Reactions of Substituted (1,3-Butadiene-1,4-diyl)magnesium, 1,4-Bis(bromomagnesio)butadienes and 1,4-Dilithiobutadienes with Ketones, Aldehydes and PhNO To Yield Cyclopentadiene Derivatives and N-Ph Pyrroles by Cyclodialkenylation

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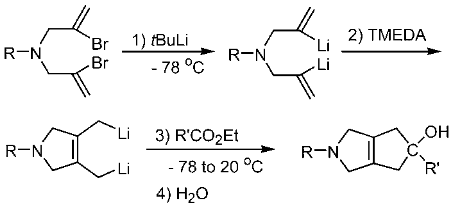
Abstract: 1,4-Dilithiobutadiene derivatives **1**, 1,4-bis(bromomagnesio)butadiene derivatives **2** and metallacyclic (1,3-butadiene-1,4-diyl)magnesium reagents **3** were prepared and their reactions with ketones, aldehydes, and PhNO were investigated. Multiply substituted cyclopentadienes and N-Ph pyrroles were formed by unprecedented reaction conditions. The carbonyl group of aldehydes and ketones was deoxygenated during the reaction and behaved formally as a one-carbon unit; the N=O moiety of PhNO was cleaved to afford N-Ph pyrrole derivatives. Furthermore, different reactivities among these three types of reagents **1**, **2** and **3** were revealed. The 1,4-dilithium reagents **1** readily reacted with both aldehydes and ketones; the 1,4-dimagnesium reagents **2** reacted with aldehydes, but not ketones; the metallacyclopentadiene reagents of magnesium **3** showed higher reactivity and did react with ketones.

Keywords: carbonyl compounds · cyclopentadienes · heterocycles · lithiation · pyrroles

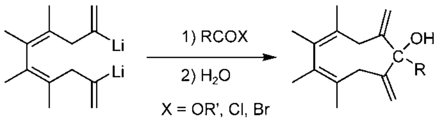
Introduction

There is an increasing interest in preparation and applications of organolithium and organomagnesium reagents in synthetic chemistry and organometallic chemistry.[1,2] Particular attention has been paid to the synthetic application of polylithium and polymagnesium reagents with carbonyl compounds, since new methods for useful cyclic and acyclic products are anticipated. Barluenga and co-workers reported that bis(2-lithioallyl)amines, a class of non-conjugated dilithio reagents, react with carboxylic esters affording cyclic alcohols after hydrolysis (Scheme 1).[3] A dilithiated dihydropyrrole was generated from bis(2-lithioallyl)amines by intramolecular carbolithiation of a lithiated double bond and served as the key intermediate.[3]



Scheme 1. An example of a reaction of dilithio reagents with carbonyl compounds.

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 2).[4] The success of this cyclization can be explained with the centered conjugated diene system which fixes the skeleton and the two alkenyllithium moieties in close proximity.



Scheme 2. Reaction of 2,9-dilithium reagents with acid chloride affording nine-membered rings.

Maercker and co-workers reported on the reaction of polylithium organic compounds.[5] 3,4-Dilithio-2,5-dimethyl-2,4-hexadiene reacted with carbonyl compounds such as diethyl carbonates, esters, aldehydes and ketones to afford acyclic compounds. Depending on electrophiles, mono- and disub-

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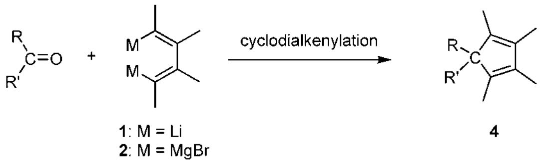
stituted derivatives with either butadiene, allene, or alkyne skeleton were obtained.[5]

Yus and co-workers have also described 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 pattern affording the expected diols after hydrolysis with water.[6]

We have recently studied the preparation and reaction chemistry of 1,4-dilithiobutadiene derivatives **1** (Figure 1) and have reported preliminary results on a novel reaction of **1** with ketones and aldehydes.[7] When treated with one equivalent of ketone or aldehyde at −78 °C for 30 min, 1,4-dilithiobutadiene derivatives **1** afforded multiply substituted cyclopentadienes **4** in good to excellent isolated yields (Scheme 3).[7] Formation of cyclopentadiene derivatives from 1,4-dilithio-1,3-dienes and aldehydes or ketones represents the first example of an unknown pattern of carbon–carbon bond formation involving deoxygenation of C=O double bonds in carbonyl compounds.[8–15]



Scheme 3. A new type of C–C bond forming reactions by cleavage of C=O double bonds of carbonyl compounds.

Although only a limited number of 1,4-bis(bromomagnesio) reagents have been reported, they have been shown to be useful in organic synthesis.[16,17] Rieke and co-workers have demonstrated that substituted 2-butene-1,4-diylmagnesium reagents, a class of metallacyclic compounds of magnesium, possess interesting and useful reactivities towards a series of electrophiles.[1e,18]

These interesting and useful reaction patterns of 1,4-dilithiobutadiene derivatives **1** with ketones and aldehydes reported from our group, and 1,4-bis(bromomagnesio) reagents and metallacyclic compounds of magnesium reported by others, prompted us to prepare 1,4-bis(bromomagnesio)-butadiene derivatives **2** and metallacyclic (1,3-butadiene-1,4-diyl)magnesium **3** and investigate their reactions. In this full paper, we report 1) reactions of **1**, **2** and **3** with ketones; 2) reactions of **1**, **2** and **3** with aldehydes; 3) reactions of **2** with CO_2, $PhNO_2$, and PhNO. Mechanistic aspects of these reactions are discussed.

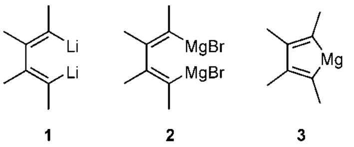
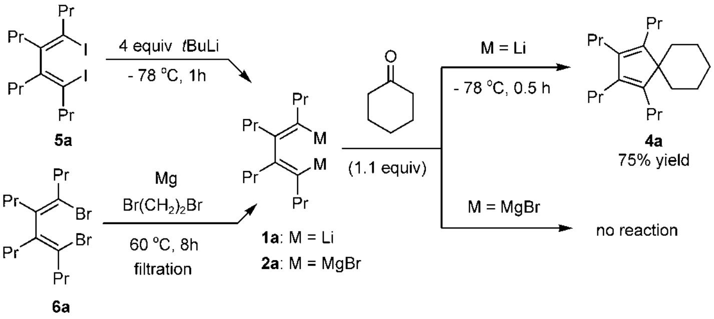


Figure 1. 1,4-Dilithio-1,3-dienes **1**, 1,4-bis(bromomagnesio)-1,3-dienes **2**, and (1,3-butadiene-1,4-diyl)magnesium **3**.

Results and Discussion

Reactions of 1,4-dilithiobutadiene derivatives 1, 1,4-bis(bromomagnesio)butadiene derivatives 2 and (1,3-butadiene-1,4-diyl)magnesium reagents 3 with ketones: 1,4-Dilithio-1,2,3,4-tetrapropyl-1,3-butadiene **1a** (1 mmol) in diethyl ether (5 mL) was generated in situ from the corresponding diiodo compound **5a** (1 mmol) and *t*BuLi (4 mmol) at −78 °C (Scheme 4),[7,19] while 1,4-bis(bromomagnesio)-1,2,3,4-tetrapropyl-1,3-butadiene **2a** (1 mmol) in tetrahydrofuran (20 mL) was generated in situ from the corresponding dibromo compound **6a** (1 mmol) and Mg powder (Scheme 4). Formation of these bimetallic reagents **1** and **2** was monitored by GC analysis or by TLC.



Scheme 4. In situ Generation of **1** and **2** and their reactions with ketones.

Reaction of organo mono-lithium compounds, including alkyl- and alkenyllithium compounds, with carbonyl groups is usually straightforward forming alcohols after hydrolysis, or forming α-deprotonation products.[1,2] Interestingly, however, the in situ generated **1a** reacted immediately with one equivalent of cyclohexanone at −78 °C to afford the cyclopentadiene derivative **4a** as the only product in 75 % isolated yield (Scheme 4).

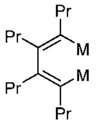
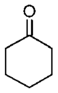
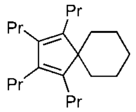
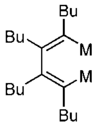
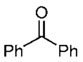
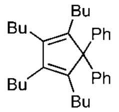
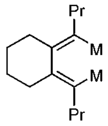
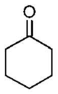
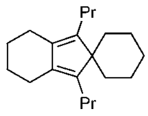
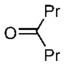
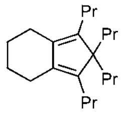
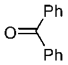
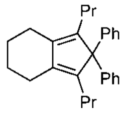
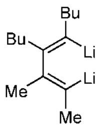
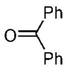
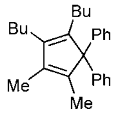
Surprisingly, however, no reaction was observed when the in situ generated **2a** was treated with cyclohexanone even at higher temperatures (Scheme 4), probably due to the existence of skeleton conjugation.

Representative results are summarized in Table 1. Both aromatic and aliphatic ketones could be applied for the preparation of a variety of cyclopentadiene derivatives of diverse structures, such as spiro compounds and tetrahydroindene derivatives.

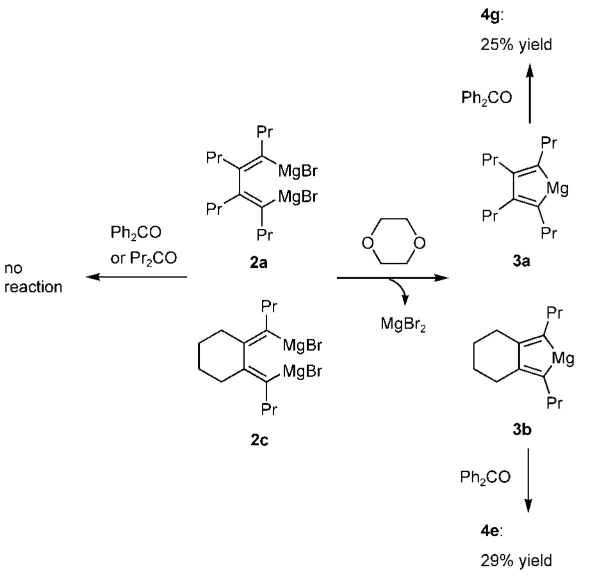
In order to compare the reactivity between **2** and **3**, and to make sure which is the real reactive species in THF solution, compounds **2a** and **2c** in THF were replaced by **3a** and **3b**, respectively, in 1,4-dioxane according to literature procedures.[20] As expected, **3a** and **3b** showed higher reactivity than **2a** and **2c**, and did react with ketones (Scheme 5).

An interaction (or chelation) of the alkenyllithium moieties with the carbonyl group is proposed to be essential in this intermolecular–intramolecular reaction between 1,4-dilithium reagents and ketones (Scheme 6). One of the two alkenyllithium moieties reacts first with the carbonyl group to form **8**, which is then intramolecularly attacked by the re-

Table 1. Reaction of 1,4-dilithio- and 1,4-bis(bromomagnesio)-1,3-dienes with ketones.[a]

Entry	Organolithium reagent or Grignard reagent		Ketone	Product		Yield [%][b]
1		**1a**: M = Li			**4a**	75
2		**2a**: M = MgBr				0
3		**1b**: M = Li			**4b**	72
4		**2b**: M = MgBr				0
5		**1c**: M = Li			**4c**	74[c]
6		**2c**: M = MgBr				0
7	**1c**				**4d**	92
8	**1c**				**4e**	75
9		**1d**			**4f**	67

[a] Reaction conditions are given in Scheme 4. [b] Yields refer to isolated amounts after column chromatography. [c] Two isomers in 3:1; the major isomer has an exocyclic double bond.

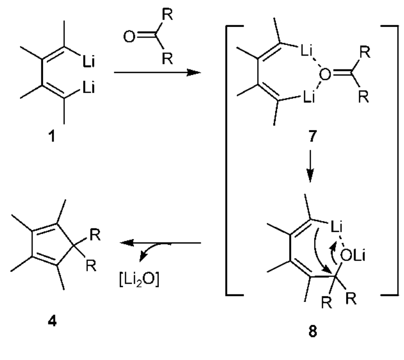


Scheme 5. Generation of magnesio-cyclopentadienes from 1,4-bis(bromomagnesio)-1,3-dienes and different reactivities.

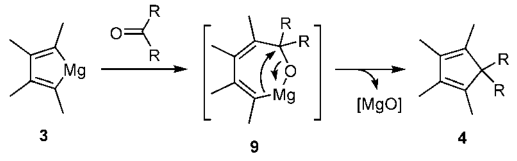
maining alkenyllithium moiety to give cyclopentadiene derivatives **4** along with release of lithium oxide.

For reactions between metallacyclic (1,3-butadiene-1,4-diyl)magnesium reagents **3** with ketones, a proposed reaction mechanism is given in Scheme 7. As usually observed for Grignard reagents, insertion of the C=O double bond of a ketone into one of the two Mg–C bonds of **3** affording **9** is proposed to be the first step.

Reactions of 1,4-dilithiobutadiene derivatives 1, 1,4-bis(bromomagnesio)butadiene derivatives 2 and (1,3-butadiene-1,4-diyl)magnesium reagents 3 with aldehydes: Probably due to higher reactivity of aldehydes towards organolithium reagents compared with ketones, aldehydes with 1,4-dilithiobutadienes **1** proceeded not as cleanly as ketones in these reactions and gave lower reaction yields. In some cases, formation of a by-product was observed. The by-products were later characterized to be polysubstituted 2,5-dihydrofurans **10**.[21] By changing the reaction conditions of 1,4-dilithio-1,3-dienes **1** with aldehydes, either polysubstituted 2,5-dihydrofurans **10** or cyclopentadienes **11** could be prepared selectively. When one equivalent of an aldehyde was added to the dilithio reagent **1** at −78 °C, 1,2,3,4,5-pentasubstituted cyclopentadienes **11** were obtained.[7] However, when two equivalents of an aldehyde were added to the dilithio

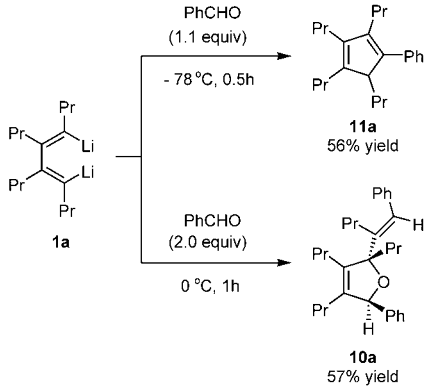


Scheme 6. Proposed reaction mechanism between 1,4-dilithium reagents and ketones.

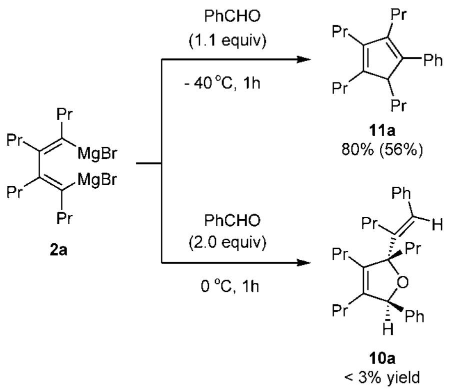


Scheme 7. Proposed reaction mechanism between metallacyclic reagents of magnesium **3** and ketones.

reagent **1** at room temperature, 2,5-dihydrofuran derivatives **10** were formed with high stereoselectivity (Scheme 8).[21]



Scheme 8. Reactions of the 1,4-dilithium reagents with aldehydes.



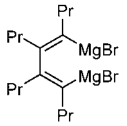
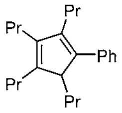
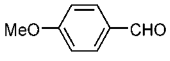
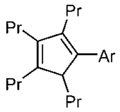
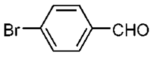
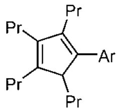
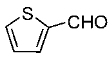
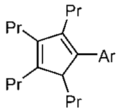
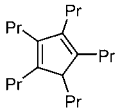
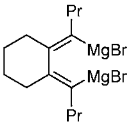
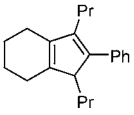
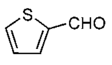
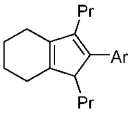
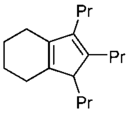
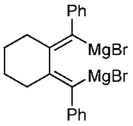
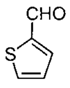
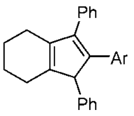
Scheme 9. Reactions of the 1,4-bis(bromomagnesio)-1,3-diene reagents with aldehydes.

It was found that the in situ generated 1,4-bis(bromomagnesio)butadienes **2** could react with aldehydes in a similar pattern to afford cyclopentadiene derivatives **11** (Scheme 9). Results are summarized in Table 2. It should be noted that reactions of **2** with aldehydes did not result in the formation of 2,5-dihydrofurans **10** as the major products, even at higher temperature and with an excessive amount of aldehydes (Scheme 9).

The metallacyclopentadiene derivatives of magnesium **3a** and **3b** reacted with aldehydes in a similar way to afford cyclopentadiene derivatives (Scheme 10). The low yields of products were due to the procedure for the in situ generation of intermediates **3**.

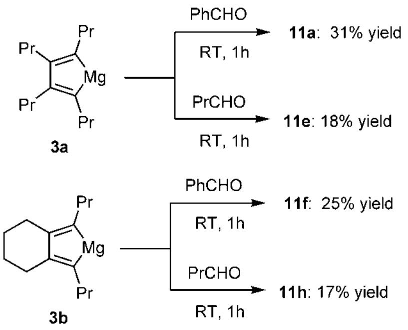
Reaction mechanisms described in Schemes 6 and 7 can be applied for reactions of **1**, **2** and **3** with aldehydes.

Table 2. Reaction of 1,4-bis(bromomagnesio)-1,3-dienes with aldehydes.[a]

Entry	Grignard reagent	Aldehyde	Product		Yield [%][b]
1	 **2a**	PhCHO		**11a**	80 (56)
2	**2a**			**11b**	72 (55)
3	**2a**			**11c**	71 (59)
4	**2a**			**11d**	67 (51)
5	**2a**	PrCHO		**11e**	53 (31)
6	 **2c**	PhCHO		**11f**	71 (53)
7	**2c**			**11g**	71 (61)
8	**2c**	PrCHO		**11h**	59 (41)
9	 **2d**			**11i**	72 (57)

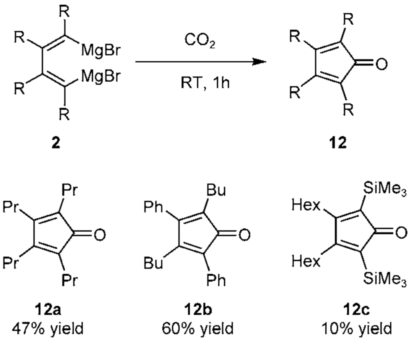
[a] Reaction conditions are given in Scheme 9. [b] GC yields. Yields refer to isolated amounts after column chromatography are given in parentheses.

Reactions of 1,4-bis(bromomagnesio)butadiene derivatives 2 with CO_2 and PhNO: Earlier, we reported an efficient and selective synthetic method of cyclopentadienone derivatives from carbon dioxide and 1,4-dilithio-1,3-dienes **1**.[22] 1,4-Bis(bromomagnesio)butadiene derivatives **2** reacted similarly



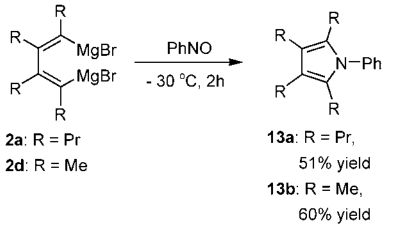
Scheme 10. Reactions of the magnesiocyclopentadienes with aldehydes.

with CO_2 affording substituted cyclopentadienones **12**, though in lower yields (Scheme 11). The reaction mechanism is assumed to be the same.

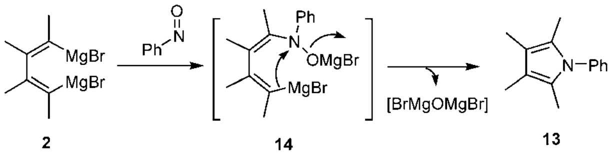


Scheme 11. Reaction of 1,4-bis(bromomagnesio)butadienes **2** with CO_2 affording cyclopentadienones.

All the above reactions of **1**, **2**, and **3** involve the C=O double bonds of aldehydes, ketones and carbon dioxide. In order to study the reaction scope, we used $PhNO_2$ as a model substrate containing N=O double bonds to investigate its reaction with **1**, **2**, and **3**. Reactions between organomagnesium reagents and nitroarenes have attracted much attention and have been recently highlighted.[23] However, we found that these organometallic reagents **1**, **2**, and **3** reacted with $PhNO_2$ to give different products. We then tried reactions of **1**, **2**, and **3** with PhNO, which is known to undergo various addition, reduction, and oxidation reactions.[24] Interestingly, we found that 1,4-bis(bromomagnesio)butadiene derivatives **2** reacted PhNO to afford substituted N-Ph pyrrole derivatives (Scheme 12). This reaction provides a new method for preparation of pyrrole derivatives.[25] Compound **3a** reacted with PhNO in a similar way to afford **13a** in 19% isolated yield. A proposed reaction mechanism is given in Scheme 13.



Scheme 12. Reaction of 1,4-bis(bromomagnesio)butadienes **2** with PhNO affording pyrrole derivatives.



Scheme 13. Proposed reaction mechanism for the reaction between 1,4-bis(bromomagnesio)butadienes **2** and PhNO affording pyrrole derivatives.

Conclusion

Multiply substituted cyclopentadienes and N-Ph pyrroles were formed from reactions of 1,4-dilithiobutadiene derivatives **1**, 1,4-bis(bromomagnesio)butadiene derivatives **2** and metallacyclic (1,3-butadiene-1,4-diyl)magnesium reagents **3** with ketones, aldehydes, and PhNO by unprecedented reaction conditions. The carbonyl group of aldehydes and ketones was deoxygenated in the reaction and behaved formally as a one-carbon unit; the N=O moiety of PhNO was cleaved to afford N-Ph pyrrole derivatives. Furthermore, different reactivities among these three types of reagents **1**, **2** and **3** were revealed. The 1,4-dilithium reagents **1** readily reacted with both aldehydes and ketones; the 1,4-dimagnesium reagents **2** reacted with aldehydes, but not ketones; the metallacyclopentadiene reagents of magnesium **3** showed higher reactivity and did react with ketones.

Experimental Section

General: Unless otherwise noted, all starting materials were commercially available and were used without further purification. All reactions involving organometallic compounds were run under a slightly positive pressure of dry N_2 with use of standard Schlenk techniques. THF, diethyl ether and dioxane were heated under reflux and distilled from sodium/benzophenone under a nitrogen atmosphere. *n*BuLi and *t*BuLi were obtained from Acros Chemical Co. Ltd. The 1,4-dibromo-1,3-diene derivatives and 1,4-diiodo-1,3-diene derivatives were synthesized by the reported procedure.[19]

^1H and ^{13}C NMR spectra were recorded at 300 and 75 MHz, respectively. All spectra were measured in $CDCl_3$ at 25 °C, with TMS as internal reference. GLC analysis was performed on a gas chromatograph (Shimadzu 14B) equipped with a flame ionization detector and a capillary column (CBP1-M25-25). GLC yields were determined using suitable hydrocarbons as internal standards.

Typical procedure for reactions of 1,4-dilithiobutadiene derivatives 1 with ketones: *n*BuLi (2.2 mmol, 1.6 M in hexane) was added to a solution of 1,4-diiodo compound **5** (1 mmol) in diethyl ether (5 mL) at −78 °C. The reaction mixture was then stirred at −78 °C for 1 h to generate **1**. After the addition of the ketone (1.1 mmol) at −78 °C, the mixture was stirred at −78 °C for 0.5 h. Hydrolysis with 3 N HCl followed by normal work up and column chromatography afforded the products.

The characterization data of **4a–f** have been reported.[7]

Typical procedure for the reactions of 1,4-bis(bromomagnesio)butadiene derivatives 2 with ketones: Magnesium powder (400 mg) in THF (5 mL) was warmed to 50 °C, and 1,2-dibromoethane (0.3 mL) was added. Ten minutes later, dibromo compound **6** (1.0 mmol) in THF (15 mL) was added dropwise while stirring via syringe. The reaction mixture was then stirred at 60 °C for 8 h. The Grignard reagent **2** was filtered under an atmosphere of nitrogen to remove the excess of magnesium. The ketone (1.1 mmol) was then added to the THF solution of **2**. No reaction was observed.

Typical procedure for the reactions of (1,3-butadiene-1,4-diyl)magnesium reagents 3 with ketones: 1,4-Bis(bromomagnesio)-1,2,3,4-tetrapropyl-1,3-diene (**2a**; 1 mmol) in THF (20 mL) was generated in situ from the corresponding dibromo compound **6a** (1 mmol) and Mg powder. Subsequently the solution of **2a** was cooled to room temperature. Dioxane (20 mL) was added and the reaction mixture was stirred at room temperature for 2 h. After the mixture was filtered under an atmosphere of nitrogen to remove the precipitate, the filtrate was evaporated in vacuo to remove the solvent. Dioxane (15 mL) was added and the reaction mixture was stirred for 2 h. Then the mixture was kept without stirring for 4 h and filtered under an atmosphere of nitrogen to remove the precipitate again to generate **3**. The ketone (1.1 mmol) was added at room temperature. The reaction mixture was then stirred for 0.5 h, quenched with saturated aqueous NH_4Cl, followed by normal work up and column chromatography afforded the products.

1,2,3,4-Tetrapropyl-5,5-diphenyl-cyclopenta-1,3-diene (4g): White solid (isolated yield: 25 %, 80 mg); b.p. 103 °C; ^1H NMR ($CDCl_3$, Me_4Si): δ = 0.63–1.48 (m, 20 H), 2.08 (t, J = 6.4 Hz, 4 H), 2.25 (t, J = 7.8 Hz, 4 H), 7.10–7.26 (m, 10 H); ^{13}C NMR ($CDCl_3$, Me_4Si): δ = 14.7, 14.8, 23.1, 23.4, 28.6, 29.6, 72.0, 126.0, 127.9, 128.5, 141.0, 141.9, 148.0; HRMS: m/z: calcd for $C_{29}H_{38}$: 386.2974, found: 386.2966.

Typical procedure for the reactions of 1,4-bis(bromagnesio)butadiene derivatives 2 with aldehydes: After 1,4-bis(bromomagnesio)-1,2,3,4-tetrapropyl-1,3-diene (**2a**; (1 mmol) in THF (20 mL) was generated, the aldehyde (1.1 mmol) was added at −40 °C. The reaction mixture was then stirred for 0.5 h at −40 °C, quenched with saturated aqueous NH_4Cl, followed by normal work up and column chromatography to afford the products.

The NMR data of **11a**,[26] **11b–c**,[27] **11d–i**[26] are consistent with the reported data.

Typical procedure for the reactions of (1,3-butadiene-1,4-diyl)magnesium reagents 3 with aldehydes: After (1,3-butadiene-1,4-diyl)magnesium reagent **3** was generation, the aldehyde (1.1 mmol) was added at room temperature. The reaction mixture was stirred for 0.5 h, quenched with saturated aqueous NH_4Cl, followed by normal work up and column chromatography to afford the products.

Typical procedure for the reactions of 1,4-bis(bromagnesio)butadiene derivatives 2 with CO_2: After 1,4-bis(bromomagnesio)-1,2,3,4-tetrapropyl-1,3-diene (**2a**; 1 mmol) in THF (20 mL) was generated, CO_2 was bubbled for 1 h at room temperature. The reaction mixture was quenched with saturated aqueous NH_4Cl and followed by normal work up and column chromatography to afford the products.

2,3,4,5-Tetrapropyl-cyclopenta-2,4-dienone (12a): Orange liquid (isolated yield: 47 %, 117 mg); ^1H NMR ($CDCl_3$, Me_4Si): δ = 0.81–0.91 (m, 12 H), 1.30–1.38 (m, 4 H), 1.45–1.55 (m, 4 H), 2.05–2.16 (m, 8 H); ^{13}C NMR ($CDCl_3$, Me_4Si): δ = 14.38, 14.42, 22.8, 23.2, 25.4, 28.4, 126.2, 154.6, 203.9. The NMR data are consistent with the reported data.[22]

2,4-Dibutyl-3,5-diphenyl-cyclopenta-2,4-dienone (12b): Orange liquid (isolated yield: 60 %, 206 mg); ^1H NMR ($CDCl_3$, Me_4Si): δ = 0.57 (t, J = 6.9 Hz, 3 H), 0.75 (t, J = 6.9 Hz, 3 H), 0.80–1.53 (m, 8 H), 2.12 (t, J = 6.9 Hz, 2 H), 2.42 (t, J = 6.9 Hz, 2 H), 7.22–7.43 (m, 10 H); ^{13}C NMR ($CDCl_3$, Me_4Si): δ = 13.4, 13.8, 22.4, 22.7, 22.8, 26.7, 29.9, 31.6, 125.0, 127.1, 127.9, 128.1, 128.2, 128.4, 128.5, 129.3, 131.7, 134.2, 153.5, 158.3, 202.5. The NMR data are consistent with the reported data.[22]

3,4-Dihexyl-2,5-bis-trimethylsilanyl-cyclopenta-2,4-dienone (12c): Orange liquid (isolated yield: 10 %, 39 mg); ^1H NMR ($CDCl_3$): δ = 0.00 (s, 18 H), 0.69–0.71 (m, 6 H), 1.13–1.22 (m, 16 H), 2.14–2.16 (m, 4 H); ^{13}C NMR ($CDCl_3$, Me_4Si): δ = 0.1, 14.0, 22.6, 28.4, 29.8, 30.7, 31.6, 128.2, 172.9, 211.2; HRMS: m/z: calcd for $C_{23}H_{44}OSi_2$: 392.2931, found 392.2927.

Typical procedure for the reactions of 1,4-bis(bromagnesio)butadiene derivatives 2 with PhNO: After 1,4-bis(bromomagnesio)-1,2,3,4-tetrapropyl-1,3-diene (**2a**; 1 mmol) in THF (20 mL) was generated, PhNO was added at −30 °C. The reaction mixture was stirred at −30 °C for 2 h, quenched with saturated aqueous $NaHCO_3$ and followed by normal work up and column chromatography to afford the product.

1-Phenyl-2,3,4,5-tetrapropyl-1*H*-pyrrole (13a): Colorless liquid (isolated yield: 51 %, 158 mg); ^1H NMR ($CDCl_3$, Me_4Si): δ = 0.69 (t, J = 7.2 Hz, 6 H), 0.99 (t, J = 7.2 Hz, 6 H), 1.12–1.26 (m, 4 H), 1.48–1.56 (m, 4 H), 2.27–2.40 (m, 8 H), 7.19–7.42 (m, 5 H); ^{13}C NMR ($CDCl_3$, Me_4Si): δ = 14.2, 14.7, 24.0, 25.4, 27.1, 27.4, 118.4, 127.2, 128.6, 128.9, 129.0, 139.8; HRMS: m/z: calcd for $C_{22}H_{33}N$: 311.2613; found: 311.2614.

1-Phenyl-2,3,4,5-tetramethyl-1*H*-pyrrole (13b): Red-orange liquid (isolated yield: 60 %, 119 mg); ^1H NMR ($CDCl_3$, Me_4Si): δ = 1.96 (s, 6 H), 2.01 (s, 6 H), 7.16–7.45 (m, 5 H); ^{13}C NMR ($CDCl_3$, Me_4Si): δ = 9.39, 10.57, 113.83, 123.64, 127.177, 128.44, 128.90, 139.46. The NMR data are consistent with the reported data.[25]

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