# Interaction of Azobenzene and Benzalaniline with Strong Amido Bases

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S *Supporting Information*

ABSTRACT: The interaction of azobenzene with lithium dicyclohexylamide (Cy_2NLi) in THF or Et_2O afforded the ion−radical salt of azobenzene (**1**) structurally characterized for the first time and dicyclohexylaminyl radical, which begins a novel chain of transformations leading eventually to the imino−enamido lithium complex (**3**). Benzalaniline, being a relative of azobenzene, reacted with Cy_2NLi without electron transfer by a proton-abstraction mechanism to form the dilithium salt of $N^1,N^2,1,2$-tetraphenylethene-1,2-diamine quantitatively.
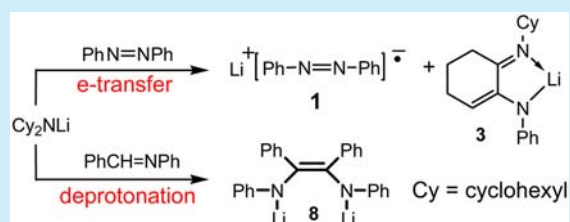
Azobenzene is known to exhibit dual reactivity toward strong bases. Organolithium (PhLi, *n*-, *s*-, or *t*-BuLi, Ph_3SiLi) and organopotassium reagents (Ph_2CHK, $PhCH_2K$, Ph_3SiK) can be added smoothly to the N=N bond of azobenzenes at low temperatures to give the derivatives of the trisubstituted hydrazines.[1]

Certain efforts were initially directed toward the interaction of sterically hindered lithium amide bases with azobenzene. It was found that lithium diisopropylamide (LDA) does not add to the N=N bond but acts as a reductor.[2] The reaction, however, proceeds sluggishly as evidenced by a meager ∼30% yield of quenching products. The probable mechanism was given[3] using transfer of a hydride ion within the transient complex **A*** resulting in the reduction of the N=N bond leading to lithium 1,2-diphenyl hydrazide (Scheme 1). In some cases, LDA may

Scheme 1. Proposed Mechanism for the Reaction of Azobenzene with LDA
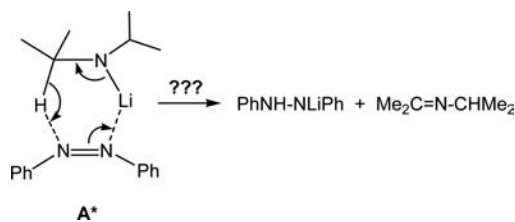
serve as a hydrogen donor. Thus, it was shown that hydrogen involved in reducing benzophenone by LDA is the *α*-hydrogen of the isopropyl group. The byproduct of the reduction in this case is *N*-isopropylacetone imine.[4] However, the formation of lithium 1,2-diphenyl hydrazide and transient complex **A*** in the reaction of azobenzene with LDA was not definitively proven. On the other hand, there is much evidence for radical involvement in the

reactions of LDA with various classes of organic compounds: with polynuclear hydrocarbons,[5] aromatic ketones,[4a] heterocyclic compounds,[6] *α*-bromo imines.[7]

In this paper, we provide such evidence for the reaction of azobenzene with LDA and Cy_2NLi, which affords the ion-radical salt of azobenzene and a novel chelate compound containing fragments of azobenzene and dicyclohexylamide. For comparison, we carried out a similar reaction of Cy_2NLi with a related compound, benzalaniline, proceeding without participation of radicals, affording product of dimerization.

Equimolar amounts of azobenzene and Cy_2NLi in diethyl ether were allowed to react at room temperature. Deep cherry coloration arose immediately followed by precipitation of deep-cherry fine crystals of ion-radical salt of azobenzene, $Li^+[PhNNPh]^{•−}$ (**1**). We succeed in separation of **1** in the form of single crystals by slow crystallization from diluted THF solution. Whereas many investigators observed formation of **1** in different reactions, its separation in monocrystalline form was problematic because of the polymeric nature of **1**. The structure of **1** is shown in Figure 1; the crystal data and details of the data collection and refinement are given in Table S1 (Supporting Information).

X-ray analysis indicates that ion-radical salt **1** is a coordination polymer in which the lithium ion acts as a bridging group. The distances between lithium ion and the nitrogen atoms of both azobenzene molecules (2.003(1) Å) are equal. Lithium has additional coordination with THF and short contacts with carbon atoms of benzene rings, both 2.650(1) Å. The N−N bond length in **1** (1.349(2) Å) is longer than those observed in azobenzene (1.18−1.25 Å)[8a,b] but notably shorter than in hydrazobenzene (1.394 Å).[9] This is in accordance with the
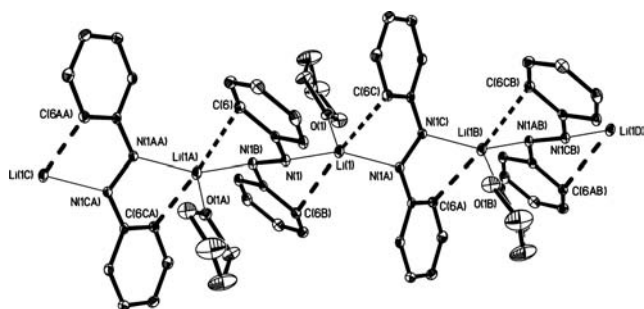
Figure 1. Chain structure of **1** together with the atomic numbering system (ellipsoids at the 30% probability level). Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Li(1)−N(1) 2.003(1), Li(1)−C(6B) 2.650(1), N(1)−N(1B) 1.349(2), N(1)−C(1) 1.384(2), C(1)−C(6) 1.403(2), C(1)−C(2) 1.404 (2), C(2)−C(3) 1.375(2); N(1)−Li(1)−N(1A) 144.3(2), N(1B)-N(1)−C(1) 113.1(1), N(1B)−N(1)−Li(1) 110.2(1).

tautomeric nature of N−N bond in the ion-radical salt. For comparison, the nitrogen−nitrogen bonds in dilithium salt of hydrazobenzene, $[\{PhN(Li)−N(Li)Ph\}_4]$ (1.467−1.469 Å),[10] are close to the rupture limit.[11]

We found that lithium diisopropylamide reacts with azobenzene in THF or diethyl ether in a similar way, that is, to afford a dark-cherry poorly soluble powder of **1** in yield ∼ 60%. However, the remaining mother liquor contained only intractable mixture of products.

The compound **1** is paramagnetic and shows a strong signal in the electron-spin resonance spectrum, identical to those observed for the sample of **1** prepared by the reaction of azobenzene with potassium.[12] Note also that Wittig for the first time prepared radical salt of azobenzene by the reaction of dilithium salt of hydrazobenzene with 1 equiv of azobenzene.[13]

It is also known that the anion-radical salt of azobenzene undergoes disproportionation in solution to the free azobenzene and dianion.[14] This determines the yield of products in substitution reactions. In any case, 50% of azobenzene should be recovered. We confirmed this assumption by the reaction of **1** with PhMe$_2$SiCl, which afforded 50% of azobenzene and 50% of disubstituted hydrazobenzene, $[Ph(PhMe_2Si)N]_2$ (**2**). Formation of **2** was confirmed by X-ray analysis. The structure of **2** is shown in Figure S1; the crystal data and details of the data collection and refinement are given in Table S1 (Supporting Information).

Whereas the reaction of azobenzene with lithium dicyclohexylamide gives radical salt **1**, it is reasonable to assume that Cy$_2$NLi provides one electron and lithium ion for the first step of the reaction (Scheme 2).

The remaining dicyclohexylaminyl radical (Cy$_2$N•) begins a novel chain of transformations (Scheme 3). In the course of our investigations, we succeeded in the isolation and characterization of one more major product **3**, composed of aromatic and alicyclic fragments.

**Scheme 2. First Step of Reaction of Azobenzene with Cy$_2$NLi**
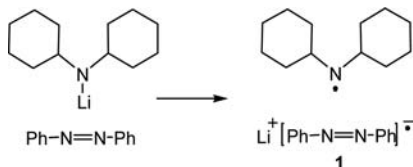
Scheme 3. Probable Chain of Transformations of Dicyclohexylaminyl Radical (Cy$_2$N•)
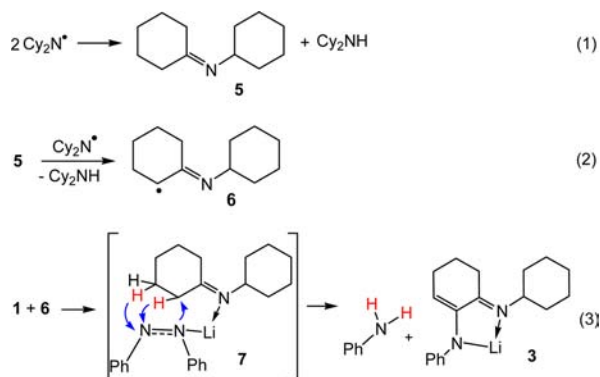
Imino-enamido lithium complex **3** was extracted from reaction mixture with hexane and isolated in 30% yield as pale green crystals.

The quality of the crystals was suitable for X-ray analysis. The structure of **3** is shown in Figure 2; the crystal data and details of
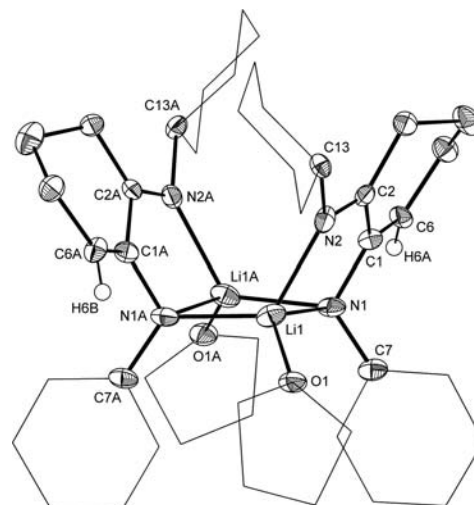

Figure 2. Molecular structure of **3** together with the atomic numbering system (ellipsoids at the 30% probability level). Hydrogen atoms have been omitted for clarity except for H(6A) and H(6B). Selected bond lengths (Å) and angles (deg): Li(1)−N(1A) 2.058(4), Li(1)−N(2) 2.062(4), Li(1)−N(1) 2.092(4), N(1)−C(7) 1.384(2), N(1)−C(1) 1.423(2), N(2)−C(2) 1.289(3), C(1)−C(6) 1.344(5), C(1)−C(2) 1.479(3); N(1A)−Li(1)−N(2) 122.3(2), N(1A)−Li(1)−N(1) 105.6(2), N(2)−Li(1)−N(1) 82.0(1), C(7)−N(1)−C(1) 116.0(2), C(7)−N(1)−Li(1A) 126.1(2), C(1)−N(1)−Li(1A) 113.3(1), C(7)−N(1)−Li(1) 107.9(2), C(1)−N(1)−Li(1) 109.2(1), Li(1A)-N(1)−Li(1) 74.0(2), C(2)−N(2)−Li(1) 114.0(2).

the data collection and refinement are given in Table S1 (Supporting Information). Compound **3** exists as a dimer in the crystal with Li$_2$N$_2$ core. Every lithium atom is surrounded by three nitrogen atoms and one oxygen atom of THF molecule. The cyclohexyl groups in the dimer and both THF molecules are disordered over two positions.

The anionic Li(1)−N(1) bond distance in the five-membered ring (2.092(4) Å) is not much longer than the coordination bond length Li(1)−N(2) (2.062(4) Å). The planar geometry of the chelate cycle is determined by the rigid framework, containing sp^2 carbons with the N(1)C(1)C(2)N(2) torsion angle of

$-1.2(3)°$. After the sparingly soluble in ether complex **1** was separated, we distilled off the volatile products in vacuo for analysis. Chromatography−mass spectrometry measurements allowed us to detect dicyclohexylamine (the major product), aniline, and *N*-cyclohexylidenecyclohexanamine **5** as a minor product since it reacts further with dicyclohexylaminyl radical (Scheme 3, eq 2). In order to detect the other products formed in the reaction of Cy₂NLi with azobenzene, we performed hydrolysis of the residue in anaerobic conditions and found the expected free base **4** (Scheme 4), aniline, and azobenzene

Scheme 4. Hydrolysis of 3
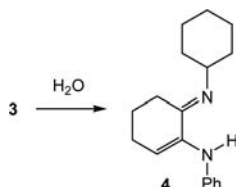
(formed from reaction of remaining **1** with water) (Figure S3, Supporting Information). No hydrazobenzene was found. The mechanism rationalizing the formation of **3** and the other products is shown in Scheme 3 (eqs 1−3).

It is known that aminyl radicals can easily disproportionate to give amines and imines[15] (eq 2). On the other hand, these radicals possess strong hydrogenative properties and abstract allylic hydrogens preferrably[15b] (eq 3).

Using chromatography−mass spectrometry measurements, we found only negligible amounts of 1,2-diphenylhydrazine in the products of the reaction. Hence, no hydrogen transfer from Cy₂NLi to azobenzene occurred. In the control experiment, we confirmed that aniline is formed before hydrolysis of the reaction mixture. It is reasonable to assume that the transient complex **7** turned to **3** with aniline extrusion according to eq 3 (Scheme 3 and Scheme S1). Nevertheless, we cannot exclude the related formation mechanisms of **3** involving enamide anion, which might add to azobenzene to form the hydrazide anion and following processes including aniline extrusion (Supporting Information, Scheme S1). Enamide anion may appear due to deprotonation of **5** or reduction of **6** by Cy₂NLi:
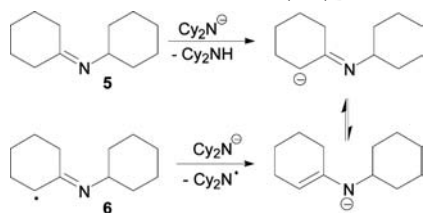

We have previously shown that cleavage of the nitrogen−nitrogen bond in anionic hydrazide complexes is promoted by a negative charge at the hydrazido nitrogen.[16] It should be noted also that this charge is increased by coordination of a donor atom to a metal (N → Li in our case). On the other hand, a computational evaluation showed that the six-membered ring 1,2-imine−enamines are more thermodynamically stable than the other tautomers (1,2-bis-imines, 1,2-bis-enamines).[17] These data are in agreement with the structure of the separated product **3**.

Subsequently, we tested the reactivity of benzalaniline (closely related to azobenzene compound) toward Cy₂NLi. This clean reaction proceeds slowly (24 h at room temperature) to form the

dilithium salt of $N^1,N^2,1,2$-tetraphenylethene-1,2-diamine **8** (Scheme 5). No EPR signals were detected.

**Scheme 5. Reaction of Benzalaniline with Cy₂NLi**
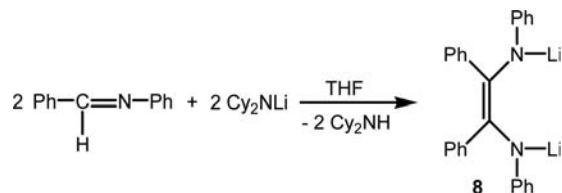
In order to elucidate the structure of compound **8** (since it has not been possible to isolate single crystals), the resulted solid was treated with an excess of chlorotrimethylsilane. The silylated product **9** was obtained in nearly quantitative yield (Scheme 6). No other products were detected in this reaction.

Scheme 6. Preparation of 9
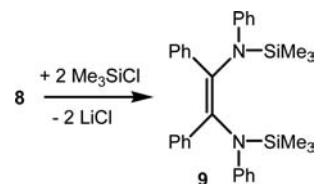
The X-ray crystal structure of **9** (Figure S2 and Table S1, Supporting Information) reveals the formation of the *Z*-isomer of $N^1,N^2,1,2$-tetraphenyl-N^1,N^2-bis(trimethylsilyl)ethene-1,2-diamine.

The nitrogen atoms in **9** exhibit a trigonal planar geometry with sum of angles $359.2°$. The alkene core has a little deviation from idealized planar geometry. The angle between planes C(9)C(2)N(2) and C(3)C(1)N(1) is $10.9(1)°$.

Interestingly, substituted Schiff bases having an $-RC{=}N-$ group instead of $-HC{=}N-$ react with LDA by an addition mechanism or α-hydrogen abstraction from the R substituent (Scheme 7).[18]

Scheme 7. Reactions of Schiff Bases with LDA[18]
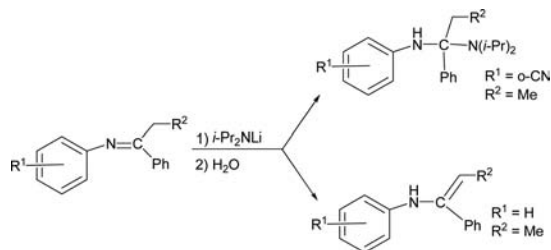
It should be noted that a more sterically hindered base, lithium 2,2,6,6-tetramethylpiperidide, reacts only as a proton abstractor.

It is also known that some nucleophilic bases, such as cyanide anions, may catalyze intermolecular aldimine coupling (Scheme S2, Supporting Information)[19] to form six possible isomeric products including optical isomers (Scheme S3, Supporting Information). In our case, lithiation and association of lithium cations with nitrogen atoms exclusively promoted the formation of *Z*-isomer. We tend to consider proton ($-HC{=}N-$) abstraction by Cy₂NLi as the first step of the reaction since there was no addition product observed (Scheme 8).

Scheme 8. Proposed Mechanism of Benzalaniline Coupling with Cy$_2$NLi
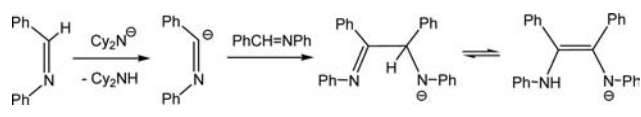
Dicyclohexylamide anion seems to be more hindered than diisopropylamide, and its behavior is similar to that of the 2,2,6,6-tetramethylpiperidide anion, which gave no addition product with aldimines.[17]

In summary, we have shown that the interaction of azobenzene with lithium dicyclohexyl- and diisopropylamides proceeded via an electron-transfer step to form the ion-radical salt of azobenzene (**1**), which is a coordination polymer in crystal. Imino—enamido lithium complex (**3**), the second product of the reaction of Cy$_2$NLi with azobenzene, resulted from the consecutive transformation of dicyclohexylaminyl radical. On the contrary, benzalaniline reacted with Cy$_2$NLi without electron transfer by a proton-abstraction mechanism to form the dilithium salt of N^1,N^2,1,2-tetraphenylethene-1,2-diamine quantitatively.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.5b02860.

> Experimental procedures and characterization data of new compounds **1**−**3**, **8**, and **9** (PDF)
> X-ray data for **1**−**3** and **9** (CIF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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