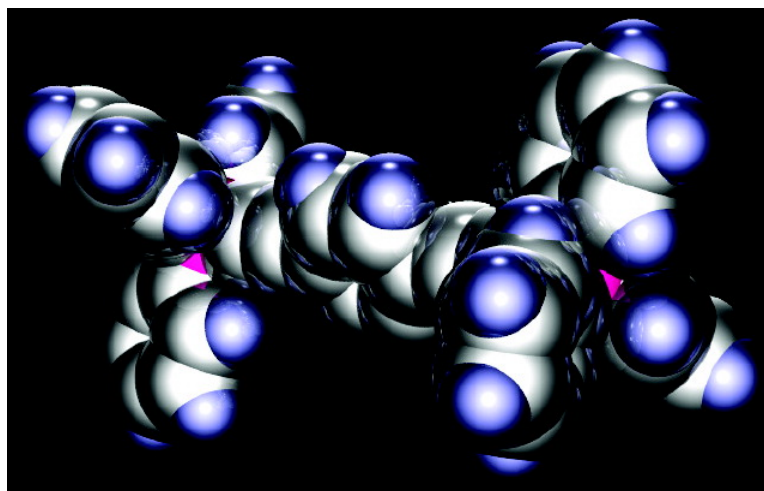## Communication

Ionic Rotors. Preparation, Structure, and Dynamic Solid-State D NMR Study of the 1,4-Diethynylbenzenebis(triphenylborate) Dianion

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Ionic Rotors. Preparation, Structure, and Dynamic Solid-State ²D NMR Study of the 1,4-Diethynylbenzenebis(triphenylborate) Dianion

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The incorporation of moving parts into molecular compounds is a topic of current interest with regard to the development of molecular machines.[1] This interest is fueled in part by the desire to manipulate matter on the small scale. Since macroscale gyroscopes can be used in guidance systems, similar functions can be envisioned in micro- or nanoscale devices. Therefore, research into developing molecular "gyroscopes" has attracted considerable interest as of late.[2] Molecular gyroscopes consist of rotors encased in a protective scaffold to allow freedom of motion to the internal component. Recently, elegant work by Garcia-Garibay's group on systems with a diethynylphenylene rotor connected between two trityl groups (middle of Figure 1) has shown that it is possible to control the rate that the central phenyl ring rotates in the solid state by appropriately substituting groups on the ligand periphery.[3] Crystal packing interactions (such as CH−π and π−π interactions) involving these charge-neutral compounds or their solvates dictate the rotational velocity of the central phenylene ring; the more substituted the trityl/trypticenyl end groups, the more isolated the central rotors, and the faster the central phenylene rotation.[4] This is clearly evident in the 10^5 increase in room temperature phenylene rotation rates between the p-$(Ph_3CC_2)_2C_6H_4$ and p-$[(3,5\text{-}^tBu_2C_6H_3)_3$-$CC_2)_2C_6H_4]$ derivatives.[3]

In the late 1970s, the tin and lead congeners of the type p-$(Ph_3MC_2)_2C_6H_4$ (M = Sn, Pb) were reported but for purposes other than studying the rotation of the central phenylene spacer.[5] Likewise, in the early 1990s, Stang reported the preparation of the cationic species based on phosphonium derivatives (Figure 1, above) starting from the bis(phenyliodonium)acetylene triflate.[6] Surprisingly, the isoelectronic borate counterpart (Figure 1, right) has not yet been reported. Our interest in the synthesis and supramolecular chemistry of boron alkynyl compounds led us to consider this promising class of ionic derivatives as alternatives to the charge-neutral carbon-based rotors for the design of electromagnetically responsive materials. Ionic-based compounds may allow for better separation of rotors due to Coulombic repulsion, and ultimately, the crystal structure of such species may be fine-tuned by incorporating different cations that will serve to direct the supramolecular structure of the resulting solids. We now wish to communicate our initial endeavors in preparing a compound that contains the p-$(Ph_3BC_2)_2C_6H_4$ dianion, the heretofore missing member of the isoelectronic series of molecular rotors (Figure 1, right).

The compound $[Li(THF)_4]_2[p\text{-}(Ph_3BC_2)_2C_6H_4]$ and its deuterio counterpart were prepared in 65−70% yield by reacting p-$(LiC_2)_2$-C_6H_4 (generated in situ from butyllithium and dialkynylbenzene)
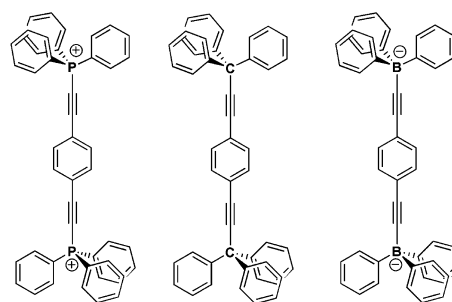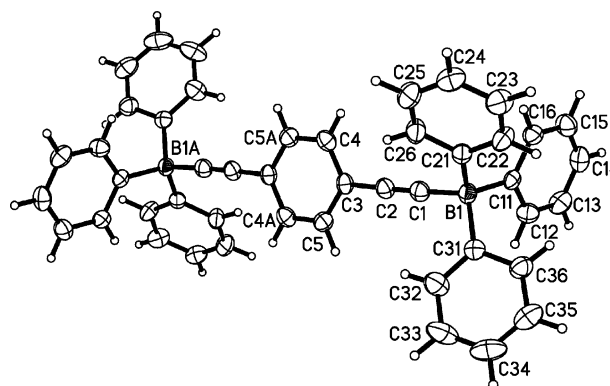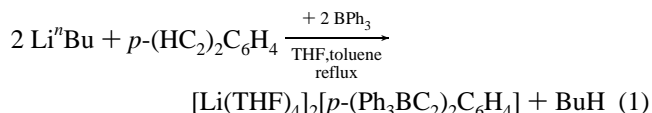

Figure 1. Isoelectronic rotors.

Figure 2. ORTEP drawing of the $[p\text{-}(Ph_3BC_2)_2C_6H_4]^{2-}$ dianion. Thermal ellipsoids are drawn at the 50% probability level.

with 2 equiv of triphenylborane, according to eq 1. The diborate salt is soluble in polar solvents

$$2\,Li^nBu + p\text{-}(HC_2)_2C_6H_4 \xrightarrow[\substack{\text{THF,toluene} \\ \text{reflux}}]{+\ 2\ BPh_3} [Li(THF)_4]_2[p\text{-}(Ph_3BC_2)_2C_6H_4] + BuH \quad (1)$$

such as acetone or acetonitrile, moderately soluble in THF, but is insoluble in hydrocarbons and diethyl ether, and decomposes in chlorinated solvents.

An ORTEP diagram of the dianion in $[Li(THF)_4]_2[p\text{-}(Ph_3BC_2)_2C_6H_4]$ is given in Figure 2. The dianion is well-behaved with a typical sp³-boron−alkynyl carbon bond distance of 1.60 Å,[7] but one of the THF molecules in the $Li(THF)_4$ cation suffers a disorder, as outlined in the Supporting Information.

As expected, the Coulombic repulsion of dianions and the presence of the atoms of the cation leads to a greater separation of rotors in $[Li(THF)_4]_2[p\text{-}(Ph_3BC_2)_2C_6H_4]$ in the solid state compared to those found in the structures of p-$(Ph_3CC_2)_2C_6H_4$ or its benzene solvate.[3] As detailed in Figure 3 and elaborated on in the discussion of the supramolecular structure found in the Supporting Information, the rotors of the borate derivative are well separated from one
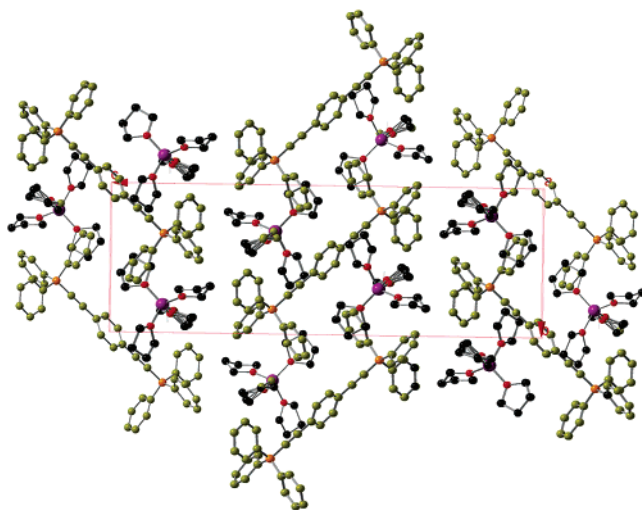
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Figure 3. Packing diagram of [Li(THF)$_4$]$_2$[p-(Ph$_3$BC$_2$)$_2$C$_6$H$_4$] viewed into the bc plane.

another, while those in the charge-neutral derivatives are interpenetrated to different extents. It is anticipated that the isolation of the rotors in the title compound should lead to high rates of phenylene rotation.

Crystals of the diborate salt rapidly (minutes) turn opaque when removed from the mother liquor at room temperature. Integration of the resonances obtained in the solution ^{1}H NMR spectrum of the opaque samples dissolved in acetone-d_6 confirms that the salt readily loses its coordinated THF. The ^{1}H NMR spectra for samples of the diborate salt that were dried under vacuum for 1 h consistently revealed the presence of only 4 of the expected 8 equiv of THF, indicating that [Li(THF)$_2$]$_2$[p-(Ph$_3$BC$_2$)$_2$C$_6$H$_4$] was sufficiently stable for further analyses, although the exact structural nature of the desolvated form remains unclear. The samples of the borate salts lose all coordinated THF at the expense of coordinating water over the period of weeks when kept in air, as indicated by NMR spectroscopy and elemental analyses. The hydrated salt is insoluble in most weakly coordinating solvents and is prone to hydrolytic decomposition in solution. Thus, this hygroscopic diborate salt is best stored protected from atmospheric moisture.

A sample of desolvated diborate salt with the composition [Li-(THF)$_2$]$_2$[p-(Ph$_3$BC$_2$)$_2$C$_6$D$_4$] (NMR) that was protected from atmospheric moisture (by manipulation in a nitrogen-filled drybox) was subjected to a variable-temperature solid-state ^{2}D spin−echo NMR spectroscopic study to determine whether and at what rate the central phenylene ring rotates (via 180° ring flips)[8] in the solid state. The results of the NMR study are summarized in Figure 4, full details are provided in the Supporting Information. The molecular motion of the central phenylene of the diborate dianion can best be modeled as a two-site system that contains a fast (≥10 MHz) and a slower (10 kHz to 1 MHz) moving component. In general, the slower component of phenylene rotation in the borate derivative is faster than, but comparable to, that of the carbon-based analogues over comparable temperature range. For instance, the rotation in the borate has a rate of 300 kHz at 294 K versus 15 kHz at 297 K for its ditrityl counterpart. The slower component of phenylene rotation reaches the MHz regime at only 308 K in the borate complex, whereas the carbon analogue was reported to achieve a rate of 1.3 MHz at 348 K.[2a,b] Thus, even with the structural collapse involving the desolvation of [Li(THF)$_4$]$_2$[p-(Ph$_3$-BC$_2$)$_2$C$_6$D$_4$], the Coulombic repulsion of anions and the mere presence of cation atoms likely afford greater separation between rotors than that in the trityl system and allows for faster rotation
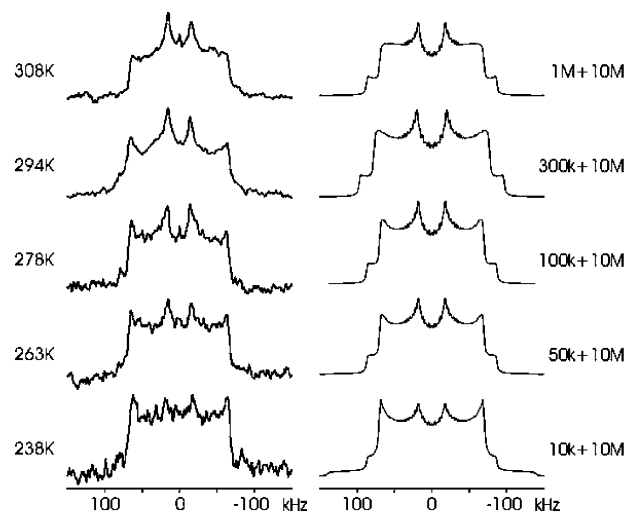

Figure 4. Experimental (left) and calculated (right) solid-state ^{2}D NMR spectra for central phenylene rotation in the [p-(Ph$_3$BC$_2$)$_2$C$_6$D$_4$] dianion at various temperatures. The calculated spectra on the right were obtained by considering a two-site model with fast (≥10 MHz) and slow (10 kHz−1 MHz) moving components.

than that of the carbon analogue. The two-site system indicates the complex structural nature of the desolvated compound: either different domains with both compact (slow rotation) and more-separated (fast rotation) local environments coexist or the desolvated compound has a new supramolecular structure with symmetry independent rotors. These details will be addressed further in the full report and in future reports, where we will delineate the role of cation substitution on (1) increasing the air stability of the rotor, and (2) how the supramolecular organization of the borate rotors effects phenylene rotation rates. It is hoped that we will learn how to control the supramolecular organization of these potentially electroresponsive borate-based solid architectures.

Supporting Information Available: Crystallographic information file (CIF), additional structural information and figures, including the supramolecular organization, and experimental procedures. This material is available free of charge via the Internet at http://pubs.acs.org.

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