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1,4-Dilithio-1,3-dienes: Reaction and Synthetic Applications

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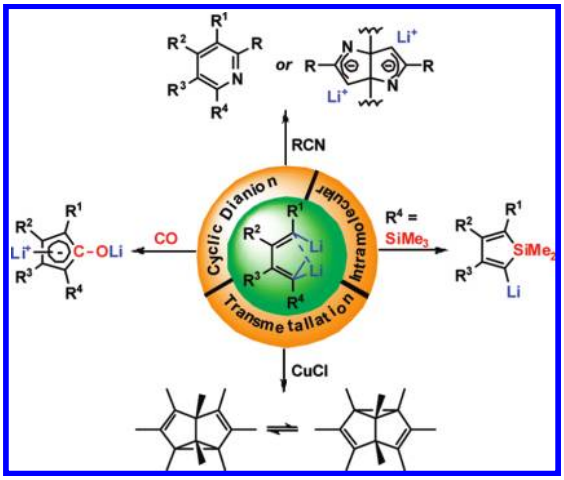

The development of organometallic reagents remains one of the most important frontiers in synthetic chemistry. Commonly used organometallic reagents (such as RLi and RMgBr) are typically monometallic compounds, although they aggregate in many cases. When two carbon—metal bonds are in the same molecule in close proximity, however, these two carbon—metal moieties may exhibit novel reactivity. In this Account, we outline our work on new reactions and synthetic applications of the organo-dilithio reagents 1,4-dilithio-1,3-butadienes.

The 1,4-dilithio-1,3-butadienes can be accessed readily in high efficiency with a wide variety of substitution patterns on the butadienyl skeleton. The configuration has been predicted and demonstrated to favor a double dilithium bridging structure in both solution and solid states. The two Li atoms are bridged by a butadiene moiety and are in close proximity. By taking advantage of this unique configuration, we have developed useful and interesting synthetic methodologies.

Three types of reactions of 1,4-dilithio-1,3-butadienes, termed dilithio reagents here, have been developed and are discussed. An intramolecular reaction is introduced in the first section. The reaction is a result of the intracooperative effect among the two C—Li moieties, the butadienyl bridge, and the substituents. A useful transformation from silylated 1,4-dilithio-1,3-butadienes to α-lithio siloles is described.

Second, we discuss an intermolecular reaction that results from the intercooperative effect of the two C—Li moieties toward substrates. As an example of the formation of functionalized cyclic dianions from the linear dianions of the dilithio reagents and organic substrates, we describe the isolation and structural characterization of a novel type of cyclic dianion; that is, fully substituted oxy-cyclopentadienyl dilithium formed via the reaction of dilithio reagents with CO. We also describe diverse reactions of dilithio reagents with nitriles to form substituted pyridines, tricyclic 1-bipyrrolines, and siloles, demonstrating the remarkable effect of substituents on the butadienyl skeleton.

Third, we discuss transmetalation of dilithio reagents to generate other organo-dimetallic compounds. This section focuses on organo-dicopper compounds and their reactivity toward the synthesis of strained ring systems, such as semibullvalenes and twisted four-membered rings, with the metal-mediated C—C bond-forming approach. In addition to these three representative reactions, other useful applications are also briefly introduced.

The dimetallic 1,4-dilithio-1,3-butadienes and their transmetalated derivatives provide unique synthetic organometallic reagents that are very different from monometallic reagents, both in terms of reactivity and synthetic application. These organo-dimetallic reagents provide access to interesting and useful compounds that are not available by other means. Moreover, given the possibilities afforded, the study of organo-dimetallic and organo-polymetallic compounds should yield further synthetic applications in the near future.

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1. Introduction

It is widely recognized that practical and efficient organometallic reagents, such as organolithium (RLi), Grignard reagents (RMgX), and organocopper (RCu) reagents, etc., can greatly accelerate the advancement of synthesis and related subjects. Consequently, the research and development of organometallic reagents continues to be one of the most important areas in synthetic chemistry. Commonly used organometallic reagents such as RLi and RMgBr are mostly monometallic compounds, although they aggregate in many cases. Conceptually, when two carbon−metal bonds are in the same molecule and in close proximity, these two carbon−metal moieties may exhibit novel reactivity.

Some dilithium or even polylithium compounds show interesting reactivity.[1−3] For example, bis(2-lithioallyl)amines,[3a] 2,9-dilithio-1,4,6,9-decatetraenes,[3b] 3,4-dilithio-2,4-hexadienes,[3c] and lithiophenylalkyllithiums[3d−f] have been prepared, and their reactivities toward carbonyl compounds have been reported. A few of 1,4-dilithio compounds are also known and used as 1,4-dianion precursors for the preparation of main group metalloles.[4]

In 1999, we serendipitously found that substituted 1,4-dilithio-1,3-butadienes (Figure 1, dilithio reagents for short hereafter), exhibit different reactivity patterns than their monolithium analogues toward organic carbonyl compounds.[5,6] We gradually recognized that the cooperative effect between the two C−Li moieties and the butadienyl bridge is essential for realizing such reaction patterns.[6] Since then, our study of the reactions of these dilithio reagents and analogous organodimetallic compounds, such as 1,4-bis(bromomagnesio)-1,3-butadiene derivatives,[7] with various organic substrates has demonstrated that they are useful building blocks and can be applied for the synthesis of diversified cyclic compounds.

Shown in Figure 1 are three representative skeletons of dilithio reagents, to which a wide variety of substitutions on the butadienyl skeleton can be readily introduced. During our research on dilithio chemistry, we have also developed preparative methods for various dihalo compounds, which are used as precursors for dilithio reagents and will not be included in this Account.[8] Herein we would like to discuss the recent accomplishments on dilithio reagents in our group. We will focus on three major reaction patterns: (1) intramolecular reactions, (2) intermolecular reactions, and (3) transmetalations. The reactions illustrate the unique cooperative reactivity of these dilithio reagents, as well as the remarkable effect of substituents on the butadienyl skeleton. Additionally, several other useful applications will be also briefly introduced.

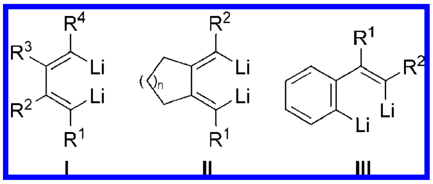


FIGURE 1. Representative skeletons of dilithio reagents. R^1, R^2, R^3, and R^4 can be H, alkyl, alkenyl, aryl, silyl, etc.; the substituents and the size of the ring may be different.

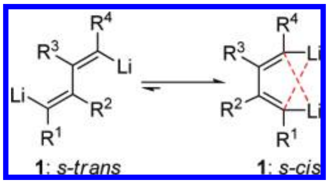


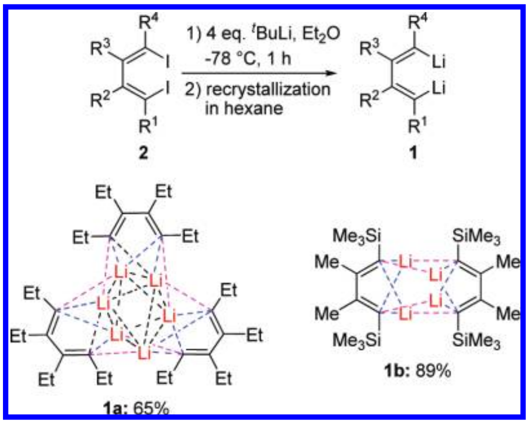
FIGURE 2. 1,4-Dilithio-1,3-butadiene, **1**, favors a double dilithium bridged structure (*s-cis* configuration) in both solution and solid states.

2. Structural Characteristics of 1,4-Dilithio-1,3-butadienes

1,4-Dilithio-1,3-butadienes, **1**, are readily accessible in high efficiency with a wide variety of substitution patterns on the butadienyl skeleton. It has been predicated and structurally shown to favor a double dilithium bridging structure (*s-cis* configuration) in both solution and solid states (Figure 2). The first dilithio compound of type **I**, 1,2,3,4-tetraphenyl 1,4-dilithio-1,3-butadiene, was prepared by Schlenk and Bergmann in 1928 by reaction of diphenylacetylene with Li.[9] An initial ab initio molecular orbital (MO) study of **1** by Schleyer et al in 1980 revealed that a symmetrically bridged structure (*s-cis*) was energetically favored over nonbridged conformations.[10] The theoretical predictions with double lithium bridges were confirmed by the single-crystal X-ray structure of 2,2′-dilithiobiphenyl in 1982.[11] Structures of several other dilithio compounds were also determined by single-crystal X-ray structural analysis and shown to have double lithium bridges.[12] These compounds are generally stabilized with coordinated DME or TMEDA.

Since we have found that 1,4-dilithio-1,3-butadienes demonstrate different reactivity than commonly used mono-Li reagents, we have tried to establish an efficient synthetic method to obtain pure dilithio compounds, aiming at developing such compounds as useful organo-dilithio reagents, and characterizing their single-crystal structures. Although some previous reports had shown structures of some dilithio compounds,[11,12] no structural information of more general all-alkyl substituted **1** as well as other higher aggregation states was known until we recently reported the structure of 1,2,3,4-tetraethyl-1,4-dilithio-1,3-butadiene **1a** (Scheme 1).[13] Dilithio

SCHEME 1. Preparation and Isolation of Dilithio Reagents



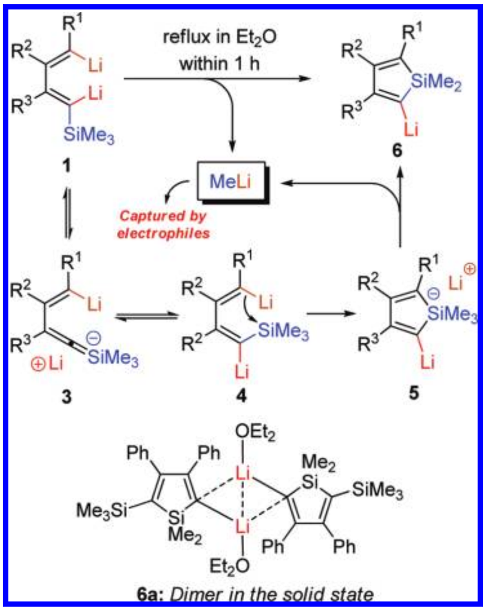
compound **1a** in diethyl ether was generated in situ from its corresponding 1,4-diiodo-1,3-butadiene, **2a**, and 4 equiv of *t*-BuLi at −78 °C for 1 h. The pure **1a** was obtained in 65% yield by extraction of in situ generated **1a** with hexane and recrystallization in hexane after removal of LiI by filtration. An X-ray structure analysis of **1a** revealed a trimeric form with a Li_6 pseudooctahedron (Scheme 1).[13] Similarly, **1b** was obtained in 89% yield and determined to be a dimer in the solid state.[14] Most analogues can be obtained in this group as fine crystalline compounds in good to excellent isolated yields on a gram scale. These compounds are kept in a cooler and used when needed as reagents.

The bridging lithium centers, found both in the solid state and in solution, enable these dilithio reagents to show cooperative effects upon reactions with substrates to form cyclic compounds in general. The two C−Li bonds may also react independently with two molecules of substrates to form acyclic compounds, depending on the type of substituents on the butadienyl skeletons and the substrates used.

3. Intramolecular Reactivity Patterns: Formation of α-Lithio Siloles from Silylated Dilithio Reagents via *E*/*Z* Isomerization Followed by Nucleophilic Attack

3.1. Reaction and Mechanistic Aspects. Normally, reactions of our dilithio reagents were carried out at low temperature. When the reaction temperature was increased to refluxing Et_2O, an interesting reaction of silylated 1,4-dilithio-1,3-butadienes **1** took place to efficiently give rise to α-lithio siloles **6**. These compounds are important building blocks for the preparation of functionalized siloles (Scheme 2).[15−17] This was the first intramolecular reaction pattern of such dilithio compounds. Mechanistic investigation demonstrated that an *E*/*Z* isomerization of one of the 1-silyl-1-lithio alkene moieties in **1** took place, positioning the silyl group *syn* to the other C−Li bond (Scheme 2).[17]

SCHEME 2. Intramolecular Reaction of Silylated 1,4-Dilithio 1,3-Butadienes To Afford α-Lithio Siloles via Configurational *E*/*Z* Isomerization and Nucleophilic Attack



Organolithium-mediated cleavage of a Si−C bond from the Si group is an interesting and fundamental topic for silicon chemistry.[18] The released MeLi moiety can be readily trapped with an external electrophile, such as an aldehyde to form its corresponding alcohol upon hydrolysis.[17a] An X-ray single crystal structure of **6a** revealed that it is dimeric with two lithium bridges. In the dimer the two carbon atoms and one Et_2O are bonded to each lithium atom. The distance between two Li atoms is 2.258 Å, which suggests a strong Li−Li interaction.[17]

3.2. Synthetic Applications. The syntheses and applications of conjugated organic π-systems containing silole units are very attractive because of their applications in organic electronics and optoelectronics.[19] It is well-known that substituents on siloles have a remarkable influence on the property of siloles. Therefore, one of the key variables is the substitution pattern of the siloles. The reaction to form **6** is general (Figure 3), affording diverse silole-containing compounds.[15−17]

Siloles with extended π systems are very useful.[19] Our protocol was successfully used to prepare dilithio bis-silole derivatives bearing different substituents (Scheme 3). For example, the linked tetralithio reagent **7**, obtained quantitatively from lithiation of its corresponding tetraiodide, could be readily transformed to linked dilithio bis-silole derivatives **8**. These compounds could afford interesting but otherwise unavail-

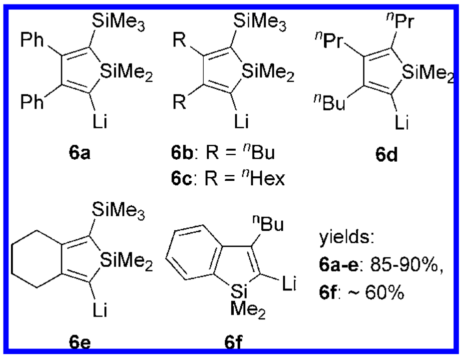


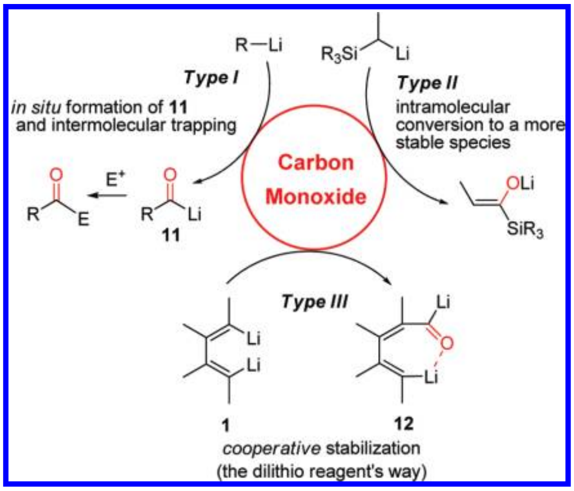
FIGURE 3. Various α-lithio siloles available from this methodology.

able bridged siloles **9** upon treatment with electrophiles. Thus, phenyl-linked bis-silole (**9a**), biphenyl-linked bis-silole (**9b**), and fluorenyl-linked bis-silole (**9c**) could be all obtained in good yields.[16,17] The bis-iodonated phenyl-linked bis-silole **9a-I** was obtained in 55% isolated yield when its corresponding dilithio bis-silole derivatives **8** were treated with I_2. Functionalized **9a-I** could be further utilized in Negishi coupling to afford the product **10** with extended conjugation in 84% yield (Scheme 3).[17]

4. Intermolecular Reactions

4.1. Carbonylation with CO To Form Cyclic Functionalized Dianions. 4.1.1. Reaction and Mechanistic Aspects. Carbonylation of organolithium compounds with CO is a fundamental reaction in organic and organometallic chemistry. This reaction results in the formation of acyllithium intermediate **11**, which has great potential in the synthesis of carbonyl compounds. Unfortunately, acyllithium species are too reactive even at very low temperatures and their applications have been severely limited (type I and type II, Scheme 4).[20−22]

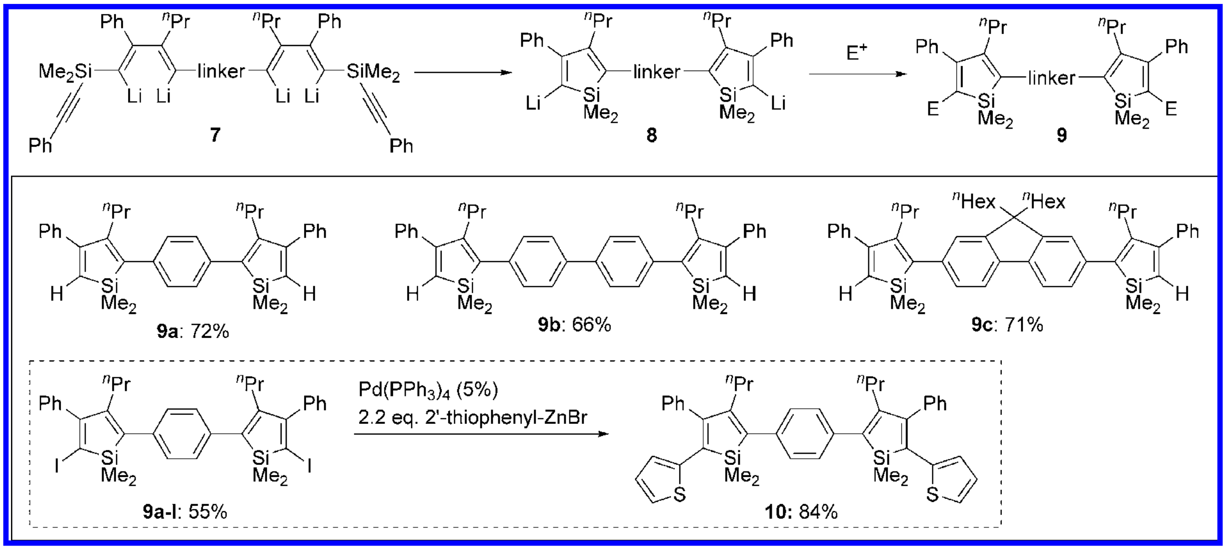
SCHEME 4. Strategies to Use Acyllithium Intermediates



Therefore, a way to stabilize such reactive species is highly demanded. We envisioned that carbonylation of one C−Li bond in **1** would form an acyllithium intermediate such as **12**, which might be stabilized by interaction with the adjacent C−Li moiety (type III, Scheme 4).[14,22]

We proposed that the stabilized acylllithium species **12** might undergo a cycloaddition reaction followed by rearrangements to afford cyclic dianions, such as **A**−**F** (Figure 4). We recently demonstrated that the cyclic dianion **D**, oxy-cyclopentadienyl dilithium (OCp for short), can be obtained in excellent yields (Scheme 5).[14] The X-ray data show that two Cp rings are connected through a "Li_2O_2" four-membered ring. The lithiums are bonded to the cyclopentadienyl moiety in an η^5 fashion and the Li−C distances fall in narrow ranges. Solution NMR of **13** also supports the oxy-cyclopentadienyl dilithium structure.[14] Although the solid state structure is **13**, it

SCHEME 3. From Linked Tetralithio Reagents to Linked Bis-siloles



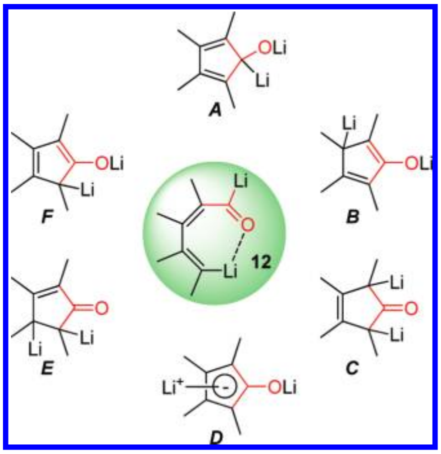
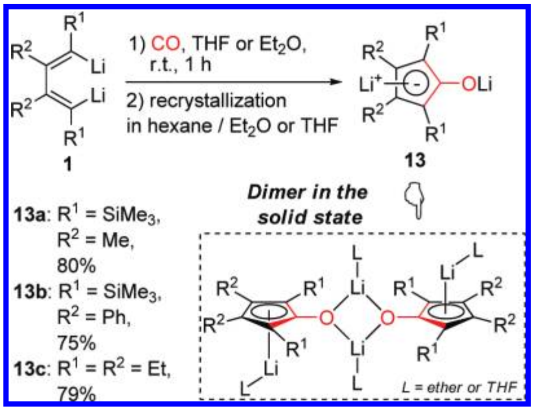


FIGURE 4. Possible cyclic dianion intermediates **A**−**F**.

SCHEME 5. Isolation of the Intermediate **13**

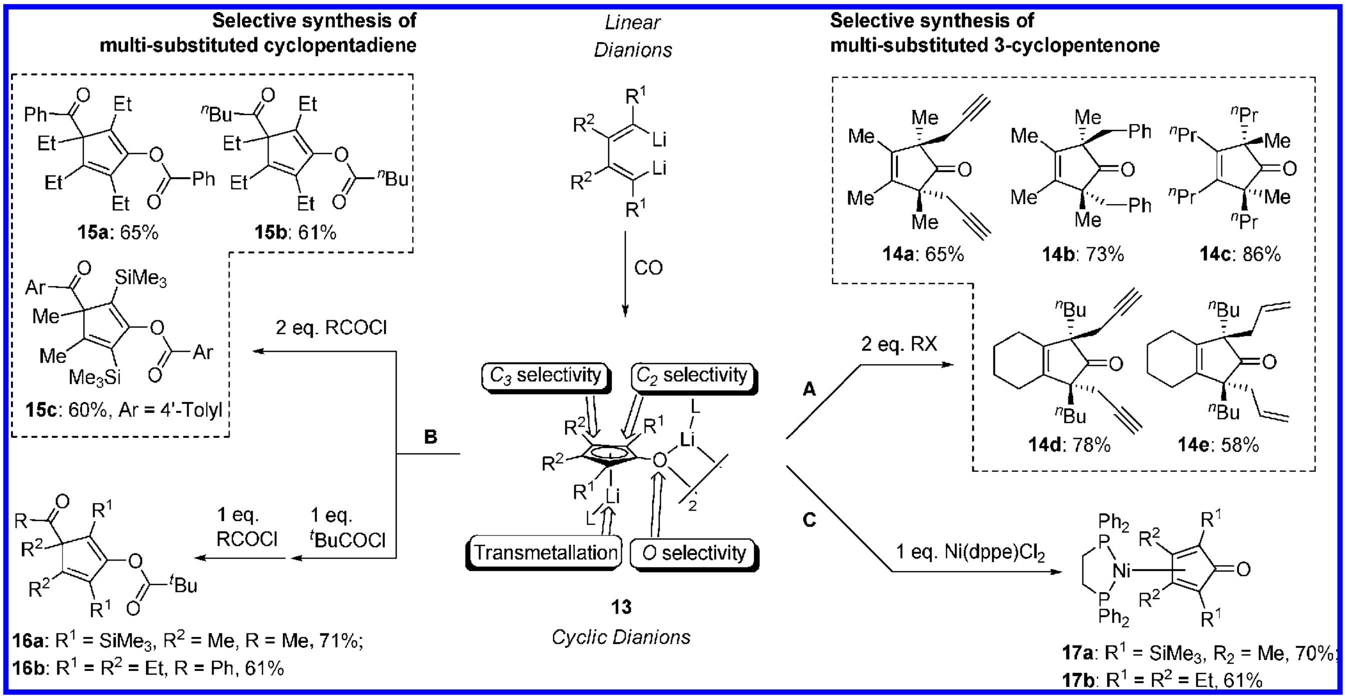


is not clear if this species is in equilibrium with the other possible structures shown in Figure 4.

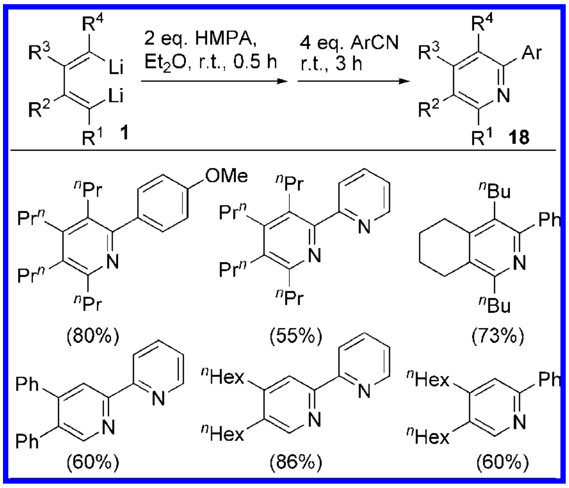
4.1.2. Further Applications. The isolation and reactivity investigation of the cyclic dianions **13** shown in Scheme 5 are of general interest in both organic synthesis and organometallic chemistry. Because of the concomitance of the CpLi moiety, the exocyclic oxy anion, and those multireactive sites, these OCp dianions **13** are structurally very unique and of novel reaction chemistry toward organic substrates and organometallic compounds. When **13** was treated with 2 equiv of MeI, Me_2SO_4, allylic bromide, benzyl halides, or propargyl halides, 3-cyclopentenone derivatives **14** were obtained in good to excellent yield with perfect chemo-, regio-, and stereoselectivity (Scheme 6A).[22] It is noted that, when the electrophiles are acid chlorides (RCOCl), the reaction affords very different products than when alkylating agents were used (Scheme 6B). Reaction of **13** with acid chlorides results in double acylated cyclopentadienes **15**. In contrast, when the bulky *t*-BuCOCl is used, only O-acylation is observed. Addition of a second, smaller acid chloride, however, provides the mixed double acylated products in good to excellent yield.[14]

Furthermore, expecting these OCp dianions **13** as precursors or ligands for transition metal complexes, we also investigated their reactivity with Ni(dppe)Cl_2 complex. This reaction afforded the cyclopentadienone−nickel complexes **17** in high isolated yields (Scheme 6C).[14] Utilization of OCp dianions **13** for the synthesis of new metallocene complexes is one of current interests in our group.

SCHEME 6. Application of Cyclic Diaions **13** in Organic Synthesis and Organometallic Chemistry

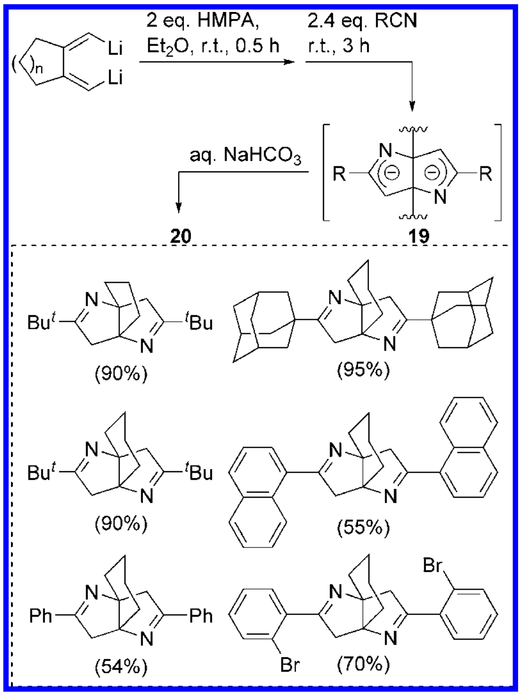


SCHEME 7. Formation of Pyridine Derivatives: Substituent-Dependent

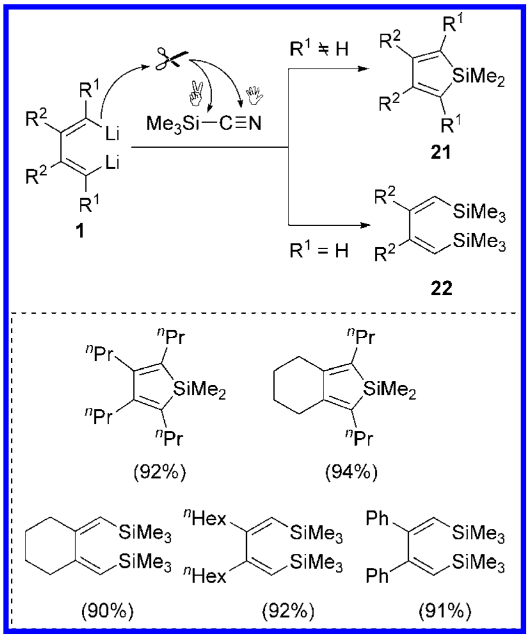


4.2. Reaction with Nitriles: Remarkable Substitution Effect of the Butadienyl Skeletons. The addition of organolithiums to nitriles to provide *N*-lithioketimines is among the fundamental processes in organometallic chemistry. Generally, the intermolecular trapping of *N*-lithioketimines with organohalides or protons yields imines and ketones. The intramolecular trapping with organohalides provides a useful route to *N*-containing heterocycles.[1,2] Interestingly, the dilithium intermediate reacts with nitriles to form pyridines, a reaction that has no prior precedence (Scheme 7).[23,24] It should be noted that the substitution pattern and nature of the substituents play a vital role in determining the structure of the products. As shown in Scheme 7, a tandem addition−cyclization of 1,2,3,4-tetrasubstituted dilithio reagents with various aromatic nitriles in the presence of HMPA gives exclusively penta-substituted pyridines in good to excellent yields. Similarly, 2,3-dialkyl- or diaryl-substituted dilithio reagents generated trisubstituted pyridines.[24] In contrast, five- or six-membered ring fused dilithio reagents reacted with various nitriles without α-hydrogens to generate the tricyclic Δ^1-bipyrrolines **20** in high yields, probably via dianions **19** (Scheme 8).[24,25] As far as we are aware, this is the first synthesis of tricyclic Δ^1-bipyrrolines.

SCHEME 8. Synthesis of Tricyclic Δ^1-Pyrroline Derivatives: Substituent-Dependent



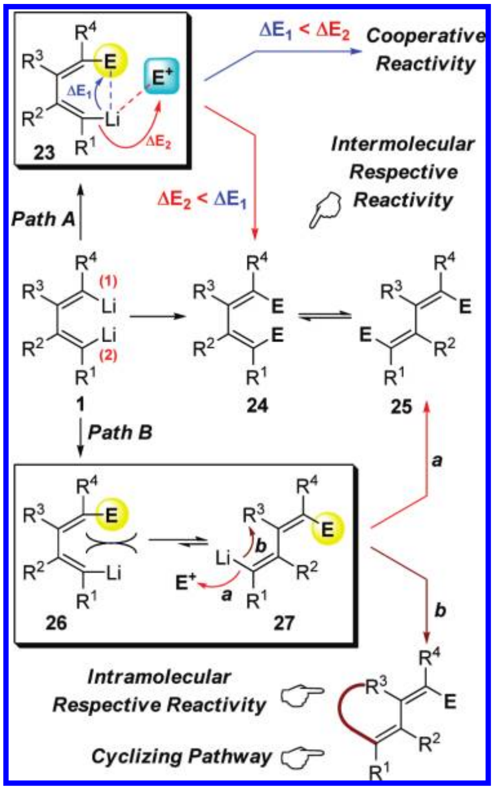
SCHEME 9. Formation of Siloles and (*Z*,*Z*)-Dienylsilanes



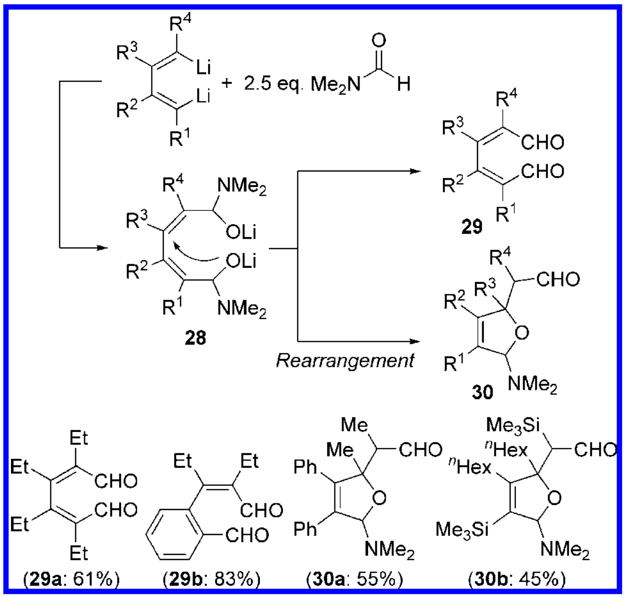
Further, when tetrasubstituted dilithio reagents were treated with Me_3SiCN, a tandem silylation−intramolecular substitution process occurred to yield siloles **21**. In contrast, the reaction of 2,3-disubstituted dilithio reagents with Me_3SiCN gave rise to (*Z*,*Z*)-dienylsilanes **22** with high stereoselectivity (Scheme 9).[24] Cleavage of the Si−C bond of Si−CN moiety was observed, in contrast to the normal reaction pattern, in which the nitriles are attacked at the C≡N triple bond. These results reveal that the formation of pyridines, tricyclic Δ^1-bipyrrolines, siloles, and (*Z*,*Z*)-dienylsilanes is strongly dependent on the substitution patterns of the dilithio reagents and the nature of the nitriles employed.

4.3. Dilithio Reagents Rarely Behave "Normally". Dilithio reagents feature unique reactivity because of the co-operation of two bridging C−Li bonds. Yet "normal" reactivity of dilithio reagents could be envisioned, in which the two C−Li

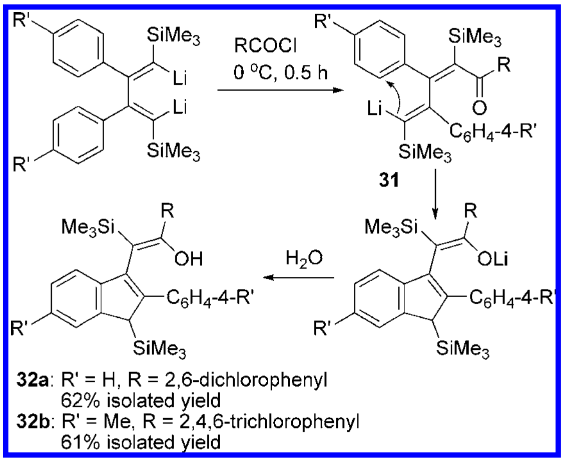
SCHEME 10. Strategies Moving the Stable *s-cis* Form to the Unstable *s-trans* Form



SCHEME 11. Reaction of Dilithio Reagent with DMF



SCHEME 12. Formation of Stable Enols



bonds react individually as in mono-Li reagents. Two different possibilities can be anticipated.

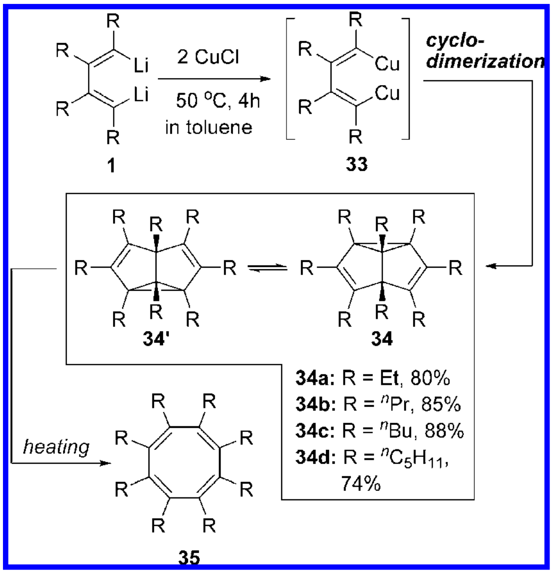
As shown in path A of Scheme 10, after the reaction of the C—Li(1) bond with an electrophile (E^+), **23** may be too stable to continue an intramolecular reaction. In this case, the interaction of the remaining C—Li(2) could react with second electrophile in an intermolecular reaction thus forming the "normal" doubly substituted product **24** (or **25**). Another possibility is shown in path B. After reaction of the C—Li(1) bond with an electrophile, intermediate **26** may strongly disfavor the sterically crowded *s-cis* form, instead forming the *s-trans* conformer **27**. In the *s-trans* conformation, interaction of the C—Li(2) with the group E will be diminished by the distance between these groups and the C—Li(2) may act on its own in an inter- or intramolecular fashion.

The products from these "normal" reaction pathways, such as 2,4-diene-1,6-bis-electrophiles **24** or **25**, contain one or two terminal functional groups on a butadienyl skeleton. They are useful building blocks for the preparation of both cyclic and linear conjugated compounds. Therefore, we have investigated reactions of these dilithio reagents with a variety of substrates, including isocyanates,[26] isothiocyanates,[26] hexafluorobenzene,[27] and different carboxylic acid derivatives, expecting the development of new reactions of these dilithio reagents.[28] However, for most electrophiles, the dilithio reagents behaved cooperatively, giving different cyclopentadiene derivatives.

Although very rarely, these dilithio reagents do react in the "normal" manner. For example, when DMF was used, the two C—Li bonds reacted with two molecules of DMF to generate the reactive intermediates **28**. Intermediate **28** either afforded multiply substituted 2,4-diene-1,6-dials **29** or 2,5-dihydrofuran derivatives **30**, depending on the substituents on the butadienyl skeleton (Scheme 11).[29,30]

Another unexpected reaction of the dilithio reagent is shown in Scheme 12.[31] To avoid the steric repulsion between the $SiMe_3$ group and the bulky R substituent derived from the acid chloride, the reactive species **31** takes the *s-trans* form instead of the *s-cis* conformation (Scheme 12). The C—Li bond in **31** then undergoes an intramolecular attack on the nearby

SCHEME 13. CuCl−Mediated Cyclodimerization of Dilithio Reagents Affording Semibullvalenes



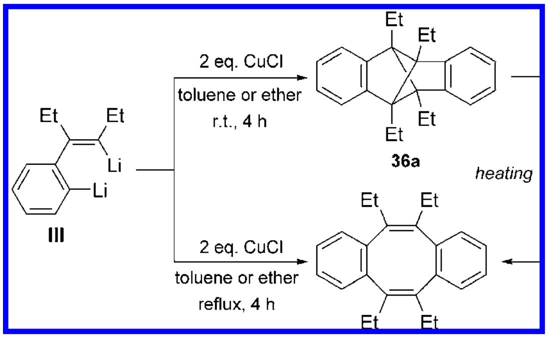
phenyl substituent to give the stable enol derivatives **32** as final products.[31]

5. Transmetalation and Further Applications

Transmetalation is one of the most basic and useful reactions in organometallic chemistry. A wide variety of different organometallic compounds can be efficiently generated via transmetalation from organolithium compounds. Dilithio reagents showed greatly different reactivity from monolithio reagents. Consequently, we envisioned interesting reactions and applications of the dimetallic reagents formed from dilithio reagents. Because organocopper reagents are widely used in organic synthesis, we set out to investigate the transmetalation of dilithio reagents with copper salts.

5.1. Copper-Promoted Cyclodimerization Leading to Semibullvalenes and Other Strained Ring Systems. Among strained ring systems, semibullvalene **34**, a valence isomer of cyclooctatetraene (COT) **35**, has attracted much attention. Semibullvalenes demonstrate extremely rapid *degenerate* Cope rearrangements and are of both theoretical and experimental interest; furthermore, efficient and practical synthetic methods are lacking. We found that dilithio reagents **1** were transformed into semibullvalenes **34** efficiently in the presence of a stoichiometric amount of CuCl (Scheme 13).[32,33] This is the first practical synthesis of semibullvalenes using the metal-mediated C−C bond forming approach. We hypothesize that transmetalation from lithium to copper occurred first, followed by the sequential reactions of Cu−C bonds, leading to the unexpected semibullvalenes **34**. These semibullvalenes could be thermally transformed to their corresponding COT derivatives **35** in quantitative yields, as shown in Scheme 13.

SCHEME 14. CuCl-Mediated Cyclodimerization of Dilithio Reagents Affording Twisted Strained Ring Systems **36**



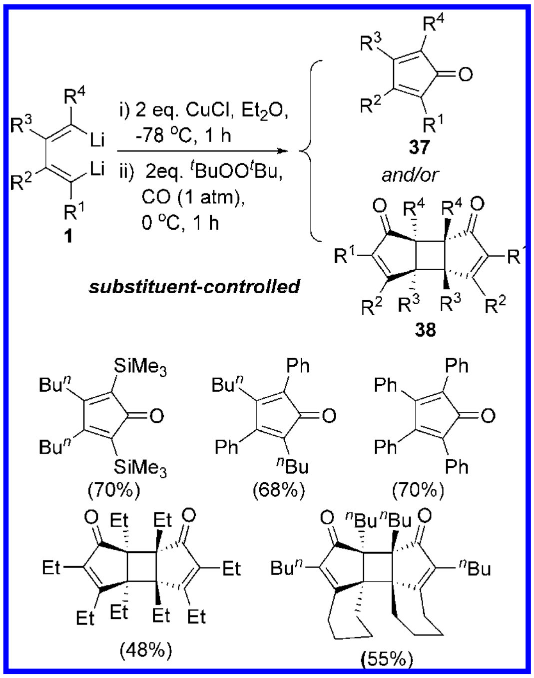
When dilithio reagents of type **III** were treated with CuCl in ether or toluene, no semibullvalenes were detected. Instead, another type of isomer of COT, dibenzotricyclo[3.3.0.0.^{2,6}]-1,2,5,6-tetraalkyloctanes **36** were formed. These could be converted cleanly into more stable dibenzo-COT derivatives as shown in Scheme 14.[34] Twisted tricyclic compound **36** is also an important member of COT valence isomers and has attracted much attention due to its highly strained ring system. It has been proposed as an intermediate between two disubstituted dibenzo-COT.[35] Our work represents the first experimental evidence for **36a**, and we have also characterized it by X-ray analysis.[34]

5.2. Tandem CO Insertion and Intra- or Intermolecular Annulation of Organo-dicopper Reagents. In order to exploit further applications of the butadienyl dicopper intermediates in the cyclo-dimerization, we used various substrates to trap the intermediates to better understand the mechanism. When carbon monoxide was introduced after transmetalation to copper, we observed an unprecedented cycloaddition reaction forming head-to-head dimers **38**, as well as the expected cyclopentadienones **37** (Scheme 15).[36] The effect of substituents again played an important role in this reaction to afford either cyclopentadienones **37** or their head-to-head dimers **38**. As in the previous reaction (Scheme 13), dicopper intermediate **33** is proposed to be formed as the first key intermediate. Elucidation of the structure of **33** is underway in our laboratories.

6. Summary and Outlook

In this Account, we describe our systematic work on the discovery and development of dilithio reagents, 1,4-dilithio-1,3-butadienes. The chemistry of the dilithio reagents shows very different reactivity from their corresponding mono-Li reagents,

SCHEME 15. Tandem CO Insertion and Annulation of Organo-dicopper Intermediates



which are commonly used in the lab and in industry. The results demonstrate that dilithio reagents are useful building blocks and can be applied to the synthesis of a wide variety of cyclic compounds with diversified structures. The unique structure of the butadienyl dilithium compounds leads to exciting cooperative reactivity. Three major reaction patterns have been observed: (1) intramolecular reactions, (2) intermolecular reactions, and (3) transmetalation to form organo-dicopper compounds have been presented. The remarkable effect of substituents on the butadienyl skeleton has also been discussed. Although some other dimetallic or polymetallic compounds have been synthesized and applied to organic synthesis, research in this area is still sporadic. We are currently developing new synthetic methods to prepare different types of organo-dimetallic compounds especially having two different metallic centers by combining main group metals, transition metals, and rare earth metals. The bridge linking the two metal centers plays a crucial role in the reaction chemistry of such organo-dimetallic compounds. Therefore, another major current interest in this group is to design and synthesize organo-dimetallic compounds with a wide variety of bridges such as longer bridges with five- or six-carbon chains or with heteroatoms inserted in the bridge. We expect interesting reaction chemistry and useful synthetic applications from such new organo-dimetallic compounds. In addition, in terms of fundamental organometallic chemistry, these organo-dimetallic compounds could show unprecedented structural information and new fundamental reactivity.

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BIOGRAPHICAL INFORMATION

Zhenfeng Xi received his B.S. degree from Xiamen University in 1983 and his M.S. degree from Nanjing University, Zhengzhou University, and the Henan Institute of Chemistry in 1989. He joined Professor Tamotsu Takahashi's group at the Institute for Molecular Sciences, Japan, in 1993 and obtained a Ph.D. degree in 1996. He took an Assistant Professor position at Hokkaido University, Japan, in 1997, after he worked as a postdoctoral research fellow with Professor Takahashi at the Catalysis Research Center, Hokkaido University. In 1998, he joined the College of Chemistry at Peking University, where he is now a Professor. He received several awards including the Outstanding Young Investigator award from the Qiu Shi Science & Technologies Foundation in 2000 and the Yaozeng Huang Organometallic Chemistry Award in 2004. He has been the holder of the Cheung Kong Professorship since 2002. Professor Xi's research interests include the development of synthetic methodologies based on selective cleavage of C−H, C−C, and C−X bonds mediated by organometallic compounds, the development of organometallic reagents, studies of reaction mechanisms involving reactive organometallic intermediates, and the synthesis of functional structures.

FOOTNOTES

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