Reaction Chemistry of 1,4-Dilithio-1,3-diene and 1-Lithio-1,3-diene Derivatives

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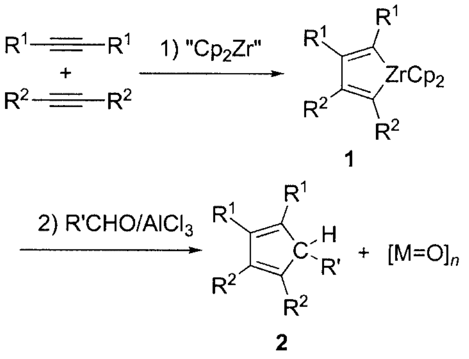
Keywords: Organolithium compounds / Bimetallic reagents / Synthetic methods

The organolithium compounds, 1,4-dilithio-1,3-diene and 1-lithio-1,3-diene derivatives, show unprecedented reaction patterns with organic substrates. The 1,4-dilithio-1,3-dienes react with aldehydes or ketones via deoxygenation of the C=O moieties to afford cyclopentadiene derivatives; pyridine derivatives are obtained in excellent yields when these organolithium reagents are treated with nitriles. In addition to novel reaction patterns, the experimental results have demonstrated that both the mono- and the dilithio reagents are synthetically useful building blocks.

1. Introduction

In April of 1998, this group initiated a research project to develop synthetically useful methodologies, by investigating Lewis acid-mediated reactions of reactive organometallic intermediates with unsaturated organic substrates such as carbonyl compounds. One year later, we found that zirconacyclopentadienes **1** react with aldehydes in the presence of Lewis acids such as $AlCl_3$ to afford cyclopentadiene derivatives **2** (Scheme 1); the C=O double bonds of the aldehydes were cleaved and the aldehydes behaved as one-carbon unit equivalents.[1]



2a: $R^1 = R^2 = Pr$,
$R' = Ph$, yield 89%

Scheme 1. The one-pot formation of multiply-substituted cyclopentadienes from two alkyne molecules and one aldehyde molecule via the Lewis acid-mediated reaction of zirconacyclopentadienes with aldehydes

Zhenfeng Xi was born in 1963 in Henan Province, China. He received his B. S. degree from the Department of Chemistry of 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, as a Ph.D. student in 1993 and obtained a Ph.D. degree in 1996. He took an Assistant Professor position at the Catalysis Research Center (CRC) of Hokkaido University, Japan, in 1997, after he worked as a postdoctoral research fellow with Professor Tamotsu Takahashi at CRC. In 1998, he joined the College of Chemistry at Peking University, where he is now a Professor and serves as the Dean of the College of Chemistry. He received the National Science Fund for Distinguished Young Scholars in 1998 and an Outstanding Young Investigator award from Hong Kong Qiu Shi Science & Technologies Foundation in 2000. He has been the holder of Cheung Kong Scholars Program Professorship since 2002. Professor Xi's research interests include development of synthetic methodologies based on selective cleavage of C−H, C−C and C−X bonds mediated by organometallic compounds, development of organometallic reagents, study on mechanisms of reactions involving reactive organometallic intermediates, and synthesis of functional structures.

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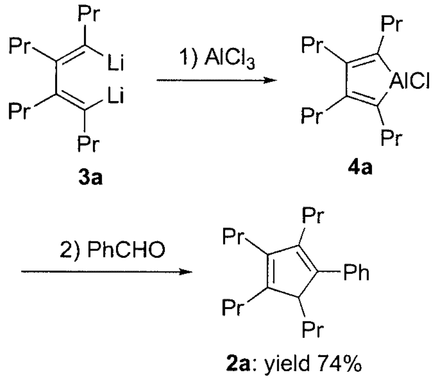
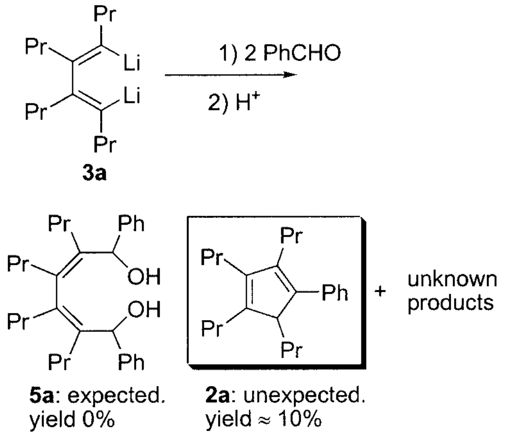
As the first example of this kind, the reaction mechanisms were of great interest. Since aluminacyclopentadienes **4** might be generated through the transmetallation of zirconacyclopentadienes **1** with $AlCl_3$ and were proposed to be the key intermediates in the above reactions,[1,2] we prepared 2,3,4,5-tetrapropylaluminacyclopentadiene **4a** from the reaction of 1,4-dilithio-1,3-diene **3a** with $AlCl_3$ according to the literature procedure (Scheme 2).[3] Treatment of **4a** with benzaldehydes afforded the same product, **2a**, which indicated the involvement of the aluminacyclopentadienes as intermediates.[1–4]



Scheme 2. Formation of cyclopentadienes from the reaction of aluminacyclopentadienes with aldehydes

As a routine experiment, benzaldehyde was added directly to 1,4-dilithio-1,3-diene **3a** without $AlCl_3$. However, the formation of the expected diol **5a** was not observed in pairs of repeated experiments (Scheme 3). In addition to the unknown products, the unexpected cyclopentadiene derivative **2a** was isolated in yields of about 10%. Although the yield of **2a** was very low, the fact that it formed at all attracted our attention and finally led us to the 1,4-dilithio-1,3-diene derivatives.



Scheme 3. Reaction of 1,2,3,4-tetrapropyl-1,4-dilithio-1,3-dienes with aldehydes

Several methods are available for the preparation of a variety of 1,4-dilithio-1,3-diene derivatives (Figure 1). Among them, the most common way is lithiation of the corresponding diiodo compounds **6** using *t*BuLi or *n*BuLi, since the diiodo compounds **6** can easily be prepared by iodination of metallacyclopentadienes **1′**, such as zirconacyclopentadienes and titanacyclopentadienes (Scheme 4).[5,6]

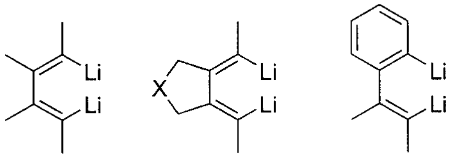
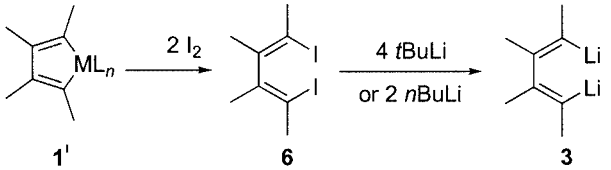


Figure 1. A variety of 1,4-dilithio-1,3-diene derivatives



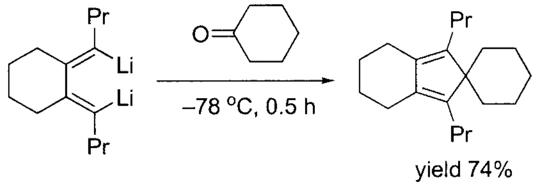
Scheme 4. Preparation of 1,4-dilithio-1,3-diene derivatives

This review will briefly summarize the novel reaction patterns of 1,4-dilithio-1,3-diene derivatives and the useful synthetic methods thus developed so far. Reactions of polylithium reagents such as 1,2-dilithium and 1,3-dilithium reagents reported by other groups will be also introduced when appropriate. In the last part of this paper, recent findings on the reaction chemistry of 1-lithio-1,3-dienes will be discussed.

2. Reactions of 1,4-Dilithio-1,3-dienes with Carbonyl Compounds

2.1 Formation of Cyclopentadiene Derivatives

As mentioned above, when treated with benzaldehydes, 1,4-dilithio-1,3-diene derivative **3a** afforded multiply-substituted cyclopentadiene **2a** in about 10% yield (Scheme 3). Optimized reaction conditions (1 equivalent of carbonyl compound, −78 °C for 30 min) afforded **2a** in 56% isolated yield.[7] Both ketones and aldehydes could be used for the preparation of a variety of cyclopentadiene derivatives of diverse structures, such as spiro compounds and tetrahydroindene derivatives (Scheme 5 and Figure 2).[7] Probably due to the higher reactivity of aldehydes than ketones towards organolithium reagents, the reactions involving the aldehydes did not proceed as cleanly as the reactions involving the ketones, and thus gave lower yields of products.



Scheme 5. Reaction of 1,4-dilithio-1,3-diene derivatives with ketones

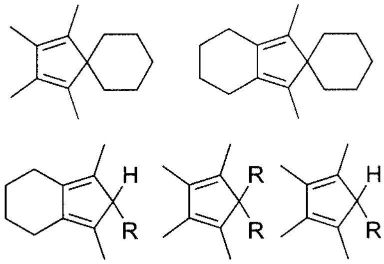
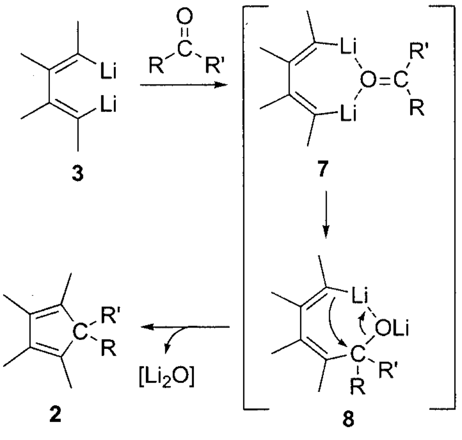


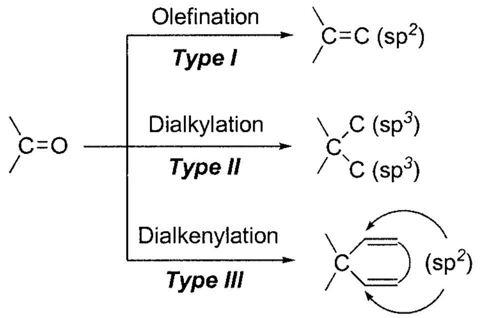
Figure 2. Cyclopentadiene derivatives prepared with diverse structures

As one of the possibilities, chelation of the two alkenyllithium moieties with the carbonyl group is proposed to be involved in this reaction (Scheme 6). One of the two alkenyllithium moieties in **7** may first react with the chelated carbonyl group to form **8**, which then undergoes an intramolecular attack by the remaining alkenyllithium moiety to give the cyclopentadiene derivatives, with the concomitant loss of lithium oxide.



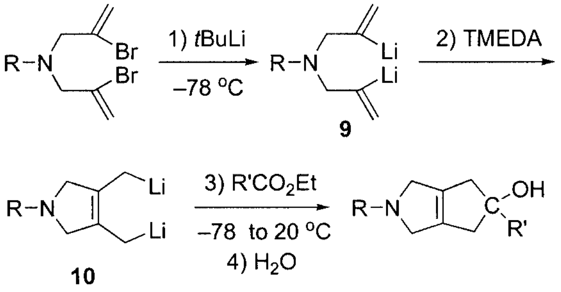
Scheme 6. A proposed reaction mechanism for the reaction of 1,4-dilithio-1,3-dienes with carbonyl compounds affording cyclopentadienes

In general, two types of carbon−carbon bond formation reactions are known via the deoxygenation of the C=O double bonds in carbonyl compounds (Scheme 7, ***Type I*** and ***Type II***). The formation of cyclopentadiene derivatives from 1,4-dilithio-1,3-dienes and aldehydes or ketones via direct cyclo-dialkenylation represents the first example of an unknown pattern of carbon−carbon bond formation involving carbonyl compounds (Scheme 7, ***Type III***).



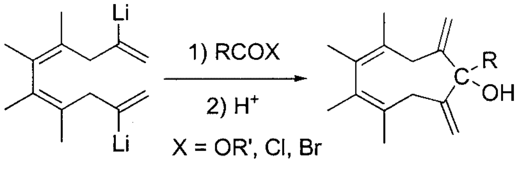
Scheme 7. Types of C−C bond forming reactions via cleavage of the C=O double bonds in carbonyl compounds

Other groups have also reported some examples of the formation of cyclic compounds from the reactions of polylithium reagents with carbonyl compounds.[8,9] Bis(2-lithioallyl)amines **9**, a class of non-conjugated dilithio reagents, were reported by Barluenga and co-workers to react with carboxylic esters affording cyclic alcohols after hydrolysis (Scheme 8).[10] A dilithiated-dihydropyrrole **10** was generated from **9** via intramolecular carbolithiation of a lithiated double bond and served as the key intermediate.[10]



Scheme 8. Reaction of bis(2-lithioallyl)amines with carboxylic esters affording cyclic alcohols after hydrolysis

Similarly, nine-membered carbocycles could be prepared from the reaction of 2,9-dilithio-1,4,6,9-decatetraenes with acyl halides or carboxylic esters (Scheme 9).[11] The success of this cyclization can be explained by the centered conjugated diene system which fixes the skeleton and the two alkenyllithium moieties in close proximity.[12]

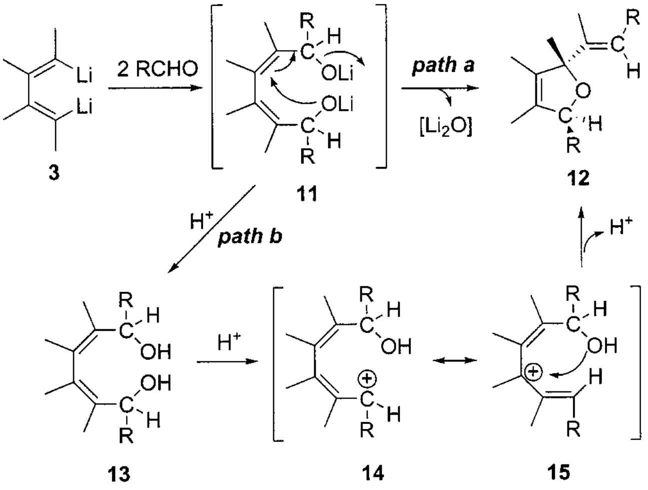


Scheme 9. Formation of nine-membered carbocycles from the reaction of 2,9-dilithio-1,4,6,9-decatetraenes with acyl halides or carboxylic esters

Maercker and co-workers reported a series of papers on reactions of polylithium organic compounds.[8] A reagent related to 1,4-dilithio-1,3-dienes is 3,4-dilithio-2,5-dimethyl-2,4-hexadiene, which reacts with carbonyl compounds such as diethyl carbonates, esters, aldehydes and ketones to afford acyclic compounds. Depending on the electrophiles used, mono- and disubstituted derivatives with either butadiene, allene, or alkyne skeletons are obtained.[13]

2.2 Formation of 2,5-Dihydrofurans

By changing the reaction conditions for the reaction of 1,4-dilithio-1,3-dienes with aldehydes, polysubstituted 2,5-dihydrofurans **12** or cyclopentadienes **2** could selectively be prepared . As mentioned above, when one equivalent of an aldehyde was added to the dilithio reagent at −78 °C, 1,2,3,4,5-pentasubstituted cyclopentadienes **2** were obtained.[7] However, interestingly, when two equivalents of an aldehyde were added to the dilithio reagent at room temperature, 2,5-dihydrofuran derivatives **12** were formed with high stereoselectivity (Scheme 10).[14] The formation of cyclopentadiene derivatives was not observed in most cases.[14] This is a new preparative method for 2,5-dihydrofurans, which are important intermediates in organic synthesis, by employing the simple and fundamental reaction pattern of organolithium compounds with aldehydes. Depending on the bulkiness of the ketones, analogous reactions with ketones afforded mixtures of 2,5-dihydrofurans and cyclopentadienes.



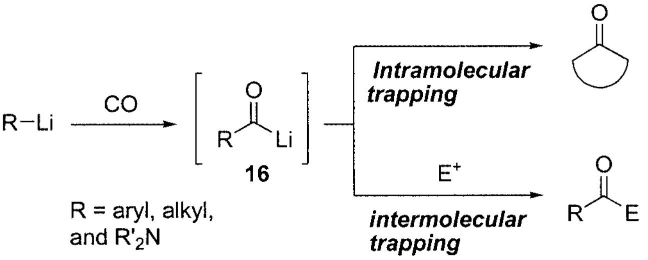
Scheme 10. Formation of 2,5-dihydrofurans from the reaction of 1,4-dilithio-1,3-dienes with aldehydes

1,6-Dialkoxide **11** is assumed to be the intermediate in this reaction (Scheme 10). Although several experimental results indicated that an intramolecular nucleophilic attack by one of the oxygen anions followed by elimination of Li_2O might be the reaction pathway leading to the final product (***path a***), the acid-promoted allylic rearrangement and sequential cyclization of 1,6-diols **13**, which were isolated in some cases,[14] could not be excluded as a reaction pathway leading to 2,5-dihydrofurans (***path b***).

Yus and co-workers have also reported reactions of dilithio compounds such as 1-lithio-3-(2-lithioethyl)benzene, 1-lithio-4-(2-lithioethyl)benzene, 1,3-dilithiopropane and 1,4-dilithiobutane, with carbonyl compounds. These reactions proceeded in the normal manner affording the expected diols after hydrolysis with water.[8,15]

3. Reactions of 1,4-Dilithio-1,3-dienes with Carbon Monoxide

The reaction of organolithium reagents with CO has long been considered to be an important approach to introduce carbonyl groups into organic molecules. However, due to the high reactivity of the initial intermediate (the carbonyllithium species **16**),[16] few useful synthetic methods have been developed from the primary carbonylation of organolithium reagents (Scheme 11). In addition to being strong nucleophiles, these species are also electrophiles, since the carbonyl function is susceptible to nucleophilic attack.

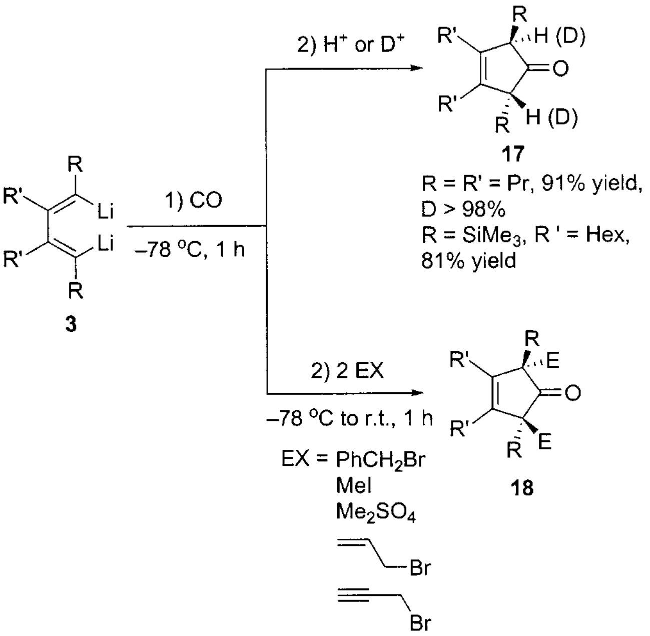


Scheme 11. Formation of carbonyllithium intermediates and their applications

As illustrated in Scheme 11, the primary adduct **16** may be trapped using electrophiles both intramolecularly and intermolecularly, to afford cyclic or linear carbonyl compounds, respectively. Efficient intermolecular trapping of the carbonyllithium species **16** under carefully controlled reaction conditions has been reported by Nudelman, Seyferth, and others.[17,18] Murai, Smith, and others have demonstrated that an intramolecular conversion of the carbonyllithium species **16** into a more stable species is a useful way to utilize the RLi/CO reaction systems for the construction of cyclic carbonyl compounds.[19−21]

As an unprecedented pattern of highly selective and efficient carbonylation of organolithium reagents, reaction of the dilithio reagents with CO at −78 °C for 1 h afforded *trans*-3-cyclopenten-1-one **17** in an excellent isolated yield and with perfect *trans* selectivity after hydrolysis (Scheme 12).[22] Deuteriolysis of the reaction mixture afforded dideuterated products with more than 98% of deuterium incorporation. In addition to the formation of high yields of the cyclopentenones, it is especially worth noting the perfect regio- and stereoselectivity of this reaction. The usefulness of this novel reaction was further demonstrated by the addition of various electrophiles such as benzyl halides, MeI, Me_2SO_4, allyl halides and propargyl halides, to the carbonylation intermediates (Scheme 12).[22] All these reactions afforded their corresponding products **18** in excellent yields with high selectivities.

Although it is not yet clear as to why the cyclopentenone derivatives **17** and **18** are formed in highly regio- and stereoselective patterns, it is obvious that one or more new dilithio intermediates are generated in the carbonylation reaction of **3**. An acyclic carbonyllithium species **19** is proposed to be

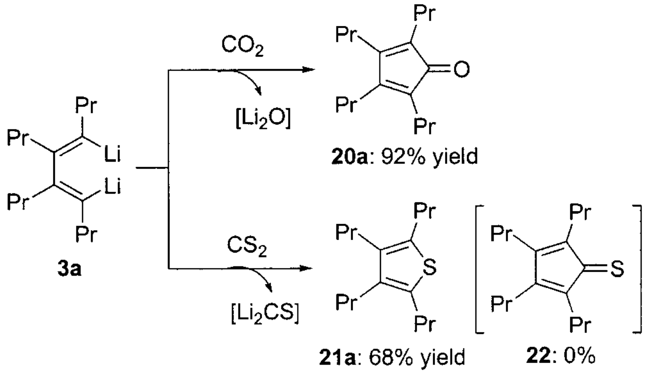


Scheme 12. Formation of cyclopentenones from the reaction of 1,4-dilithio-1,3-dienes with CO

the first reaction intermediate, which immediately undergoes intramolecular acyl-lithiation of the lithiated C=C double bond (***path a*** in Scheme 13), or intramolecular nucleophilic attack of the carbonyl group by the remaining alkenyllithium moiety (***path b*** in Scheme 13), followed by sequential rearrangement to afford cyclic dianions, such as **i**–**vi** (Scheme 13).

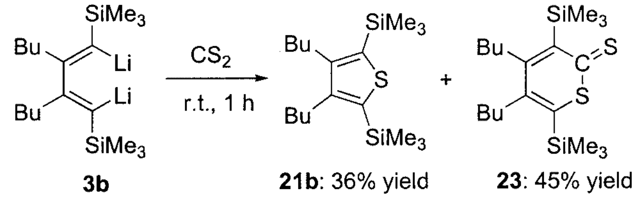
4. Reactions of 1,4-Dilithio-1,3-dienes with CO_2 and CS_2

Carbon dioxide and carbon disulfide are two heterocumulenes. Their reactions with organolithium reagents have been used in various organic syntheses. The formation of unsymmetrical ketones was reported from the reaction of CO_2 and two organolithium compounds via an intermolecular reaction pathway.[23] When 1,4-dilithio-1,3-dienes **3** was treated with CO_2, the cyclopentadienone derivatives **20** was obtained in high yields in a one-pot reaction, via cleavage of one of the C=O double bonds (Scheme 14).[24] The experimental results indicate that this intermolecular reaction pattern affords cyclopentadienones in the reaction mixture before hydrolysis.



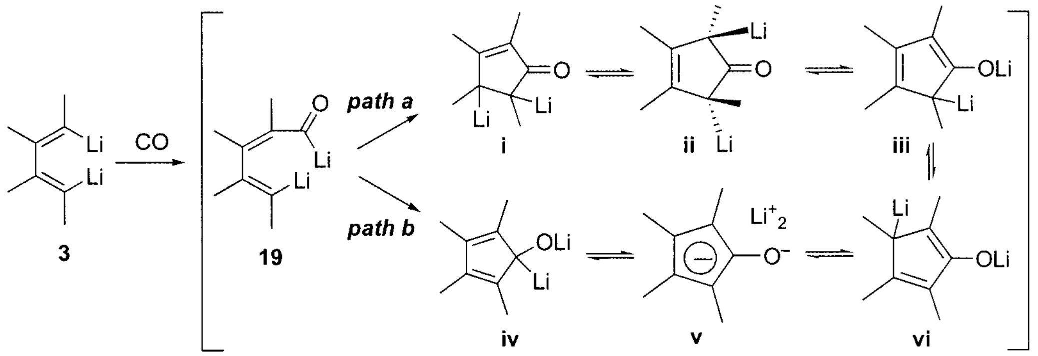
Scheme 14. Reactions of 1,4-dilithio-1,3-dienes with CO_2 and CS_2

Interestingly, however, when the 1,4-dilithio-1,3-dienes **3** were treated with CS_2, the thiophene derivatives **21** rather than the cyclopentadienethiones **22** were generated in good yields (Scheme 14).[25,26] Depending on the substituents on the dilithio compounds **3**, the above reaction afforded, in addition to the multiply-substituted thiophenes **21**, the thiopyran-2-thione derivatives **23** (Scheme 15), via cleavage of the C=S double bonds and via cycloaddition reactions, respectively.



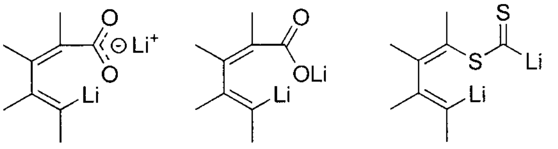
Scheme 15. Formation of substituted thiophenes and thiopyran-2-thione derivatives

The lithium carboxylates **24** and/or **25** are proposed to be the first intermediates in the reaction of **3** with CO_2 (Figure 3), while the thiophilic addition intermediate **26** is as-



Scheme 13. Proposed reaction mechanisms for the reaction of 1,4-dilithio-1,3-dienes with CO

sumed to be formed initially in the reaction of **3** with CS_2, which leads to the thiophenes **21** (Figure 3).



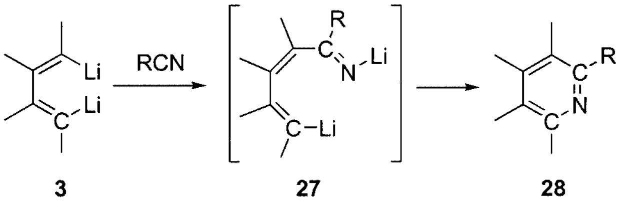
24 **25** **26**

Figure 3. Proposed reaction intermediates for the reactions of 1,4-dilithio-1,3-dienes with CO_2 and CS_2

5. Reactions of 1,4-Dilithio-1,3-dienes with Nitriles

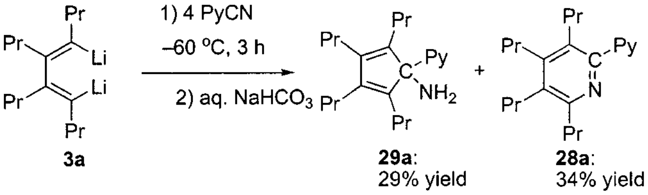
The direct cycloaddition reactions of nitriles that afford *N*-containing heterocycles such as the pyridine derivatives are very attractive, and represent the simplest method for forming these compounds. *N*-Lithioketimines, the addition reaction intermediates of organolithium compounds to nitriles, may be intramolecularly trapped to afford cyclic *N*-containing compounds such as pyridines. Thus, subsequent intramolecular nucleophilic substitution of organohalides has been used for the synthesis of *N*-containing heterocycles, as demonstrated by Kristensen, Begtrup and others.[27,28]

Surprisingly, in the 1,4-dilithio-1,3-dienes **3**, the 1,4-dianion species reacted with nitriles in the presence of HMPA at room temperature for 1 h to give the substituted pyridines **28**, as well as the 2,2′-bipyridines and tetrahydroisoquinolines in high yields (Scheme 16).[29] No dihydropyridines or related intermediate products were observed in the reaction mixtures before workup, as determined by NMR spectroscopy. This work again demonstrates that 1,4-dilithio-1,3-dienes have unique reaction properties, and thus the reaction of organolithium compounds with nitriles represents a novel and synthetically useful reaction for the formation of pyridine derivatives.



Scheme 16. Reaction of 1,4-dilithio-1,3-dienes with nitriles affording substituted pyridines

When the reaction of **3a** with 2-cyanopyridine was carried out at lower temperatures in the presence of HMPA, cyclopentadienylamine **29a** was isolated in a 29% yield, along with **28a** in a 34% yield (Scheme 17).[29] Although the reaction mechanism is not yet clear, this observation provides a useful clue for the understanding of the reaction pathway.

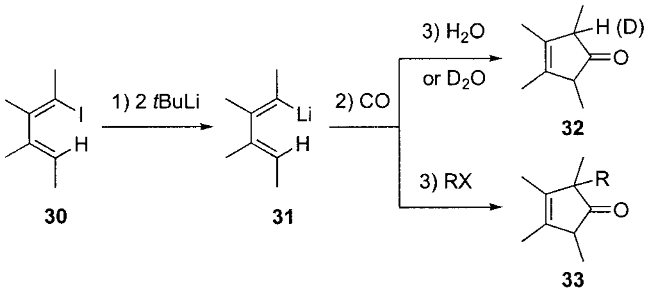


Scheme 17. Reaction of 1,4-dilithio-1,3-dienes with nitriles at lower temperatures affording both pyridines and cyclopentadienylamines

6. Reactions of 1-Lithio-1,3-dienes with CO, CS_2 and Nitriles

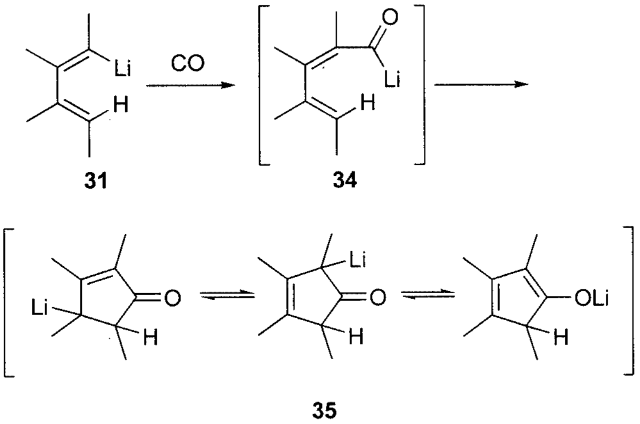
6.1 Reaction with CO Affording Cyclopentenones

1,4-Dilithio-1,3-diene derivatives **3**, generated in situ from their corresponding 1,4-diiodo-1,3-dienes **6** and BuLi, reacted with carbon monoxide to afford the 3-cyclopentenones **17** with high regio- and stereoselectivities (Scheme 12).[22] Addition of electrophiles to the carbonylation reaction mixtures led to various substituted 3-cyclopentenones **18**.[22] More interesting results were obtained during our further investigation into this novel and useful reaction. In one accidental case, when 1,4-diiodo-1,2,3,4-tetrapropyl-butadiene **6a** containing a small amount of 1-iodo-1,2,3,4-tetrapropyl-butadiene **30a** as an impurity was used, we were surprised to observe that 1-lithio-1,2,3,4-tetrapropyl-butadiene **31a** also underwent the carbonylation-cyclization reactions to give the corresponding cyclopentenones **32** or **33** with high regio- and stereoselectivities (Scheme 18).[30] A variety of 2- or 3-cyclopentenone derivatives could be prepared in good to excellent yields after hydrolysis (Scheme 18).[30] It is interesting to compare the stereochemistry of the cyclopentenones **32** with that of the cyclopentenones **17** in Scheme 12. The dilithio reagents **3** gave *trans*-3-cyclopentenones, while these monolithio reagents **31** afforded *cis*-3-cyclopentenones as the major products.



Scheme 18. Reaction of 1-lithio-1,3-dienes with CO affording cyclopentenones

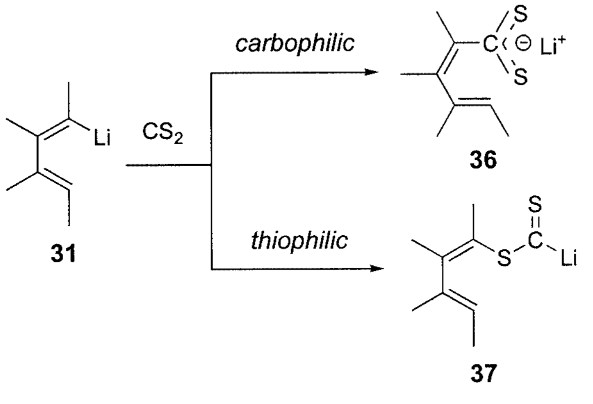
Carbolithiation of unsaturated C−C bonds is a very important approach for the formation of new C−C bonds. Conceptually, acyl-lithiation of unsaturated C−C bonds is more interesting and useful, since not only new C−C bonds but also carbonyl groups can be introduced into the products. As proposed for the reaction of the dilithio reagents **3** with CO shown in Scheme 13, a carbonyllithium species **34** might be formed in the first step of the reaction of the monolithio reagents **31** with CO, followed by intramolecular acyl-lithiation of the C=C double bond to afford **35** (Scheme 19).



Scheme 19. Proposed reaction mechanisms for the reaction of 1-lithio-1,3-dienes with CO

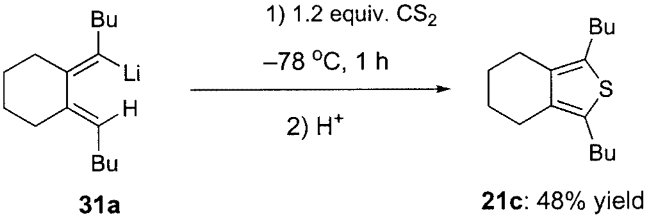
6.2 Reaction with CS_2 Affording Thiophene Derivatives

Although the selectivity of the reaction of the 1-lithiobutadienes **31** with CS_2 was found to be worse than that of the reaction of the 1,4-dilithiobutadienes **3** with CS_2, the reaction pattern was novel. As illustrated in Scheme 20, the first addition intermediates of the reaction of the 1-lithiobutadienes **31** with CS_2 may be the carbophilic addition compound **36** and/or the thiophilic addition compound **37**.



Scheme 20. Proposed reaction patterns of 1-lithio-1,3-dienes with CS_2

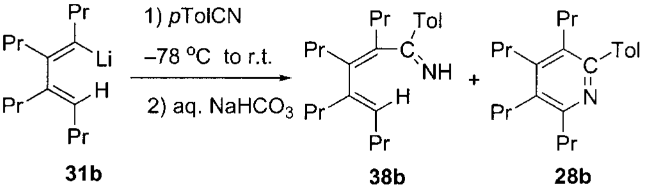
The experimental results showed that, in addition to some unknown products, the thiophene compounds **21** were formed from the reaction of the 1-lithiobuadienes **31** with CS_2 (Scheme 21).[26] Although further investigation to elucidate the reaction mechanism for the formation of the thiophene derivatives **21** is needed, it is obvious that the reaction pattern of the dilithio reagents **3** with CS_2 is different from that of the monolithio reagents **31** with CS_2.



Scheme 21. Formation of thiophene derivatives from the reaction of 1-lithiobutadienes **31** with CS_2

6.3 Reaction with Nitriles Affording Pyridine Derivatives

Addition of 1 equivalent of HMPA and 1.5 equivalent of a nitrile to the in situ-generated 1-lithio-1,3-dienes **31** caused an immediate reaction which afforded the pyridine derivatives **28** in high yields.[29] These reactions are even cleaner than those of the dilithio reagents **3** with nitriles. The experimental results suggest that, although the same pyridines **28** are formed as the final products, the reaction mechanisms for the formation of **28** from **31** might be different from those for the formation of **28** from **3**. In the reactions of the dilithio reagents **3** with nitriles, no linear imines were observed even at low temperature. However, in the reactions of the monolithio reagents **31** with nitriles, linear imines **38** were isolated at lower temperatures (Scheme 22, Table 1).[29] With the reaction temperatures increasing, the yields for the linear imine **38b** decreased, while those for the pyridine derivative **28b** increased. Finally at room temperature, the linear imine **38b** disappeared completely, and the pyridine derivative **28b** was formed in an almost quantitative yield (Scheme 22, Table 1).



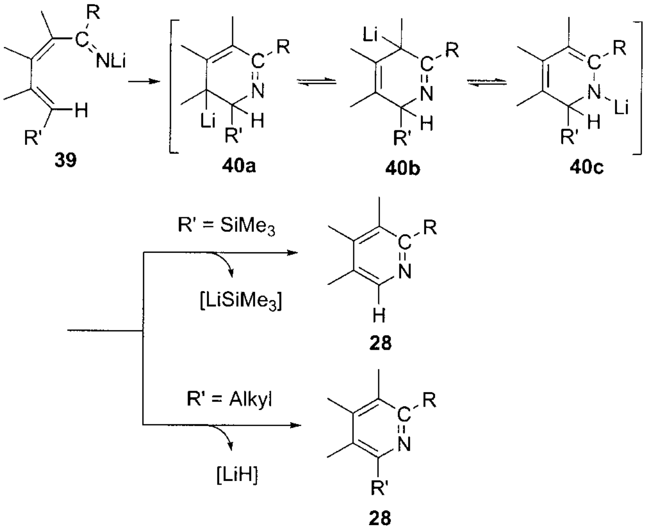
Scheme 22. Reaction of 1-lithiobutadienes with nitriles affording linear imines and pyridine derivatives

Table 1. Formation of linear imine **38b** and pyridine **28b** from the reaction of 1-lithiobutadiene **31b** with tolylnitrile

T / °C	t / min	Yield of **38b** / %	Yield of **28b** / %
−78	15	70	< 5
−60	30	23	54
−60	60	10	86
0	30	< 3	95
25	30	0	98

The formation of the linear imines **38** indicates that the *N*-lithioketimines **39** are formed as the first intermediates in the reaction of the monolithio reagents **31** with nitriles.

Intramolecular lithiation of the C=C double bond is followed, affording the cyclic intermediates **40** (Scheme 23). It is worth noting that when a trimethylsilyl group is positioned at the α-position of the N atom in **40c** (R′ = $SiMe_3$), $LiSiMe_3$ is eliminated to afford the final pyridine derivatives, while elimination of LiH takes place if R′ is an alkyl group.



Scheme 23. Formation of pyridine derivatives via cycloaddition of nitriles with organolithium compounds

7. Conclusion and Outlook

Organometallic compounds of main group metals, such as the Grignard reagents RMgX and organolithium compounds RLi, have made a great contribution to the advancement of synthetic chemistry and organometallic chemistry of transition metals. There is an increasing interest in the preparation and applications of organolithium and organomagnesium reagents in synthetic chemistry and organometallic chemistry.[8,9] Particular attention has been paid to the synthetic application of polylithium and polymagnesium reagents, since new methods for useful cyclic and acyclic products can be expected. In spite of the fact that our attention on organolithium compounds was brought about by accident, our experimental results so far have demonstrated that 1,4-dilithiobutadiene and 1-lithiobutadiene derivatives have the ability to partake in interesting and unprecedented reaction patterns with organic substrates. Current on-going projects in this group involving 1,4-dilithiobutadiene and 1-lithiobutadiene derivatives, have revealed that the nature of the substituents on the conjugated butadienyl skeletons has a remarkable influence on the reaction patterns of these organolithium reagents with various substrates.

In addition to organolithium reagents, Grignard reagents RMgX, organoaluminium reagents, organozinc reagents, and many other organometallic compounds of main group metals have often been used as reagents in synthetic chemistry and in industry. This group has recently extended the research programs from those based on 1,4-dilithiobutadiene and 1-lithiobutadiene derivatives to those involving analogous organometallic compounds of main group metals, expecting different and novel reaction patterns.[4,31] For example, analogous organoaluminium compounds can react at room temperature with both aromatic and aliphatic aldehydes to afford cyclopentadiene derivatives in good to excellent yields.[4] Unlike the dilithio and monolithio reagents, ketones do not react with aluminum reagents. 1,4-Bis(bromomagnesio)-1,3-dienes and 1-bromomagnesio-1,3-dienes, generated in situ from their corresponding bromo compounds, exhibit interesting reactivities towards a variety of organic substrates.[32]

Bimetallic compounds with the two metal centers in close proximity have been very attractive as catalysts and reagents. However, the one of the biggest problems is the dissociation of a bimetallic compound into two monometallic compounds in the reaction system. Thus, we have tried to use 1,4-dimetalbutadienes as model compounds for bimetallic regents. Preparation of 1,4-dimetalbutadienes can easily be achieved from 1,4-dilithiobutadienes or directly from 1,4-dihalobutadienes. For example, we have recently investigated the organoiron analogues and found that unactivated alkynes could react with 1,4-dilithio-1,3-diene derivatives in the presence of $FeCl_3$ affording substituted benzene derivatives via a formal [4 +2] cycloaddition. A 1,4-diironbutadiene is proposed as the reaction intermediate.[33] Synthetically useful methods and novel reaction patterns can be expected from 1,4-dimetal-butadienes, 1-metal-butadienes, and related organometallic reagents of both transition metals and main group metals.

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