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Communication

Synthesis and Reactivity of a Dipyrrinatolithium Complex

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The synthesis and characterization of the first dipyrrinato-alkali-metal complex is reported herein. The novel reactivity of this lithium complex is demonstrated in the preparation, isolation, and characterization of a heteroleptic zinc(II) complex in high yield.

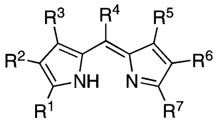

Figure 1. Dipyrrin skeleton.

Dipyrrins[1] (Figure 1) give monoanionic, conjugated, planar ligands that have attracted attention in the asymmetric synthesis of helicates,[2,3] in the formation of metal−organic frameworks,[4] as functional linkers in light-harvesting arrays,[5,6] and as the organic framework of boron dipyrrinato complexes,[7] which are used extensively as molecular probes and dyes.[8] Although dipyrrinato ligands are long respected as important intermediates in the synthesis of tetrapyrrolic macrocycles, their reactivity is rather underdeveloped and is currently experiencing a relative renaissance. Although dipyrrinato complexes of a variety of transition metals, as well as alkaline, group XII, and heavy-metal complexes thereof, are known, extensive studies regarding the reactivity of dipyrrinato ligands have not been reported.[1] As part of our work to fully investigate the utility of dipyrrins, we herein report the synthesis of the first lithium dipyrrinato derivative along with its reactivity, which is inaccessible using traditional approaches to dipyrrinato complexes.

Dipyrrinato ligands are multiply vinylogous (related through an extended π system) to β-diketiminato (NacNac) ligands[9] and offer tremendous potential as spectator ligands with tunable steric profiles. Unsymmetrical dipyrrins are usually prepared as their crystalline HBr (or sometimes HCl) salts. To access dipyrrinato complexes, the HX precursors are typically mixed with metal salts and the so-formed dipyrrinato complexes are then extracted into the organic phase during an aqueous wash. Symmetrical dipyrrins bearing aryl groups at the meso position[1] (Figure 1; R^4 = Ar) are often prepared as their nonprotonated (i.e., free-base) analogues by reacting pyrrole with aryl aldehydes under acidic conditions, followed by oxidation of the resulting dipyrromethane: complexation is achieved by reacting the free-base *meso*-aryldipyrrin with metal salts. Thus, to date, dipyrrinato complexes have been prepared using either HX salts or free bases as the source of the ligand. Clearly, these ionization states limit the potential for the synthesis of dipyrrinato complexes with a diverse array of metal fragments. With these considerations in mind, we have initiated a research program to investigate the utility of dipyrrinato lithium salts as an alternative source of the ligand.

To secure a reliable source of the anionic ligand, we used 4,4′-diethyl-3,3′,5,5′-tetramethyldipyrrin hydrobromide (**1**)[10,11] to investigate the synthesis and properties of meso unsubstituted (Figure 1; R^4 = H) dipyrrin free-bases and lithium salts. To our knowledge, there are no previous reports of alkali-metal salts involving dipyrrinato ligands, apart from a single example of a lithium derivative of a cryptand−dipyrrin in solution:[12] such derivatives of related NacNac,[13,14] porphodimethene,[15] pyrroloimine,[16,17] and aminopyrrole[18,19] skeletons are well-known.

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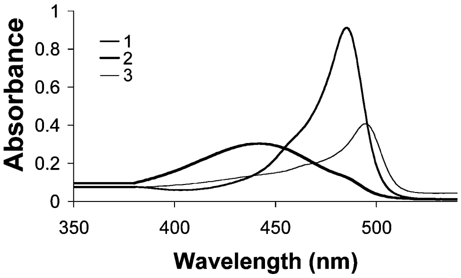
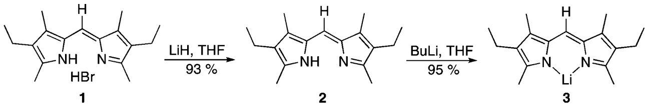


Figure 2. Absorption spectra in THF for the reaction mixture upon conversion of **1** to **2** to **3**.

Scheme 1 Preparation of Free Base **2** and Lithium Salt **3**



The free-base **2** was obtained in good yield by reacting a tetrahydrofuran (THF) solution of **1** with 4.0 equiv of LiH. Routine workup, including hexane−aqueous extraction, gave **2** as a shiny orange microcrystalline solid (Scheme 1). Alternatively, treatment of **1** with NH_4OH in ether[20] gave **2** in quantitative yield. However, using BuLi as the base, we were unable to consistently isolate a clean sample of **2**, although conversion clearly took place as was determined by analysis of the corresponding crude ^{1}H NMR spectrum.

Although 4.0 equiv of LiH was used in the preparation of **2**, solubility and absorption characteristics indicated only free-base formation. The reaction of a THF solution of the free-base **2** with 1.1 equiv of BuLi using glovebox techniques gave clean conversion to the lithium complex **3** (Scheme 1), with a concurrent color change from orange to yellow. The mixture was evaporated to dryness, and the residue was washed with hexanes to reliably give **3**. The reactions could be monitored using absorption spectroscopy (Figure 2), whereby distinct differences in absorption maxima were exhibited by a solution of **1** and the same solution after the addition of 1.0 and 2.5 equiv of BuLi, respectively, indicating the sequential formation of the free-base and the lithium complex.

^{15}N NMR spectroscopic data confirmed the formation of **3**, with a chemical shift of −231.9 ppm being distinct from the HBr salt (−209.7 ppm), free-base (−164.2 ppm), and homoleptic zinc(II) complex[11] (−167.5 ppm). Lithium incorporation was confirmed with a ^{7}Li chemical shift of 2.17 ppm. Although any of the ^{1}H NMR signals for **1**−**3** may be monitored, the distinct chemical shift region of the *meso*-H makes it of significant utility in monitoring dipyrrinato complexation reactions (Figure S1 in the Supporting Information). Quenching of **3** with DBr gave the deuterated dipyrrin (confirmed using mass spectrometry; Figure S2 in the Supporting Information), thereby verifying that both neutralization of **1** with LiH (to give the free-base) and subsequent deprotonation using BuLi (to give **3**) had been achieved.

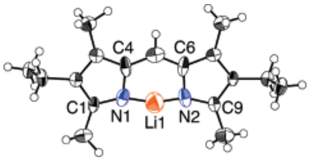


Figure 3. Structure of **3**. Selected bond lengths (Å): N1−Li1 1.42(1), N2−Li1 1.35(1), N1−C1 1.326(4), N1−C4 1.414(4), N2−C6 1.427(4), N2−C9 1.327(4).

The lithium complex was crystallographically characterized[21] twice: in both cases, red crystals were obtained from the slow evaporation of solvent from a concentrated THF solution. Both structures confirm the inclusion of a Li cation in the N,N-bidentate chelate of the deprotonated dipyrrin. However, while one structure reveals an otherwise unsupported Li cation (Figure 3), the other includes two molecules of coordinated THF (Figure S3 in the Supporting Information). The structural features of **3**•2THF are largely unremarkable, and the relevant N−Li and N−C bond lengths are consistent with closely related dipp$_2$NacNacLi structures (dipp = *N*,*N*-2,6-diisopropylphenyl; the NacNac backbone is substituted with either methyl[22] or *tert*-butyl groups[23]) that include at least one molecule of diethyl ether or THF. The N−Li−O angles in **3**•2THF are contracted (average 116.3°) relative to those of NacNacLi structures containing only one coordinated solvent molecule (average 130.8°),[22,23] likely due to steric crowding owing to the presence of two solvent molecules in the lithium coordination sphere of **3**•2THF. Additionally, while asymmetry is noted in the N−C−C−C−N backbone of both **3** and **3**•2THF, solution-phase NMR analysis reveals a typical symmetrical dipyrrinato structure.

The THF-free solid-state structure of **3** and the THF-supported structure exhibit significant differences in bond lengths and angles. For example, the N−Li average distance is 1.39 Å in **3**, compared to 1.98 Å in **3**•2THF. Furthermore, the rather short N−Li bond lengths in **3** are complimented by an elongated N1−C4 bond relative to **3**•2THF. Most interesting are the very acute C4−N1−Li and C6−N2−Li bond angles in **3** of only 96.6 and 96.9°, respectively. The bond angles, planarity of the six-membered chelate ring, and short N−Li distances in the solid-state structure of **3** substantiate that the Li atom is otherwise uncoordinated. There are limited reports of solvent-free Li atoms in an

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(21) Data for **3**: $C_{17}H_{23}N_2Li$, M = 262.32 g, golden orange needle, 0.25 × 0.14 × 0.12 mm^3, primitive orthorhombic, *Pca*21 (No. 29), a = 12.8334(5) Å, b = 13.9647(5) Å, c = 8.3343(3) Å, V = 1493.63(10) Å^3, Z = 4, T = 123 K (0.5), ρ = 1.166 g cm^{-3}, μ(Mo Kα) = 0.673 cm^{-1}, 7366 reflections (4342 unique, R_{int} = 0.024), R1 = 0.0496, wR2 = 0.0766, GOF = 1.085. Data for **4**: $C_{51}H_{69}N_6Zn_3Cl_3$, M = 1068.65 g, dark red block, 0.42 × 0.28 × 0.24 mm^3, trigonal, R-centered, *R*3*c* (No. 161), a = 33.8468(3) Å, c = 24.3950(4) Å, V = 24202.9(5) Å^3, Z = 18, T = 123 K (1.0), ρ = 1.320 g cm^{-3}, μ(Mo Kα) = 15.145 cm^{-1}, 97 247 reflections (29 902 unique, R_{int} = 0.043), R = 0.0335, R_w = 0.0363, GOF = 1.072.

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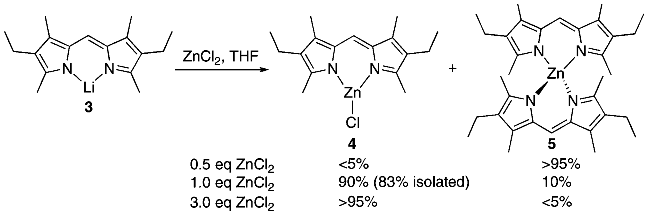
Scheme 2 Preparation of Heteroleptic Zinc(II) Complex **4**



otherwise similar bonding environment: one report[22] describes such a case where dipp$_2$NacNacLi was crystallized from hexanes. In that dipp$_2$NacNacLi structure, the structural features differ only slightly from either the THF- or diethyl ether-supported complexes, and there is clearly interaction of the Li cation of one molecule to aryl C atoms of an adjacent unit, forming an extended ladder-type structure. This makes **3**, with its unsupported Li atom, a particularly interesting complex.

To investigate the reactivity of the lithium dipyrrinato complex and to compare it to that of dipyrrin hydrobromide salts, a THF solution of **3** was added dropwise to a THF solution of ZnCl$_2$ (Scheme 2), with a concurrent color change from yellow to orange. A ^{1}H NMR spectrum of the crude reaction mixture revealed the presence of both heteroleptic **4** and the known homoleptic compound **5**,[11] both of which could be isolated. Remarkably, in the presence of both excess (3 equiv) *or* equimolar amounts of ZnCl$_2$, **4** was the major product, attesting to the preference of the lithium dipyrrinato derivative to favor heteroleptic zinc(II) complex formation (Scheme 2). In contrast, reactions employing the hydrobromide salt **1** and excess Zn(OAc)$_2$ yield only the homoleptic complex as an isolable compound.[11,24]

Evidence for the stoichiometry of **4** was obtained through reaction with AgOSO$_2$CF$_3$. After removal of quantitative AgCl, the triflate analogue of **4** was recovered in 85% yield, along with trace amounts of **5**, thereby confirming the presence of both zinc and chloride in **4**. A crystal of **4** suitable for X-ray diffraction analysis was grown from ether (Figures 4 and S4 in the Supporting Information).[21] The heteroleptic nature of **4** was unequivocally confirmed, with each Zn atom being supported in the solid state by two bridging chloro ligands, giving rise to a polymeric structure. The 2.31 Å average Zn−Cl bond length is similar to those in other Zn−μ-Cl structures, e.g., 2.32 Å in an inorganic/organic macrocycle involving a binuclear zinc(II) complex of tetra-2′-pyridylpyrazine[25] and 2.37 Å in a zinc(II) cluster complex involving bridging chloro and phosphine ligands.[26] In contrast, Zn−Cl bonds in which the chloride ligand is not bridging are distinctly shorter, averaging 2.21 Å in related κ^2-(N,N)ZnCl$_2$ complexes.[27,28] The N−Zn bonds in **4** average 1.95 Å, akin to such bonds in other zinc dipyrrinato complexes.[1]

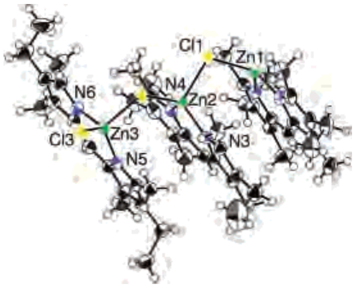


Figure 4. Structure of **4**. Selected bond lengths (Å): N1−Zn1 1.937(2), N2−Zn1 1.949(2), N3−Zn2 1.947(2), N4−Zn2 1.956(2), N5−Zn3 1.963(2), N6−Zn3 1.961(2), Zn1−Cl1 2.2853(9), Cl1−Zn2 2.3424(8), Zn2−Cl2 2.2934(9), Cl2−Zn3 2.3456(8), Zn3−Cl3 2.2918(8).

Although heteroleptic dipyrrinato complexes of copper(II),[29−32] palladium(II),[33] mercury(II),[33] rhodium(I),[34] and chromium(III)[35] are known, zinc(II) analogues are rare, although their intermediacy in the formation of homoleptic dipyrrinatozinc(II) complexes has been observed using spectroscopy.[24,36,37] A dinuclear heteroleptic head-to-tail cyclic dimer [Zn$_2$(dipyrrinato)$_2$Cl$_2$] involved each tetrahedral zinc(II) ion being coordinated to one dipyrrinato unit, one chloro ligand, and the *meso*-pyridyl moiety of the other dipyrrinato moiety.[38]

In summary, the first lithium dipyrrinato complex is reported, along with a reliable route for its synthesis. The complex exhibits unique reactivity in the field of dipyrrin chemistry and allowed for the isolation of a heteroleptic zinc(II) complex: this novel reactivity bodes well for the general utility of lithium dipyrrinato species.

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Supporting Information Available: X-ray crystallographic data in CIF format and experimental and characterization details. This material is available free of charge via the Internet at http://pubs.acs.org.

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