Rotaxanes

DOI: 10.1002/anie.201207783

Heterolytic Activation of H_2 Using a Mechanically Interlocked Molecule as a Frustrated Lewis Base**

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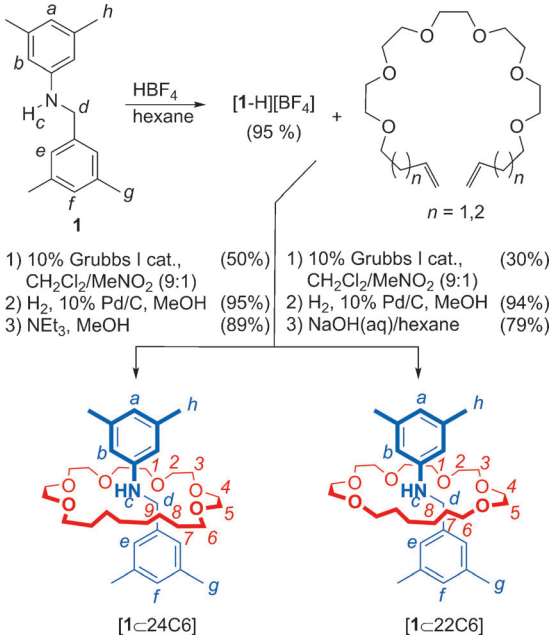
A frustrated Lewis pair (FLP) is an intra- or intermolecular combination of a Lewis acid and a Lewis base in which steric hindrance inhibits the formation of a classical Lewis donor–acceptor adduct. A consequence of the unquenched Lewis acidity and basicity is unprecedented reactivity, including the heterolytic cleavage of H_2 molecules[1] and activation of small molecules, such as CO_2,[2] N_2O,[3] NO,[4] SO_2,[5] alkenes,[6] and alkynes.[7] The FLP concept[8] has been recently exploited for the development of stoichiometric reductions of anilines to cyclohexylamines,[9] and of metal-free catalysts for hydrogenation of polar substrates[8,10] and 1,1-disubstituted olefins.[11]

The steric bulk, which inhibits the formation of Lewis acid–base adducts in FLP chemistry, has traditionally been attached directly to the Lewis acidic and basic atoms.[7a] For example, the phosphines,[1a,b] amines,[12] and boranes[1a,b] that have been used to elicit FLP reactivity all contain either bulky alkyl or aryl substituents directly bonded to the heteroatom. As this requirement can be synthetically challenging and thereby somewhat restrictive, we sought an alternate strategy to sterically encumber Lewis bases. To this end, we have considered the notion of converting a Lewis base that would normally form an adduct with the Lewis acid $B(C_6F_5)_3$ into one that participates as a partner in an FLP.

One avenue to restrict access to the reactivity of a particular functional group is to bury it inside some sort of cavity, so as to preclude access from other selected reagents. This is, of course, one of the tactics Nature utilizes to control the reactivity and selectivity of enzymes.[13] It occurred to us that the incorporation of a secondary amine into a mechanically interlocked molecule (MIM),[14] such as a [2]rotaxane,[15] might be a way to conceptually emulate Nature. This strategy would convert a simple Lewis base into a bulky Lewis base partner for FLP chemistry without the restriction of covalent modification.

The secondary amine (aniline) **1**, which contains 1,3-dimethylphenyl and 1,3-dimethylbenzyl groups, was selected as the Lewis basic axle for incorporation into a [2]rotaxane. Scheme 1 outlines the synthesis of the two neutral [2]rotaxanes [**1**⊂24C6] and [**1**⊂22C6] with differently sized macrocyclic wheels (24- and 22-membered) and the axle **1**. The key feature of the synthesis is the ring-closing metathesis reaction facilitated by Grubbs' first-generation catalyst.[16] This reaction occurs while hydrogen-bonding and ion-dipole templating interactions between the anilinium ion of the protonated axle $[\mathbf{1}\text{-H}]^+$ and the oxygen atoms of the crown ether hold the axle and wheel in close proximity; thus favoring [2]rotaxane formation.[17] [2]Rotaxanes [**1**⊂24C6] and [**1**⊂22C6] were isolated in moderate yields after reduction of the residual double bonds created from olefin metathesis and subsequent neutralization with base. This [2]rotaxane design utilizes a short axle with only two nonhydrogen atoms (NH and CH_2) between the stoppering xylene groups, so that the macrocyclic wheel can only undergo limited translational motion and



Scheme 1. Synthesis of [2]rotaxanes [**1**⊂24C6] and [**1**⊂22C6] by the clipping method converts the aniline base **1** into sterically hindered MIM bases by restricting access to the Lewis basic nitrogen atom.

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[**] This research work was supported by NSERC of Canada Discovery grants and Canada Research Chair awards (S.J.L. and D.W.S.). C.B.C. and V.N.V. are grateful to NSERC of Canada for the awarding of Alexander Graham Bell Graduate Scholarships and V.N.V. to the International Center for Diffraction Data for a Ludo Frevel Scholarship.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201207783.

cannot simply slide along the axle and expose the reactive nitrogen center. Preparation of [2]rotaxanes with smaller macrocycles was not possible because of ring strain, and of those with larger macrocycles was not possible because the rings are too large to be trapped by the xylyl stoppers. An additional feature of an anilinium [2]rotaxane is the ease of deprotonation compared to more commonly utilized secondary ammonium analogues.[15i,18]

The ^{1}H NMR spectra (500 MHz, CD_2Cl_2, 298 K) of [**1**⊂24C6] and [**1**⊂22C6] show very significant downfield shifts for the NH protons (*c*) as compared to the axle **1** because of NH···O hydrogen bonding between the NH group and the oxygen atoms of the crown ether. The NH resonance (*c*) for **1** is observed at 3.96 ppm (Figure 2) but shifts to 5.12 and 5.61 ppm for [**1**⊂24C6] and [**1**⊂22C6], respectively (Figure 3). Other axle resonances that are affected by rotaxane formation are the benzyl protons (*d*) and *ortho* protons (*b*) and (*e*), which are involved in weaker CH···O interactions. The slightly larger shifts for each resonance in [**1**⊂22C6] as compared to [**1**⊂24C6] can be attributed to more significant hydrogen bonding, which might be expected to occur as a result of the smaller size of the 22-membered macrocycle.

The X-ray structure of [**1**⊂24C6] was determined and is shown in Figure 1. The 24C6 macrocycle encircles the central

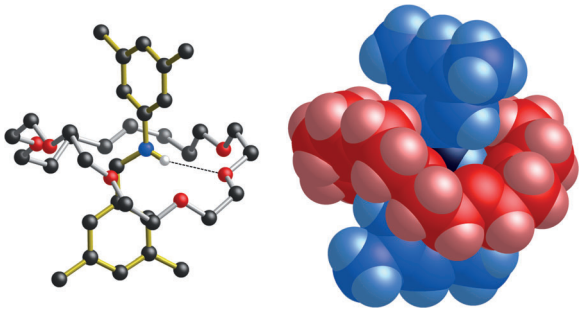
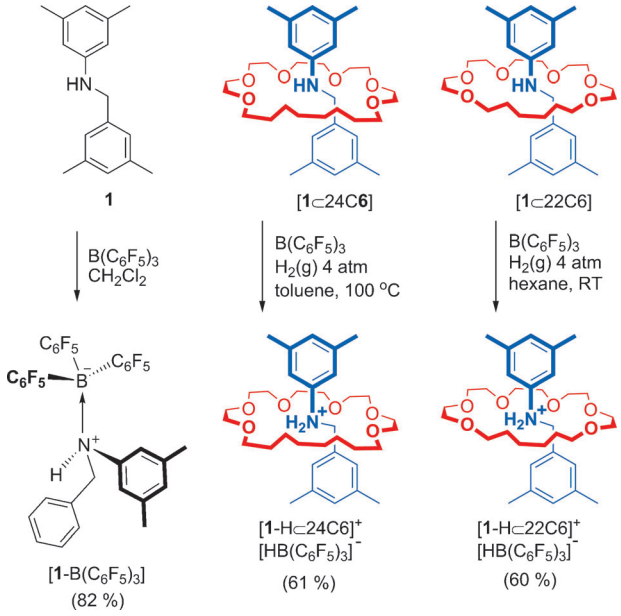


Figure 1. Left: ball-and-stick representation of the X-ray structure of [**1**⊂24C6]. Only the amine H atom involved in H bonding is shown, all others are omitted for clarity. Right: space-filling model of the same view with all H atoms showing the axle in blue and the macrocyclic wheel in red. The aniline N atom colored dark blue is barely visible.

$NHCH_2$ unit as designed, and a single NH···O hydrogen bond (N···O 3.27 Å, N–H···O 161°) is the only substantial non-covalent interaction between the two interlocked components. In the space-filling model of the structure of [**1**⊂24C6] (Figure 1, right), the nitrogen atom of the aniline is colored dark blue, but only a small portion of the atom is visible, thus emphasizing how the macrocycle provides significant steric hindrance to the close approach of any incoming reagent.

Reaction of the sterically unencumbered *N*-benzylaniline **1** with one equivalent of $B(C_6F_5)_3$ in CH_2Cl_2 results in formation of the classical Lewis acid–base adduct [**1**-$B(C_6F_5)_3$] in 82% yield (Scheme 2). The ^{1}H NMR spectrum of [**1**-$B(C_6F_5)_3$] (Figure 2b) shows that the NH resonance is shifted downfield to 7.67 ppm, and that a distinct splitting of the benzylic CH_2 group occurs from a solitary doublet into two



Scheme 2. Reactions of **1**, [**1**⊂24C6], and [**1**⊂22C6] with Lewis acid $B(C_6F_5)_3$ in the presence of H_2(g).

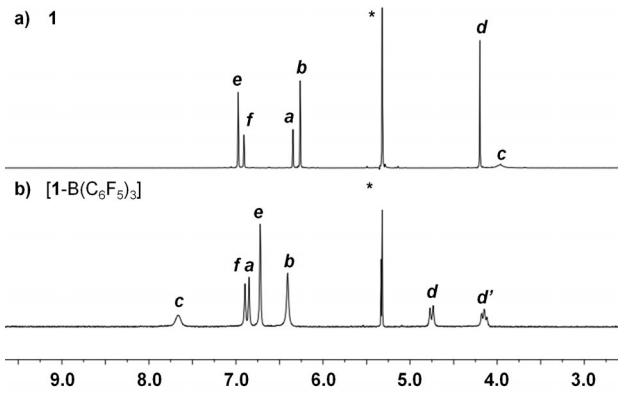


Figure 2. ^{1}H NMR spectra (500 MHz, CD_2Cl_2, 298 K) of a) the aniline **1**, and b) the adduct [**1**-$B(C_6F_5)_3$] formed from **1** and $B(C_6F_5)_3$.

sets of resonances, a doublet at 4.76 ppm and a triplet at 4.15 ppm. These observations are indicative of the dissymmetry that is created when the B–N bond is formed. The ^{11}B NMR spectrum (see the Supporting Information) shows a broad singlet at −2.50 ppm, which is also consistent of B–N bond formation.[19] The signals in the ^{19}F NMR spectrum (Supporting Information) are broad as a result of restricted rotation around the B–N bond, resulting from the steric congestion created by the large substituents on both the B and N atoms, and the gap between the ^{19}F resonances of the fluorine atoms in *meta* and *para* position is only 6.38 ppm, indicative of a four-coordinate borate species.[13] Upon cooling to 233 K, the ^{19}F NMR spectrum resolves, so that 13 of the 15 individual fluorine signals (some overlap) could be observed, again indicating strong adduct formation. Heating of [**1**-$B(C_6F_5)_3$] to 100 °C under 4 atm of H_2(g) pressure overnight resulted in no evidence for hydrogen activation.

To probe whether the macrocyclic ring of a [2]rotaxane could impart enough steric bulk to a Lewis base to prevent adduct formation and potentially produce FLP reactivity, [**1**⊂24 C6] was combined with one equivalent of $B(C_6F_5)_3$ in toluene. Initial ^{1}H NMR spectra indicated that the two species were reacting very slowly to give a complex mixture of unidentifiable products. This is presumed to be an equilibrium mixture of weak Lewis adducts resulting from the approach of $B(C_6F_5)_3$ to the oxygen atoms of the crown ether. This notion was further supported by the observation that exposure of this reaction mixture to 4 atm of H_2(g) at 100 °C led to the clean formation of the protonated [2]rotaxane cation [**1**-H⊂24 C6]$^+$ and the hydridoborate anion $[HB(C_6F_5)_3]^-$ (Figure 3) consistent with FLP activation of H_2. When this reaction was carried out in hexanes, the [**1**-H⊂24 C6][$HB(C_6F_5)_3$] salt cleanly precipitated from the solution as a yellow/orange oil in 60 % yield (Scheme 2). The ^{1}H NMR spectrum showed a broad but definitive NH_2 signal at 9.15 ppm and a benzyl CH_2 signal at 4.81 ppm, matching a sample of [**1**-H⊂24 C6][BF_4]. The ^{11}B NMR spectrum (Supporting Information) showed a distinctive doublet at −25.46 ppm ($^1J_{BH} = 92$ Hz), corresponding to formation of the hydridoborate anion $[HB(C_6F_5)_3]^-$, which was corroborated by the existence of a small *meta–para* gap of 2.84 ppm in the ^{19}F NMR spectrum (Supporting Information). Presence of the H_2-activated species was also verified by high-resolution ESI mass spectrometry in positive and negative mode, which clearly showed *m/z* values for the cation and anion, respectively (see the Supporting Information).

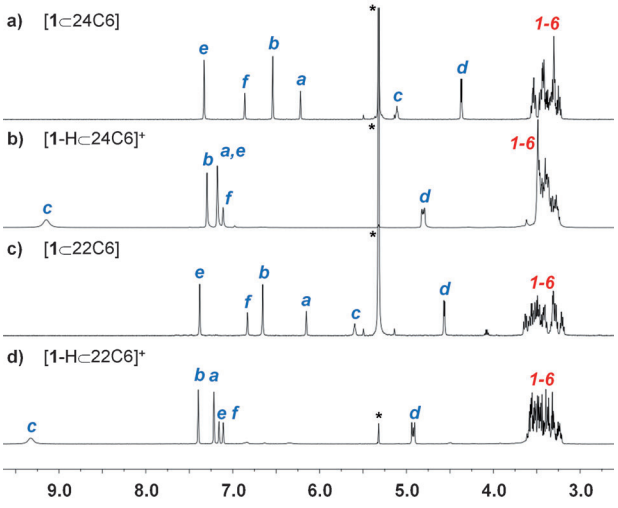


Figure 3. ^{1}H NMR spectra (500 MHz, CD_2Cl_2, 298 K) of a) [**1**⊂24 C6], b) [**1**-H⊂24 C6]$^+$ (product of the reaction of [**1**⊂24 C6] with $B(C_6F_5)_3$ and H_2(g)), c) [**1**⊂22 C6], and d) [**1**-H⊂22 C6]$^+$ (product of the reaction of [**1**⊂22 C6] with $B(C_6F_5)_3$ and H_2(g)).

The corresponding reaction of [**1**⊂24 C6] and $B(C_6F_5)_3$ under 4 atm of D_2 under analogous conditions afforded an oil, which was isolated and determined to be the corresponding deuterium-incorporated salt [**1**-D⊂24 C6][$DB(C_6F_5)_3$]. This observation was confirmed by the ^{1}H NMR spectrum, which gave an NH_2 proton integration of less than 1H, indicating deuterium incorporation, while the remaining chemical shifts indicated clean protonation of the [2]rotaxane. The corresponding ^{2}H NMR spectrum showed signals at 9.06 and 3.47 ppm corresponding to the ND and BD fragments. The ^{11}B NMR spectrum also showed a broad resonance at −25 ppm, the same region in which the borohydride anion normally shows up. This data unambiguously demonstrates that [**1**⊂24 C6] is capable of acting as a bulky Lewis base in the FLP-mediated heterolytic cleavage of molecular hydrogen in the presence of the bulky Lewis acid $B(C_6F_5)_3$.

Given this success with [**1**⊂24 C6], the impact of a smaller crown ether macrocycle was of interest, as it might reduce the flexibility of the ring and concomitantly increase the steric restrictions around the nitrogen center. The reaction of [**1**⊂22 C6] containing a smaller 22-membered crown ether ring with $B(C_6F_5)_3$ without an atmosphere of hydrogen gas led to similar results as observed with the larger crown ether. However, once the reaction mixture was placed under an atmosphere of hydrogen gas at room temperature, an oily product immediately began to precipitate. The product was characterized and confirmed to be the hydrogen-activated product [**1**-H⊂22 C6][$HB(C_6F_5)_3$]. The ^{1}H NMR spectrum shows the NH_2 resonance as a broad singlet at 9.33 ppm as well as a multiplet for the benzyl CH_2 at 4.92 ppm. The ^{11}B NMR spectrum (Supporting Information) is also indicative of H_2 cleavage, because a borohydride signal was observed at −25.48 (d, $^1J_{BH} = 90$ Hz). The product was also characterized by high-resolution ESI mass spectrometry (see the Supporting Information).

In conclusion, the heterolytic activation of H_2(g) using [**1**⊂22 C6] or [**1**⊂24 C6] and $B(C_6F_5)_3$ demonstrates that the concept of incorporating a Lewis base into a mechanically interlocked molecule (MIM) is a valid methodology for generating a sterically hindered base. Moreover, the increased reactivity with H_2 observed for [**1**⊂22 C6] versus [**1**⊂24 C6] confirms that the degree of steric protection experienced by the Lewis basic nitrogen atom can be fine-tuned by judicious choice of the encircling macrocycle. Thus, the present results outline a strategy for the transformation of a sterically unencumbered base for entry into the FLP reactivity regime, without covalent modification. The further exploitation of this approach is the subject of ongoing efforts in our laboratories.

Experimental Section

NMR experiments were recorded on Bruker Avance-III 400 MHz and Bruker Avance 500 MHz NMR spectrometers. Details of the syntheses and spectroscopic characterization of all new compounds can be found in the Supporting Information.

X-ray data for [**1**⊂24 C6]: $C_{35}H_{57}NO_6$, $M = 587.82$, colorless prisms (0.38 × 0.28 × 0.20 mm), monoclinic, $P2_1/c$, $a = 20.613(5)$, $b = 19.349(5)$, $c = 18.562(4)$ Å, $\beta = 105.105(3)°$, $U = 7148(3)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.092$ g cm^{-3}, $\mu = 0.073$ mm^{-1}, min/max trans. = 0.9857, $Mo_{K\alpha}$ $\lambda = 0.71073$ Å, $T = 173.0(2)$ K, 66297 total reflections (R(int) = 0.0685), $R1 = 0.1066$, $wR2 = 0.1946$ [$I > 2\sigma I$], $R1 = 0.2740$, $wR2 = 0.3549$ [all data], GoF(F^2) = 1.014, data/variables/restraints = 12574/757/0. The SHELXTL library of programs[20] was used for X-ray solutions and figures were drawn with CrystalMaker software.[21] CCDC 902860 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The

Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Received: September 26, 2012
Published online: November 26, 2012

Keywords: frustrated Lewis pairs · hydrogen activation · interlocked molecules · macrocycles · rotaxanes

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[21] Images generated using CrystalMaker: CrystalMaker Software Ltd, Oxford, England (http://www.crystalmaker.com).

