of coplanarity around zinc is indicated by the sum of the three bond angles, which equals 359.2 (8)°. Three coordination is rare for zinc,[4] and $\{\eta^2\text{-}H_2B(3\text{-}Bu^tpz)_2\}ZnC(CH_3)_3$ represents the first structurally characterized monomeric organozinc complex that exhibits such coordination.

The reactivity of the complexes $(\{\eta^2\text{-}H_2B(3\text{-}Bu^tpz)_2\}ZnR$ is shown in Scheme I. Protic reagents (H_2O and CH_3CO_2H) react specifically at the Zn–C bond to give $[\{\eta^2\text{-}H_2B(3\text{-}Bu^tpz)_2\}ZnX]_n$ (X = OH, $\eta^2\text{-}O_2CCH_3$) and eliminate the alkane. The hydroxo complex $[\{\eta^2\text{-}H_2B(3\text{-}Bu^tpz)_2\}Zn(\mu\text{-}OH)]_3$ has been characterized as a cyclic trimer by an X-ray diffraction study (Figure 2), and the molecule possesses approximately C_3 symmetry, with each hydroxo group bridging to zinc centers.[5] Although the X-ray structure determination did not reveal the location of the hydroxo hydrogen atoms, convincing evidence for their presence is provided by the absorption at 3611 cm^{-1} that is assigned to ν_{O-H} on the basis of the shifts observed for the isotopomers $[\{\eta^2\text{-}HB(3\text{-}Bu^tpz)_2\}Zn(\mu\text{-}OD)]_3$ and $[\{\eta^2\text{-}HB(3\text{-}Bu^tpz)_2\}Zn(\mu\text{-}^{18}OH)]_3$. The hydroxo bridge between each pair of zinc centers is asymmetric, and the lengths of the Zn–O bonds alternate in a short-long fashion around the Zn_3O_3 ring. Thus, it appears that the short Zn(1)–O(1), Zn(2)–O(2), and Zn(3)–O(3) bonds (average $Zn\text{–}O_{short}$ = 1.909 (21) Å) more closely represent normal covalent interactions (i.e., Zn–O), with the longer Zn(1)–O(3), Zn(2)–O(1), and Zn(3)–O(2) bonds (average $Zn\text{–}O_{long}$ = 1.970 (13) Å) more closely representing dative covalent interactions (Zn ← O).[6,7]

These metathesis reactions are analogous to those of the four-coordinate complexes, $\{\eta^3\text{-}HB(3\text{-}Bu^tpz)_3\}ZnR$. However, whereas the tris(3-*tert*-butylpyrazolyl)hydroborato complexes $\{\eta^3\text{-}HB(3\text{-}Bu^tpz)_3\}ZnR$ only show reactivity at the Zn–C bond, the bis(3-*tert*-butylpyrazolyl)hydroborato derivatives also exhibit reactivity at an additional site, namely, the B–H bond. Thus, the bis(3-*tert*-butylpyrazolyl)hydroborato complexes $\{\eta^2\text{-}H_2B(3\text{-}Bu^tpz)_2\}ZnR$ (R = CH_3, CH_2CH_3) react with aldehydes and ketones, $(CH_2O)_n$, CH_3CHO, and $(CH_3)_2CO$, to give the derivatives $\{HB(OR')(3\text{-}Bu^tpz)_2\}ZnR$ (R′ = CH_3, CH_2CH_3, $CH(CH_3)_2$), as a result of insertion into the B–H bond. We have not yet determined whether the alkoxo substituents on boron are also coordinated to the zinc center, i.e., $\{\eta^2\text{-}HB(OR')(3\text{-}Bu^tpz)_2\}ZnR$ vs $\{\eta^3\text{-}HB(OR')(3\text{-}Bu^tpz)_2\}ZnR$. Although other bis(pyrazolyl)hydroborato metal complexes have also demonstrated the capability of reducing ketones to alcohols, functionalized bis(pyrazolyl)hydroborato products were not isolated.[8]

Thus, in conclusion, the bis(3-*tert*-butylpyrazolyl)hydroborato derivatives $\{\eta^2\text{-}H_2B(3\text{-}Bu^tpz)_2\}ZnR$ exhibit two different reactivity pathways. The Zn–C bonds are the sites of reactivity with protic reagents such as H_2O and CH_3CO_2H, and the B–H bonds are the preferred sites of reactivity for insertion with ketones and aldehydes.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research, and we thank Professor Arne Haaland for discussions.

Supplementary Material Available: Tables of spectroscopic data for all new compounds and tables of crystal and intensity collection data, atomic coordinates, bond distances and angles, and anisotropic displacement parameters and ORTEP drawings for $\{\eta^2\text{-}H_2B(3\text{-}Bu^tpz)_2\}ZnC(CH_3)_3$ and $[\{\eta^2\text{-}H_2B(3\text{-}Bu^tpz)_2\}Zn(\mu\text{-}OH)]_3$ (29 pages); tables of observed and calculated structure factors for $\{\eta^2\text{-}H_2B(3\text{-}Bu^tpz)_2\}ZnC(CH_3)_3$ and $[\{\eta^2\text{-}H_2B(3\text{-}Bu^tpz)_2\}Zn(\mu\text{-}OH)]_3$ (30 pages). Ordering information is given on any current masthead page.

(4) (a) Gruff, E. S.; Koch, S. A. *J. Am. Chem. Soc.* **1989**, *111*, 8762–8763. (b) Al-Juaid, S. S.; Buttrus, N. H.; Eaborn, C.; Hitchcock, P. B.; Roberts, A. T. L.; Smith, J. D. S.; Sullivan, A. C. *J. Chem. Soc., Chem. Commun.* **1986**, 908–909. (c) Bell, N. A.; Shearer, H. M. M.; Spencer, C. B. *Acta Crystallogr.* **1983**, *C39*, 1182–1185. (d) Petersen, R. B.; Ragosta, J. M.; Whitwell, G. E., II; Burlitch, J. M. *Inorg. Chem.* **1983**, *22*, 3407–3415. (e) Romanenko, V. D.; Shul'gin, V. F.; Skopenko, V. V.; Markovskii, L. N. *Zh. Obshch. Khim.* **1984**, *54*, 2791–2792.

(5) Crystal data for $[\{\eta^2\text{-}H_2B(3\text{-}Bu^tpz)_2\}Zn(\mu\text{-}OH)]_3$: Orthorhombic, $Pc2_1n$ (No. 33, nonstandard setting for $Pna2_1$), a = 12.302 (2) Å, b = 20.057 (6) Å, c = 22.110 (2) Å, V = 5455 (2) Å^3, Z = 4, ρ(Mo Kα) = 125 g cm^{-3}, μ(calcd) = 13.8 cm^{-1}, λ(Mo Kα) = 0.71073 Å (graphite monochromator); 4948 unique reflections with $3° < 2\theta < 50°$ were collected, of which 2946 reflections with $F_o > 5\sigma(F_o)$ were used in refinement; R = 7.72%, R_w = 6.37%, GOF = 1.20.

(6) The reference value for a pure single covalent Zn–O bond has been adopted to be 1.89 Å. Haaland, A. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 992–1000.

(7) Other structurally characterized zinc hydroxo complexes include $[(Me_2PhSi)_3CZn(\mu\text{-}OH)]_2$ (1.899 (9) Å, ref 7a) and $[Zn_2(Bu^t_2P)_2(OH)(\mu\text{-}OH)]_2$ (2.30 (2) and 2.32 (2) Å, ref 7b). (a) Al-Juaid, S. S.; Buttrus, N. H.; Eaborn, C.; Hitchcock, P. B.; Roberts, A. T. L.; Smith, J. D. S.; Sullivan, A. C. *J. Chem. Soc., Chem. Commun.* **1986**, 908–909. (b) Arif, A. M.; Cowley, A. H.; Jones, R. A.; Koschmieder, S. U. *J. Chem. Soc., Chem. Commun.* **1987**, 1319–1320.

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^{6}Li and ^{15}N Nuclear Magnetic Resonance Spectroscopic Studies of Lithiated Cyclohexanone Phenylimine Revisited. Aggregation-State Determination by Single-Frequency ^{15}N Decoupling

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Received December 26, 1989

^{6}Li and ^{15}N NMR spectroscopy has proven to be a powerful probe of the atom connectivities and aggregation states of lithium dialkylamides and lithiated imines in solution.[1-4] Multiplicities consistent with monomers, cyclic oligomers, ion triplets, and mixed aggregates (Chart I; **1**–**4**) have all been recorded on substrates isotopically enriched in ^{6}Li and ^{15}N. The two major limitations of the double-labeling technique are as follows: (1) topologically equivalent cyclic oligomers—cyclic dimers, trimers, and tetramers—cannot be rigorously distinguished; and (2) the ^{15}N and ^{6}Li multiplets are not readily correlated when several chemically inequivalent sites are observed. We will demonstrate that ^{6}Li–^{15}N resonance correlations resulting from very simple single-frequency decoupling distinguishes cyclic dimers from higher oligomers for the lithiated phenylimine of cyclohexanone (**5**).[1,5]

^{6}Li and ^{15}N NMR spectroscopic studies of [^{6}Li,^{15}N]-**5** have been described previously; representative spectra are illustrated in Figure 1A,B.[1] The two ^{6}Li 1:2:1 triplets (J_{N-Li} = 3–4 Hz each) and the two 1:2:3:2:1 ^{15}N quintets (J_{N-Li} = 3–4 Hz) appear to derive from cyclic aggregate structural units. The 2:1 ratio of aggregate-derived resonances remains constant with changes in the concentration of either **5** or THF (using toluene-d_8 as diluent).[6] The two ^{6}Li triplets and two ^{15}N quintets are consistent with either a mixture of stereoisomeric cyclic dimers **6** and **7** or cis,trans trimer **8** (*Cy* = 1-cyclohexenyl). Colligative measurements,[7] crystallographic analogies,[7] the absence of resonances expected for the all-cis stereoisomeric trimer **9**, and ab initio calculations on $(H_2NLi\text{·}S)_n$ oligomers[8] all implicate dimers **6** and **7**. Nevertheless,

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(5) Determination of ^{13}C–^{6}Li correlations in alkyllithiums using two-dimensional techniques, as well as use of a ^{2}H lock channel to observe lithium, have been reviewed. Günther, H.; Moskau, D.; Bast, P.; Schmalz, D. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1212.

(6) At substantially elevated THF concentrations, the aggregate resonances are replaced by a ^{6}Li doublet (J_{N-Li} = 6.3 Hz) and the 1:1:1 ^{15}N triplet (J_{N-Li} = 6.1 Hz) fully characteristic of a monomer.[1]

(7) See ref 2 for leading references.

(8) Armstrong, D. R.; Mulvey, R. E.; Walker, G. T.; Barr, D.; Snaith, R.; Clegg, W.; Reed, D. *J. Chem. Soc., Dalton Trans.* **1987**, 617.

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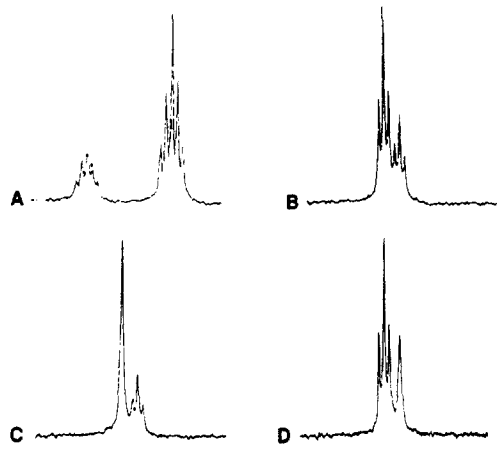
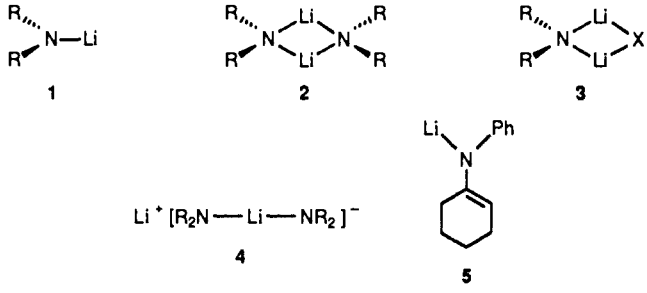
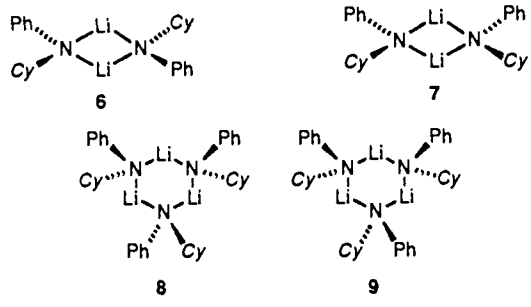


Figure 1. NMR spectra recorded at −93 °C of a 0.3 M solution of lithiated imine **5** in toluene-d_8 containing 2.0 equiv of THF/lithium: (A) ^{15}N NMR spectrum (30.42 MHz); (B) ^{6}Li NMR spectrum (44.19 MHz) observed via the ^{2}H lock channel as described in the text; (C) ^{6}Li NMR spectrum observed via the ^{2}H lock channel with concomitant irradiation of the upfield (major) ^{15}N resonance in spectrum A; (D) ^{6}Li NMR spectrum observed via the ^{2}H lock channel with concomitant irradiation of the downfield (minor) ^{15}N resonance in spectrum A.

Chart I



we were unable to unequivocally exclude trimer **8**. The inability to distinguish dimers from higher oligomers has haunted subsequent structural and mechanistic studies of N-lithiated species.[4,9]



The hardware modifications needed to achieve single-frequency decoupling of ^{15}N are straightforward. The ^{109}Ag–^{31}P broadband probe of a Bruker AC300 NMR spectrometer equipped with an X-nucleus decoupler is modified by the addition of a variable capacitor in the ^{2}H lock circuitry. This allows the ^{2}H lock channel to function as a ^{6}Li observe (or decoupling) channel operating at 44.19 MHz.[5] A proton filter in the ^{2}H lock circuitry was removed to improve sensitivity. Substantial noise introduced by the X-nucleus decoupler necessitates inclusion of quarter wavelength coaxial cable filters at the frequency ranges of ^{6}Li and ^{15}N. A decoupling power of 30–50 μW proved sufficient to achieve decoupling without perturbing resonances ≥50 Hz away.

The results of single-frequency irradiations are illustrated in Figure 1C,D. Irradiation of the major ^{15}N quintet centered at 134.6 ppm causes clean collapse of the major ^{6}Li resonance to a singlet. Similarly, irradiation of the minor ^{15}N quintet causes the minor ^{6}Li triplet to collapse to a singlet. The decouplings are consistent with two chemically distinct isomeric dimers **6** and **7**.[10] Furthermore, if cis,trans trimer **8** had been the predominant aggregate in solution, irradiation of the major ^{15}N resonance would have caused the major and minor ^{6}Li triplets to collapse to a doublet and singlet, respectively. Similarly, irradiation of the minor ^{15}N resonance would have caused collapse of the major ^{6}Li triplet to a doublet without change in the minor ^{6}Li triplet. Thus, the results of the single-frequency decouplings are consistent with stereoisomeric dimers **6** and **7** *and* inconsistent with a trimer structure.

^{6}Li and ^{15}N resonance correlations, when placed in the context of the stereochemical consequences of aggregation, provide a direct probe of aggregate structure. The exclusion of cyclic trimers in this specific case strengthens the dimer assignments for other solvated lithium amide species as well. As we continue to uncover lithium amide aggregates and mixed aggregates of increasing complexities,[11] such ^{6}Li–^{15}N resonance correlations will become essential components of solution structure determinations.

Acknowledgment. We thank Jim Simms of MIT and Brian Andrew of Bruker for several very helpful discussions. We acknowledge the National Science Foundation Instrumentation Program (CHE 7904825 and PCM 8018643), the National Institutes of Health (RR02002), and IBM for support of the Cornell Nuclear Magnetic Resonance Facility. D.B.C. and J.H.G. thank the National Institutes of Health for support of this work.

Registry No. 5, 101773-95-9; ^{6}Li, 14258-72-1.

(9) In several other instances wherein N-lithiated species display a concentration-independent pair of ^{6}Li resonances,[2,3] ratios closer to 1:1 further argue against cyclic trimers.

(10) In contrast to the irradiations of the ^{15}N multiplets separated by 55 Hz, irradiation of each of the narrowly spaced (11 Hz) ^{6}Li triplets failed to afford fully selective decoupling.

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Enantioselective Total Synthesis of Neooxazolomycin

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Received January 10, 1990

Neooxazolomycin (**1**) is a structurally novel $C_{34}H_{47}N_3O_9$ oxazole polyene lactam–lactone antitumor antibiotic isolated from several *Streptomyces* strains.[1a,b] The structures and absolute configurations of this compound[1a] and its β-lactone congener, oxazolomycin (**2**),[1c] were described in 1985. Neooxazolomycin (**1**) is an acid-, base- and light-sensitive molecule that may be regarded as an amide formed between a *Z,Z,E* oxazole triene acid left half (**22**) and a highly functionalized lactam–lactone amino diene (**37**, R_1 = H) right half (Chart I). We now report the first enantioselective total synthesis of neooxazolomycin.[2]

The oxazole triene acid left half of the antibiotic was synthesized from the known[3] (*Z*)-3-bromo-2-methyl-2-propenol (**3**), converted to the *Z* aldehyde **5** in 84% yield by a four-step sequence (Scheme I): (1) O-silylation, (2) Pd-catalyzed coupling[4] with (trimethylsilyl)acetylene to produce the enyne **4**, (3) selective O-

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