ORGANOMETALLICS

DFT Studies on the Reaction Mechanisms of 1,4-Dilithio 1,3-Dienes with Nitriles

Fei Zhao,[†] Ming Zhan,[†] Wen-Xiong Zhang,[†] and Zhenfeng Xi*,^{†,‡}

[†]Beijing National Laboratory for Molecular Sciences (BNLMS), Key Laboratory of Bioorganic Chemistry and Molecular Engineering of Ministry of Education, College of Chemistry, Peking University, Beijing 100871, People's Republic of China

[‡]State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Shanghai 200032, People's Republic of China

Supporting Information

ABSTRACT: Mechanisms for the reactions of 1,4-dilithio-1,3-butadienes and nitriles are explored through both experiments and DFT calculations. The computational results suggest that the selectivity of these reaction systems is strongly affected by the structures of the substrates. As the first step of all reaction pathways, the addition intermediate of one C–Li bond to the nitrile is formed. When tetraalkyl-substituted 1,4dilithio 1,3-dienes and 2-cyanopyridine are used, the intermediate gives the cyclopentadienyl amine product as the kinetic product because of the coordination of the pyridyl N



atom to the lithium atoms (system B). This addition intermediate also undergoes a second nitrile insertion into the C–Li bond, giving the dilithio ketimine intermediate. When tetraalkyl-substituted 1,4-dilithio 1,3-dienes and aryl nitriles are used, the dilithio ketimine intermediate undergoes a 1,6-cyclization, generating pyridine and triazine products through thermodynamically favored pathways (systems A and B). When cyclic 1,4-dilithiobutadiene and tertiary aliphatic nitriles are used, the dilithio ketimine intermediate undergoes two sequential 1,5-cyclization steps with a lower energy barrier, generating tricyclic Δ^1 -bipyrrolines (system C). Experimentally, the lithium-containing triazine intermediate 10 and Δ^1 -bipyrroline intermediate 19 have been isolated and their structures investigated through NMR and quenching experiments. The calculation results clearly show the mechanism details of these reactions and are in good agreement with the experimental observations.

INTRODUCTION

The reaction of organolithium reagents with nitriles is of fundamental interest in organometallic chemistry and organic synthesis.^{1,2} In recent years, we have systematically studied the reactions of 1,4-dilithio 1,3-dienes.^{3,4} Among these, the reaction of 1,4-dilithio 1,3-dienes with nitriles have interested us very much.^{4c,j} It was found that, depending on the substitution pattern of the dilithio skeleton and the nitrile used, three types of reactions took place: the reaction of 1,2,3,4-tetrasubstituted 1,4-dilithio 1,3-diene 1a with various nitriles (e.g., benzonitrile) afforded the pyridine derivative 2a in good yields. Along with the formation of 2a (Scheme 1, type I), the triazine 3a was also formed with 1, 2, or 3 equiv of benzonitrile (PhCN).^{4c} A 4 equiv amount of benzonitrile should be used to ensure high yields of product 2a. When 2-cyanopyridine was used and the reaction was carried out at a lower temperature $(-60 \ ^{\circ}C)$, the cyclopentadienyl amine 4a was isolated in 23% yield, along with a 66% yield of 2b (Scheme 1, type II). Increasing the reaction temperature from -60 °C to room temperature or even 50 °C did not change the yields of products 4a and 2b, indicating that the formation of 2b might be independent of the precursor of 4a. In this case 4 equiv of 2-cyanopyridine was also required and the triazine 3b was obtained in over 70% yield. However, when cyclic 1,4-dilithio 1,3-dienes 5 were applied, their reactions with 2 equiv of various nitriles resulted in the formation of a series of tricyclic Δ^1 -bipyrrolines 6 in good yields (Scheme 1, type III). No formation of the triazine derivative 3c was observed even with 4 equiv of nitrile, indicating the reaction mechanism for the formation of 6 should be different from that for the pyridine derivatives 2a,b.

The observed diverse reaction patterns of the dilithio reagents with nitriles prompted us to investigate the reaction mechanisms in depth. In this paper, we report our experimental and computational analysis on possible reaction pathways.

RESULTS AND DISCUSSION

Experimental Results. In 1980, Schleyer studied the structure of 1,4-dilithio 1,3-dienes via computation.⁵ It is revealed that a symmetrically bridged structure should be the most stable. The existence of the double lithium bridge has been proved by several crystal structures.⁶ A series of experiments have been carried out to explore the mechanism of the reaction of 1,4-dilithio 1,3-dienes with nitriles.

The 1,4-dilithio 1,3-diene derivative **1b** contains two C–Li bonds; thus, it could react with one or two molecules of nitriles,

Received: September 10, 2012 Published: March 19, 2013







Scheme 3. Formation and Isolation of Intermediate 10



Scheme 4. Quenching Reactions of 10



generating one or two *N*-lithio ketimine groups, respectively. To obtain the information about the intermediates, the reaction of benzonitrile with **1b** was performed at -78 °C for 30 min. After quenching, the reaction mixture was analyzed by GC-MS and a new product **8** was observed with an m/z value of 269. These results supported the formation of the *N*-lithio ketimine intermediate **9b** with one C–Li bond unreacted (Scheme 2).

Scheme 5. Proposed Mechanism for the Formation of the Pyridines and Triazines



Scheme 6. Proposed Mechanism for the Formation of the Cyclopentadienyl Amine



Scheme 7. Mechanism for the Formation of the Tricyclic Δ^1 -Bipyrrolines



Scheme 8. Substrates of Three Reaction Systems



To obtain the organolithium intermediates before quenching, **1b** was allowed to react with benzonitrile in diethyl ether for 3 h at room temperature. Workup of this reaction mixture in a glovebox separated the pyridine derivative 2c and the unknown product **10**. The ¹³C NMR spectrum of **10** showed only a

Scheme 9. Nitrile Insertion Steps and Relative Energies^a



^aCoordinated solvent molecules are omitted for clarity.



Figure 1. DFT-optimized structures of doubly lithium bridged intermediates IMA1, IMA2a, and IMA3 and singly lithium bridged intermediate IMA2c. Coordinated solvent molecules are omitted for clarity. Selected atom distances (in Å): IMA2a, C1-C5 = 3.260; IMA2c, C1-C5 = 2.924.

Scheme 10. Proposed Reaction Pathway from IMA2a to IMA5



broad peak at 120-130 ppm, indicating that the product **10** should contain only sp²-C bonds. According to the in situ NMR spectra, pyridines were formed in the reaction process, which indicates that product **10** is an organolithium compound. Quenching of **10** afforded triazine **3a** as the only organic product.⁷ On the basis of all these observations, the structures of **10** are proposed and shown in Scheme **3**.

We had tried our best to obtain the crystal structure of **10** in the glovebox many times. However, only quenched product triazine **3a** was obtained, probably because **10** is highly reactive. We then turned to explore **10** via quenching with different electrophiles.

Several commonly used electrophiles, such as MeI, Et_3OBF_4 , and alkyl bromides, have been tested, affording 11a-e as the corresponding products. However, these products were not stable and quickly turned to triazine 3a (Scheme 4). The driving force to form the aromatic ring might explain the instability of 11a-e.

On the basis of the experimental results above, a plausible mechanism is proposed (Scheme 5). Insertion of the nitrile into one C–Li bond of 1 generates *N*-lithio ketimine intermediate 9. Then a similar process between 9 and a second molecule of nitrile results in the 1,8-dilithium intermediate 11. 6π cyclization of 11 affords 12. After 12 is formed, another two molecules of nitriles participate in the reaction to give 14 with a long side chain. Cyclization of this side chain generates another six-membered ring in the molecule and gives 15a or 15b. Finally, the key intermediate 10 is eliminated from 15a or 15b, generating the aromatic pyridine derivative 2. Quenching of 10 with water affords triazine 3.



Figure 2. DFT-calculated potential energy surfaces of pathways a and b in system A. Coordinated solvent molecules are omitted for clarity.



Figure 3. DFT-calculated potential energy surfaces of pathway c in system A. Coordinated solvent molecules are omitted for clarity.



Figure 4. DFT-optimized structures of transition states in system A. Coordinated solvent molecules are omitted for clarity.

Using 2-cyanopyridine instead of benzonitrile would generate multisubstituted pyridine, triazine, and cyclopentadienyl amine as products (reaction type II). The proposed mechanism of the formation of cyclopentadienyl amine was reported by our group in 2008 (Scheme 6).^{4a}

The reaction of cyclic 1,4-dilithio 1,3-dienes 5 and 2 equiv of trimethylacetonitrile forms Δ^1 -bipyrroline 6a in good yields after quenching. We tried to get the corresponding lithium-containing intermediate. After washing with Et₂O, a solid product was collected. Quenching this solid with DCl yielded 6a-D as the sole product. The ¹H NMR spectrum of this solid showed no alkenyl hydrogen, indicating lithium atoms are adjacent to carbon atoms. As the precursor of 6a, the structure of 19 is proposed as shown in Scheme 7.

Computational Results. To further investigate mechanisms of these processes, DFT calculations were carried out to find these reaction pathways leading to three different types of products. According to the experimental results, the reaction between 1,4-dilithio-1,3-butadienes and nitriles would result in three pathways after quenching: (a) pyridine derivatives, (b) bipyrrolines, and/or (c) cyclopentadienyl amine. To our knowledge, one of the most dominant factors affecting the chemoselectivity is the structure of substrates. Thus, we focused on three structurally different substrate systems (Scheme 8). The calculations were carried out at the PBE1PBE/6-31G(d) level,⁸ and the results are discussed in the following sections.

At first, we tried to explore the potential energy surfaces of the reaction pathways using 1,2,3,4-tetramethyl-1,4-dilithio-1,3-

Article



Figure 5. DFT-calculated potential energy surfaces of pathways a and b in system B. Coordinated solvent molecules are omitted for clarity.



Figure 6. DFT-calculated potential energy surfaces of pathway c in system B. Coordinated solvent molecules are omitted for clarity.

butadiene (with two diethyl ethers as coordinated solvent molecules) and benzonitrile as the substrates (Scheme 8, system A). Previously, both experimental⁶ and computational^{5,9} studies have showed that the doubly lithium bridged structure **IMA1** is the most stable configuration. Insertion of the first nitrile into one C–Li bond generates the 1,6-dilithium intermediate **IMA2a**. A similar process between **IMA2a** and the second nitrile results in the 1,8-dilithium intermediate **IMA3** (Scheme 9). Our calculations suggest that **IMA2a** and **IMA3** also show doubly lithium bridged configurations (Figure 1). Each insertion of a nitrile molecule decreases the free energy of the whole system, suggesting that these nitrile insertion processes are thermodynamically favored.

The two cyclization types of **IMA3** lead to two different pathways: 1,6-cyclization results in the six-membered-ring product **IMA7**, and 1,5-cyclization results in the bicyclic product **IMA9**. Experimentally, the pyridine derivative **IMA6** is formed before quenching, and 1,3,5-triazine was found after workup. On the basis of this result, intermediate **IMA7** is proposed to undergo further reaction. A PhC(Li)=NLi moiety is eliminated from **IMA7** and reacts with benzonitrile to form



Figure 7. DFT-optimized structures of **IMB2a**, **IMB2c**, **IMB4**, and **TSB4**. Coordinated solvent molecules are omitted for clarity. Selected atom distances (in Å): **IMB2a**:, C1–C5 = 3.170; **IMA2c**, C1–C5 = 2.924, C1–Li1 = 2.081, N1–Li1 = 2.006, N1–Li2 = 1.916, N2–Li2 = 2.021; **TSB4**, C1–C5 = 2.084, C1–Li1 = 2.124, N1–Li1 = 2.126, N1–Li2 = 1.864, N2–Li2 = 2.008.

triazine derivative **IMA10**. This process decreases the Gibbs free energy even more (Figure 2, pathway a).

It is too difficult for **IMA2a** to transform to pyridine derivative **IMA5** via 6π cyclization, as lithium-adjacent carbon and nitrogen atoms both contain a negative charge. The transition state of 6π cyclization of **IMA2a** is also not found (Scheme 10).

On the other hand, 1,5-cyclization of IMA3 gives intermediate IMA8, which undergoes another 1,5-cyclization process to generate bicyclic intermediate IMA9 (Figure 2, pathway b). In this system, the pyridine pathway gives more stable products, although the energy barrier is higher than for the bipyrroline pathway. The calculation results above are in



Figure 8. DFT-calculated potential energy surfaces of pathways a and b in system C. Coordinated solvent molecules are omitted for clarity.



Figure 9. DFT-calculated potential energy surface of pathway c in system C. Coordinated solvent molecules are omitted for clarity.

agreement with the fact that only pyridine and triazine products are formed in the type I reaction.

The potential energy surface of pathway c is shown in Figure 3. The intermediate IMA2a changes to the isomer IMA2c before the formation of cyclopentadienyl amine IMA4. Since one of the lithium bridges is broken, the energy of IMA2c is higher than that of IMA2a. The C1–C5 distances in IMA2a and IMA2c are 3.366 and 2.924 Å, respectively (Figure 1). These data clearly indicate that IMA2c is more sterically favored for the intramolecular addition, despite the lack of stabilization from the double lithium bridge. However, the Gibbs free energy of IMA4 is similar to that of IMA2a and is much higher than that of IMA3. This is probably because of the destruction of the double lithium bridge in IMA2c. As a result, IMA4 cannot be formed as the final product. Optimized structures of all transition states of system A are shown in Figure 4.

In system B, the pathways to the pyridine and the bipyrroline products are found to be similar to those in system A. The Gibbs free energy in solution of **TSB3** is -28.3 kcal/mol, 6.5 kcal/mol lower than **TSB6**, indicating that pathway a has a lower energy barrier than pathway b. The final products of pathway a (**IMB6** and **IMB10**) are also thermodynamically more stable than that of pathway b (Figure 5). These results

clearly show that pathway a is more favored than pathway b and are in agreement with the experiments.

In the experiments, system B is the only case to afford the cyclopentadienyl amine product. This result is also supported by DFT calculations. The result indicates that **IMB2c** is more stable than **IMB2a** in free energy (Figure 6). Although the C1–C5 distances in these two structures are almost the same (3.170 Å for **IMB2a** and 3.195 Å for **IMB2c**), the N2–Li2 distances in **IMB2c** and **TSB4** clearly show the strong coordination effect of the pyridyl group to the lithium atom (Figure 7). This could explain the stabilization of **IMB2c**. For the same reason, the free energy of **IMB4c** is lower than that of either **IMB2c** or **IMB2a**. The barrier of each step toward **IMB4** is reasonable. The results above show that **IMB4** could be formed under the appropriate conditions as the kinetic product.

In system C, the pathways leading to the pyridine derivative and the bipyrroline derivative also diverge at the stationary point IMC3. The energy barriers of pathway b starting from IMC3 to IMC9 (13.1 kcal/mol) are much lower than that of pathway a starting from IMC3 to IMC7 (21.4 kcal/mol). Consideration of the entire pathways gives a similar result: for pathway a, the rate-determining step is the cyclization step (via TSC3) with an energy barrier of 21.4 kcal/mol; for pathway b, the rate-determining step is the addition of the first ^tBuCN (via TSC1) with an energy barrier of 15.4 kcal/mol. These results show that the bipyrroline product is kinetically favored in system C and are in good agreement with the experimental results (Figure 8).

The energy profiles of system C with cyclic 2,3-disubstituted 1,4-dilithiobutadiene and *tert*-butyl cyanide as the starting materials is shown in Figure 9. Pathway c leading to cyclopentadienyl amine is strongly thermodynamically disfavored, since the free energy of IMC4 is too high. The large C1–C5 distance in IMC2a (3.306 Å) also shows that transformation of IMC2a to IMC4 is disfavored. It should be noted that the structure of IMC2c does not exist as a stationary point, probably due to the steric hindrance of the ^tBu group in IMC2a.

In DFT calculations, it is found that the six-membered ring could have either a chair or a boat configuration. In the structure of **IMC1**, the cyclic ring exhibits a boat configuration, because the boat configuration could keep the butadiene moiety coplanar and thus minimize the energy of the lithium



Figure 10. DFT-optimized structures of stationary points in system C. Coordinated solvent molecules are omitted for clarity. Selected atom distance (in Å): IMC2, C1-C5 = 3.306.

bridges. In other stationary points, it is not necessary for the butadiene moiety to be coplanar; thus, the chair configuration is most favored (Figure 10).

Although triazines are obtained along with pyridines after quenching, the structures of the precursors of triazines, however, are still unknown in the experiments. We have proposed two types of precursors: one involves three nitriles, and the other involves four. Both types of structures should involve two lithium atoms. After full optimization, **IMA10**, **IMB10**, and **IMC10** show similar configurations, while **IMA11**, **IMB11**, and **IMC11** look much different: **IMA11** involves a dilithio bridge moiety; the configuration of **IMB11** is almost planar with all rings and lithium atoms involved; **IMC11** does not have any lithium bridge, and the triazine ring shows boat configuration (this configuration is similar to **IMA5**). For systems A and C, IM10 is more stable than IM11. For system B, IMB11 has a lower free energy than IMB10. Still, the structures with higher free energy could not be ruled out. Taking the case of system A, calculations show that IMA10 is 16.4 kcal/mol more stable than IMA11. In the structure of IMA10, the two lithium atoms are chelated by three nitrogen atoms. In the structure of IMA11, it seems that the lithium atoms are coordinated with "aza-allylic" systems (Figure 11). IMA11 is more in line with the experimental fact that the intermediate "lithium triazine" is highly sensitive to air and moisture and is difficult to test by XRD. Hence, both structure types are possible and the real structures of the "lithium triazine" need further crystallographic work.



Figure 11. Structures and potential energies of IM10 and IM11. Coordinated solvent molecules are omitted for clarity. ΔG_{sob} , ΔG_{gas} (in parentheses), and ΔH_{gas} values (in brackets) are given in kcal/mol.

CONCLUSIONS

In summary, we have investigated mechanisms for the reactions of 1,4-dilithio-1,3-butadienes and nitriles through both experiments and DFT calculations. In the type I reaction, the pyridine derivatives are formed before quenching. The lithiumcontaining triazine intermediates have been isolated and their structures explored through various quenching experiments. The computational results suggest that the selectivity of these reaction systems is strongly affected by substrates: tetraalkylsubstituted 1,4-dilithio-1,3-butadienes and aryl nitriles (e.g., benzonitrile and pyridylnitrile) give pyridine and triazine products (systems A and B), while cyclic 2,3-disubstituted 1,4-dilithiobutadiene 5 and tertiary aliphatic nitriles generate Δ^1 -bipyrrolines (system C). In system B, the cyclopentadienyl amine product is formed as the kinetic product due to the coordination of the pyridyl group to a lithium atom. These calculation results are in good agreement with experimental observations.

EXPERIMENTAL SECTION

General Methods. All reactions were conducted under a slightly positive pressure of dry nitrogen using standard Schlenk line techniques or under a nitrogen atmosphere in a Mikrouna Super (1220/750) glovebox. The nitrogen in the glovebox was constantly circulated through a copper/molecular sieves catalyst unit. The oxygen and moisture concentrations in the glovebox atmosphere were monitored by an O_2/H_2O Combi-Analyzer to ensure both were always below 1 ppm. Unless otherwise noted, all starting materials were commercially available and were used without further

purification. Solvents were purified by an Mbraun SPS-800 Solvent Purification System and dried over fresh Na chips in the glovebox. "BuLi and 'BuLi were obtained from Acros.

Organometallic samples for NMR spectroscopic measurements were prepared in the glovebox by use of J. Young valve NMR tubes (Wilmad 528-JY). 1 H and 13 C NMR spectra were recorded on a Bruker-400 spectrometer (FT, 400 MHz for 1 H; 100 MHz for 13 C) or a JEOL-AL300 spectrometer (FT, 300 MHz for 1 H; 75 MHz for 13 C) at room temperature, unless otherwise noted.

Synthesis and Isolation of Dilithium Triazine (10). 1,2,3,4-Tetraethyl-1,4-dilithiobuta-1,3-diene (1b) was prepared according to the literature.^{3a} To a solution of 1b (1.78 g, 10.0 mmol) in 50.0 mL of Et₂O in a 200 mL Schlenk tube was added PhCN (4.12 g, 40.0 mmol) at -78 °C (dry ice/acetone); the mixture was stirred for 5 min and then was warmed to room temperature. After the mixture was stirred for 3 h, the Schlenk tube was transferred to the glovebox. Then 175.0 mL of Et₂O was added to the mixture with vigorous stirring. Filtration separated the mixture to the filtrate and a solid part. The solid part was washed with a solvent mixture (petroleum ether/ethyl ether 4/1). The solvent was evaporated under vacuum to give product 10.

Procedure for the Trapping of 9b. To a solution of 1b (178 mg, 1.0 mmol) in 5.0 mL of Et_2O in a 50 mL Schlenk tube was added PhCN (412 mg, 4.0 mmol) at -78 °C (dry ice/acetone). After it was stirred for 30 min at -78 °C, the mixture was quenched with saturated aqueous NaHCO₃. When the sample was analyzed by GC-MS, the new product 8 was found with an m/z value of 269 except for PhCN and 1,2,3,4-tetraethylbuta-1,3-diene. These results indicated the formation of the N-lithio ketimine intermediate **9b** with one C–Li bond left.

Procedure for Quenching Reactions of 10. To a solution of 10 (338 mg, 1.0 mmol) in 5.0 mL of Et_2O in a 50 mL Schlenk tube was added an electrophile (MeI, Et_3OBF_4 , RBr, etc.) at -78 °C (dry ice/

Organometallics

acetone). Then the mixture was warmed to room temperature and stirred for 2 h. Because the product is easily decomposed into triazine 3, the solvent mixture was evaporated under vacuum directly. The crude products were characterized by NMR.

Computational Methods. All calculations were carried out with the GAUSSIAN 03 program package.¹⁰ All the minima and transition states were fully optimized at the PBE1PBE level¹¹ using the 6-31G(d) basis set. Harmonic frequency calculations were performed at the same level for every structure to confirm it as a local minimum or transition state and to derive the thermochemical corrections for enthalpies and free energies. The intrinsic reaction coordinate (IRC) analysis¹² was carried out throughout the pathways to confirm that all stationary points are smoothly connected to each other. Solvent effects in Et₂O ($\varepsilon = 4.335$) were evaluated by single-point calculations using the PCM model¹³ for all the stationary points. All enthalpies and Gibbs free energies in the text are given in kcal/mol and were calculated under standard conditions (298 K, 1 atm). All distances are given in Å.

ASSOCIATED CONTENT

Supporting Information

Text, figures, and tables giving experimental procedures and computational details. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*E-mail for Z.X.: zfxi@pku.edu.cn.

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by the NSFC and the 973 Program (2011CB808700). We thank Prof. Zhi-Xiang Yu of Peking University and Prof. Yuxue Li of Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, for insightful discussions and comments.

REFERENCES

(1) (a) Kamau, M. G.; Harikrishnan, L. S.; Finlay, H. J.; Qiao, J. X.; Jiang, J.; Poss, M. A.; Salvati, M. E.; Wexler, R. R.; Lawrence, R. M. Tetrahedron 2012, 68, 2696. (b) Sasada, T.; Aoki, Y.; Ikeda, R.; Sakai, N.; Konakahara, T. Chem. Eur. J. 2011, 17, 9385. (c) Lysen, M.; Madden, M.; Kristensen, J. L.; Vedso, P.; Zoellner, C.; Begtrup, M. Synthesis 2006, 3478. (d) Hansen, H. M.; Lysen, M.; Begtrup, M.; Kristensen, J. L. Tetrahedron 2005, 61, 9955. (e) Foubelo, F.; Yus, M. Curr. Org. Chem. 2005, 9, 459. (f) Langer, P.; Freiberg, W. Chem. Rev. 2004, 104, 4125. (g) Coleman, C. M.; O'Shea, D. F. J. Am. Chem. Soc. 2003, 125, 4054. (h) Najera, C.; Sansano, J. M.; Yus, M. Tetrahedron 2003, 59, 9255. (i) Ichikawa, J.; Wada, Y.; Miyazaki, H.; Mori, T.; Kuroki, H. Org. Lett. 2003, 5, 1455. (j) Kristensen, J. L.; Vedso, P.; Begtrup, M. J. Org. Chem. 2003, 68, 4091. (k) Lysen, M.; Kristensen, J. L.; Vedso, P.; Begtrup, M. Org. Lett. 2002, 4, 257. (1) Pawlas, J.; Begtrup, M. Org. Lett. 2002, 4, 2687. (m) Pawlas, J.; Vedso, P.; Jakobsen, P.; Huusfeld, P. O.; Begtrup, M. J. Org. Chem. 2001, 66, 4214. (n) Ball, S. C.; Davies, R. P.; Raithby, P. R.; Shields, G. P.; Snaith, R. J. Organomet. Chem. 1998, 550, 457. (o) Seyferth, D.; Hui, R. C.; Wang, W. J. Org. Chem. 1993, 58, 5843. (p) Armstrong, D. R.; Clegg, W.; MacGregor, M.; Mulvey, R. E.; O'Neil, P. A. J. Chem. Soc., Chem. Commun. 1993, 608. (q) Jakiela, D. J.; Helquist, P.; Jones, L. D. Org. Synth. 1984, 62, 74. (r) Cook, L. S.; Wakefield, B. J. J. Chem. Soc., Perkin Trans. 1 1980, 2392. (s) Cook, L. S.; Wakefield, B. J. Tetrahedron Lett. 1976, 17, 147. (t) Berry, D. J.; Cook, J. D.; Wakefield, B. J. J. Chem. Soc., Perkin Trans. I **1972**, 2190. (u) Berry, D. J.; Wakefield, B. J. J. Chem. Soc. (C) **1971**, 642. (v) Scala, A. A.; Bikales, N. M.; Becker, E. I. J. Org. Chem. **1965**, 30, 303. (w) Anker, R. M.; Cook, A. H. J. Chem. Soc. **1941**, 323.

(2) For recent progress on di- and polylithium chemistry, see: (a) Fraenkel, G.; Chen, X.; Chow, A.; Gallucci, J. J. Org. Chem. 2013, 78, 1149. (b) Screttas, C. G.; Steele, B. R.; Micha-Screttas, M.; Heropoulos, G. A. Org. Lett. 2012, 14, 5680. (c) Smith, K.; El-Hiti, G. A.; Alshammari, M. B. J. Org. Chem. 2012, 77, 11210. (d) Fischer, R.; Suxdorf, R.; Görls, H.; Westerhausen, M. Organometallics 2012, 31, 7579. (e) Ichibakase, T.; Nakajima, M. Org. Lett. 2011, 13, 1579. (f) Le, T. T.; Chau, N. T. T.; Nguyen, T. T.; Brien, J.; Thai, T. T.; Nourry, A.; Castanet, A.-S.; Nguyen, K. P. P.; Mortier, J. J. Org. Chem. 2011, 76, 601. (g) Aillaud, I.; Olier, C.; Chapurina, Y.; Collin, J.; Schulz, E.; Guillot, R.; Hannedouche, J.; Trifonov, A. Organometallics 2011, 30, 3378. (h) Lee, V. Ya.; Sekiguchi, A. Inorg. Chem. 2011, 50, 12303. (i) Ma, G.; Ferguson, M. J.; McDonald, R.; Cavell, R. G. Inorg. Chem. 2011, 50, 6500. (j) Ma, G.; Ferguson, M. J.; McDonald, R.; Cavell, R. G. Organometallics 2010, 29, 4251. (k) Aharonovich, S.; Botoshanski, M.; Rabinovich, Z.; Waymouth, R. M.; Eisen, M. S. Inorg. Chem. 2010, 49, 1220. (l) Hsu, Y.-L.; Liang, L.-C. Organometallics 2010, 29, 6201. (m) De Vries, T. S.; Bruneau, A. M.; Liou, L. R.; Subramanian, H.; Collum, D. B. J. Am. Chem. Soc. 2013, 135, 4103.

(3) For recent reviews, see: (a) Xi, Z. Acc. Chem. Res. 2010, 43, 1342.
(b) Zhang, W.-X.; Xi, Z. Pure Appl. Chem. 2009, 81, 235. (c) Xi, Z.; Zhang, W.-X. Synlett 2008, 2557. (d) Xi, Z. Bull. Chem. Soc. Jpn. 2007, 80, 1021. (e) Xi, Z. Eur. J. Org. Chem. 2004, 2773. See also: (f) Varela, J. A.; Saá, C. Chem. Rev. 2003, 103, 3787.

(4) (a) Liu, L.; Zhang, W.-X.; Wang, C.; Wang, C.-Y; Xi, Z. Angew. Chem., Int. Ed. 2009, 48, 8111. (b) Luo, Q.; Wang, C.; Zhang, W.-X.; Xi, Z. Chem. Commun. 2008, 1593. (c) Yu, N.; Wang, C.; Zhao, F.; Liu, L.; Zhang, W.-X.; Xi, Z. Chem. Eur. J. 2008, 14, 5670. (d) Wang, C.; Luo, Q.; Sun, H.; Guo, X.; Xi, Z. J. Am. Chem. Soc. 2007, 129, 3094. (e) Wang, C.; Yuan, J.; Li, G.; Wang, Z.; Zhang, S.; Xi, Z. J. Am. Chem. Soc. 2006, 128, 4564. (f) Fang, H.; Li, G.; Mao, G.; Xi, Z. Chem. Eur. J. 2004, 10, 3444. (g) Wang, C.; Song, Q.; Xi, Z. Tetrahedron 2004, 60, 5207. (h) Li, G.; Fang, H.; Zhang, S.; Xi, Z. Tetrahedron Lett. 2004, 45, 8399. (i) Li, G.; Fang, H.; Xi, Z. Tetrahedron Lett. 2003, 44, 8705. (j) Chen, J.; Song, Q.; Wang, C.; Xi, Z. J. Am. Chem. Soc. 2002, 124, 6238. (k) Chen, J.; Song, Q.; Xi, Z. Tetrahedron Lett. 2002, 43, 3533. (1) Chen, J.; Song, Q.; Li, P.; Guan, H.; Jin, X.; Xi, Z. Org. Lett. 2002, 4, 2269. (m) Xi, Z.; Song, Q.; Chen, J.; Guan, H.; Li, P. Angew. Chem., Int. Ed. 2001, 40, 1913. (n) Song, Q.; Chen, J.; Jin, X.; Xi, Z. J. Am. Soc. Chem. 2001, 123, 10419. (o) Xi, Z.; Song, Q. J. Org. Chem. 2000, 65, 9157. See also: (p) Seyferth, D.; Weinstein, R. M. J. Am. Soc. Chem. 1982, 104, 5534. (q) Seyferth, D.; Hui, R. C.; Wang, W.-L. J. Org. Chem. 1993, 58, 5843. (r) Tacke, M. Chem. Ber. 1995, 128, 1051. (s) Tacke, M. In Organosilicon Chemistry III: From Molecules to Materials; Wiley-VCH: Weinheim, Germany, 1998; Chapter 12, p 70. (5) Kos, A. J.; Schleyer, P. v. R. J. Am. Chem. Soc. 1980, 102, 7928. (6) (a) Liu, L.; Zhang, W.-X.; Luo, Q.; Li, H.; Xi, Z. Organometallics 2010, 29, 278. (b) Saito, M.; Nakamura, M.; Tajima, T.; Yoshioka, M. Angew. Chem., Int. Ed. 2007, 46, 1504. (c) Pauer, F.; Power, P. P. J. Organomet. Chem. 1994, 474, 27. (d) Ashe, A. J., III; Kampf, J. W.; Savla, P. M. Organometallics 1993, 12, 3350. (e) Bauer, W.; Feigel, M.; Müller, G.; Schleyer, P. v. R. J. Am. Chem. Soc. 1988, 110, 6033. (f) Schubert, U.; Neugebauer, W.; Schleyer, P. v. R. J. Chem. Soc., Chem. Commun. 1982, 1184.

(7) For references on the trimerization of nitriles to triazines, see: (a) Zhou, M.; Qiao, X.; Tong, H.; Gong, T.; Fan, M.; Yang, Q.; Dong, Q.; Chao, J.; Guo, Z.; Liu, D. Inorg. Chem. 2012, 51, 4925. (b) Aharonovich, S.; Botoshansky, M.; Waymouth, R. M.; Eisen, M. S. Inorg. Chem. 2010, 49, 9217. (c) Hitchcock, P. B.; Khvostov, A. V.; Lappert, M. F.; Protchenko, A. V. Z. Anorg. Allg. Chem. 2008, 634, 1373. (d) Boesveld, W. M.; Hitchcock, P. B.; Lappert, M. F. J. Chem. Soc., Perkin Trans. 1 2001, 1103. (e) Boesveld, W. M.; Hitchcock, P. B.; Lappert, M. F. T. J. Chem. Soc., Dalton Trans. 1999, 4041. (f) Davies, R. P.; Raithby, P. R.; Shields, G. P.; Snaith, R.; Wheatley, A. E. H. Organometallics 1997, 16, 2223. (g) Armstrong, D. R.; Henderson, K. W.; MacGregor, M.; Mulvey, R. E.; Ross, M. J.; Clegg, W.; O'Neil, P.
A. J. Organomet. Chem. 1995, 486, 79. (h) Berry, D. J.; Cook, J. D.;
Wakefield, B. J. J. Chem. Soc., Perkin Trans. 1 1972, 2190. (i) Ritter, J.
J.; Anderson, R. D. J. Org. Chem. 1959, 24, 208.

(8) For the calculations on organolithium chemistry, PBE1PBE has been proved to be more accurate than B3LYP and many other DFT calculations; see: Ramachandran, B.; Kharidehal, P.; Pratt, L. M.; Voit, S.; Okeke, F. N.; Ewan, M. J. Phys. Chem. A **2010**, *114*, 8423.

(9) Shainyan, B. A.; Sekiguchi, A. J. Mol. Struct. (THEOCHEM) 2005, 728, 1.

(10) Frisch, M. J.; et al. Gaussian 03, Rev. E.01; Gaussian, Inc., Wallingford, CT, 2004.

(11) Perdew, J. P.; Burke, K.; Ernzerhof, M. Phys. Rev. Lett. 1997, 78, 1396.

(12) (a) Fukui, K. Acc. Chem. Res. **1981**, *14*, 363. (b) Gonzalez, C.; Schlegel, H. B. J. Chem. Phys. **1989**, *90*, 2154. (c) Gonzalez, C.; Schlegel, H. B. J. Phys. Chem. **1990**, *94*, 5523.

(13) (a) Barone, V.; Cossi, M. J. Phys. Chem. A **1998**, 102, 1995. (b) Barone, V.; Cossi, M.; Tomasi, J. J. Comput. Chem. **1998**, 19, 404.