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Facile Synthesis of Multiply Substituted Cyclopentadienes and Conjugated Dienals through Reactions between 1,4-Dilithio-1,3-dienes and Carboxylic Acid Derivatives Including Acyl Chlorides, Anhydrides, and DMF

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Keywords: Cyclopentadienes / Dienals / 2,5-Dihydrofurans / 1,4-Dilithio-1,3-dienes / Organo-bimetallic reagents

Multiply substituted cyclopentadienes were formed through reactions between phenyl-substituted 1,4-dilithio-1,3-dienes such as **1b** and **1c** and two molecules of acyl chlorides. The phenyl substituents on the skeletons of the dilithiobutadiene derivatives played an essential role in the reaction pattern. Interestingly, when anhydrides were used, normal alkyl-substituted 1,4-dilithio-1,3-dienes such as **1a** could also react similarly to the phenyl-substituted **1b** and **1c**, affording analogous types of multiply substituted cyclopentadienes in excellent isolated yields. Esters were found to afford mixtures of products when treated with **1a–c**. When 1,4-dilithio-1,3-dienes were treated with DMF, multiply substituted 2,4-diene-1,6-dials and/or 2,5-dihydrofuran derivatives were obtained in good yields, depending on the substitution patterns of the butadienyl skeletons.

Introduction

2,4-Diene-type 1,6-bis-electrophiles such as dienals are useful building units for the preparation of both cyclic and linear conjugated compounds,[1–9] because these compounds contain a butadienyl conjugated skeleton and one or two terminal functional groups for potential manipulation. New types of conjugated materials and functional structures might be expected from further applications. As part of our ongoing exploration of synthetic applications of 1,4-dilithio-1,3-butadienyl reagents,[10] we recently began to investigate reactions between these dilithio compounds and DMF,[11] isocyanates,[12] isothiocyanates,[13] dialkyl oxalates,[14] acyl chlorides, esters, and anhydrides, expecting the development of synthetic methods for 2,4-diene-1,6-bis-electrophiles, which are very useful but not otherwise readily available. Here we would like to report: (1) the synthesis of multiply substituted cyclopentadienes through reactions between 1,4-dilithio-1,3-dienes and two molecules of acyl chlorides or anhydrides, and (2) the synthesis of multiply substituted stereodefined *cis*,*cis*-2,4-diene-1,6-dials and/or 2,5-dihydrofuran derivatives from 1,4-dilithio-1,3-dienes and DMF.

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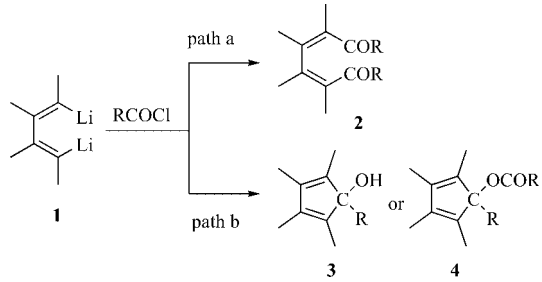
Results and Discussion

Reactions between 1,4-Dilithio-1,3-diene Derivatives and Acyl Chlorides or Anhydrides, Affording Multiply Substituted Cyclopentadienes

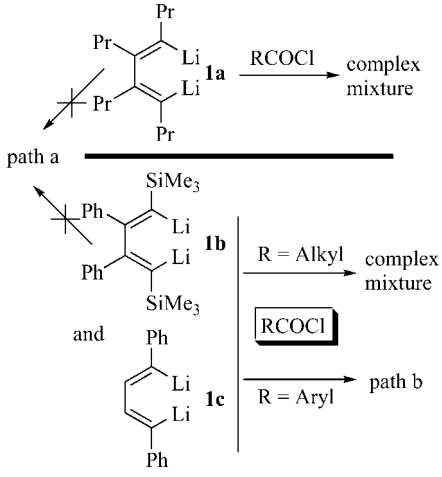
We have recently reported the formation of multiply substituted cyclopentadienes, cyclopentadienones, cyclopentenones, and cyclopentadienyl imines through reactions between 1,4-dilithio-1,3-dienes and aldehydes and ketones, carbon dioxide, carbon monoxide, and isocyanates, respectively.[10a] From the reactions between 1,4-dilithio-1,3-dienes **1** and acyl chlorides we expected the formation of *cis*,*cis*-2,4-diene-1,6-diones **2** (path a, Scheme 1) and/or cyclopentadiene derivatives **3** or **4** (path b, Scheme 1).



Scheme 1. Potential products of reactions between 1,4-dilithio-1,3-dienes and acyl chlorides.

Unfortunately, though, when 1,2,3,4-tetraalkyl-substituted dilithium reagents, such as the 1,2,3,4-tetrapropyl-substituted 1,4-dilithio-1,3-diene **1a**, were used, both aliphatic and aromatic acyl chlorides such as MeCOCl and PhCOCl generally gave messy reaction mixtures, probably

due to the high reactivity of these organic substrates. During the course of our screening of substrates, however, we found that those dilithium reagents possessing phenyl substituents on their butadienyl skeletons were capable of reacting cleanly with aromatic acyl chlorides, affording cyclopentadiene derivatives **4** in high isolated yields, although no formation of the expected *cis*,*cis*-2,4-diene-1,6-diones **2** and cyclopentadiene derivatives **3** was observed (Scheme 2).



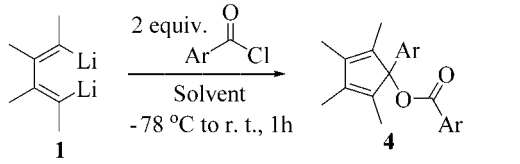
Scheme 2. Selectivity of reaction between **1** and RCOCl.

Results are listed in Table 1. It is inferred that the phenyl groups on the butadienyl skeletons are essential for such clean reactions, probably because the phenyl groups lowered the reactivity of those dilithium reagents. Changes of solvents did not have much influence on the yields (Entries 2–4). The structure of **4b** was determined by single-crystal X-ray structural analysis (Figure 1, CCDC-606926). Cyclopentadienes of this type, otherwise difficult to prepare, might be expected to have applications as building units for conjugated organic materials.[15,16]

In addition to acyl chlorides, we also treated these dilithiodienes with esters and anhydrides. The results showed that the reactions between dilithiodienes such as **1a**–**c** and esters such as $PhCO_2Me$, $PhCO_2Et$, and AcOEt generally afforded mixtures of products, probably because of further reactions of the intermediates generated in situ. Interestingly though, when anhydrides such as $(PhCO)_2O$ and $(PrCO)_2O$ were used, normal alkyl-substituted 1,4-dilithio-1,3-dienes such as **1a** were also able to react smoothly, like the phenyl-substituted **1b**, to afford analogous types of multiply substituted cyclopentadienes **4** in excellent isolated yields (Scheme 3).

Obviously, these cyclopentadiene derivatives were formed from two molecules of the acyl chloride or anhydride; a proposed reaction mechanism is given in Scheme 4. The first intermediate is assumed to be monoacylated **5**, which must be stabilized through the coordination of lithium with the carbonyl group. Cyclopentadienyl oxylithium **6**, which may be formed through intramolecular nucleophilic attack, would then react with another molecule of ArCOCl or $(RCO)_2O$ to afford the product **4**.

Table 1. Reactions between 1,4-dilithio-1,3-dienes **1** and acyl chlorides.



Entry	**1**	ArCOCl	Solvent	Product **4** isol. yield (%)
1	**1b**	PhCOCl	Et_2O	**4a**, 80
2	**1b**	*p*-tolylCOCl	Et_2O	**4b**, 79
3	**1b**	*p*-tolylCOCl	Et_2O / THF 1 : 1	**4b**, 71
4	**1b**	*p*-tolylCOCl	THF	**4b**, 74
5	**1b**	1'-naphthylCOCl	Et_2O	**4c**, 78
6	**1b**	4'-biphenylCOCl	Et_2O	**4d**, 62
7	**1c**	*p*-tolylCOCl	THF	**4e**, 68

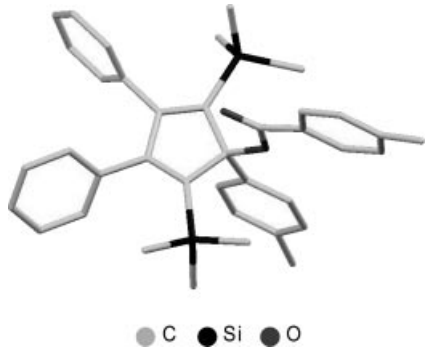
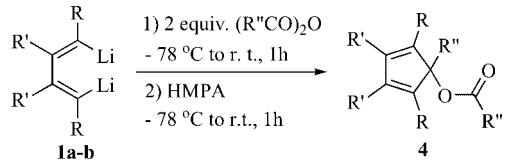
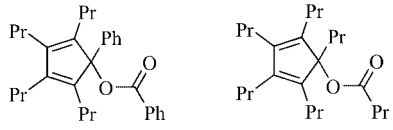
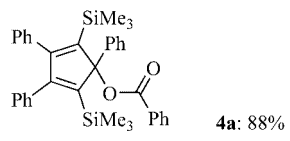


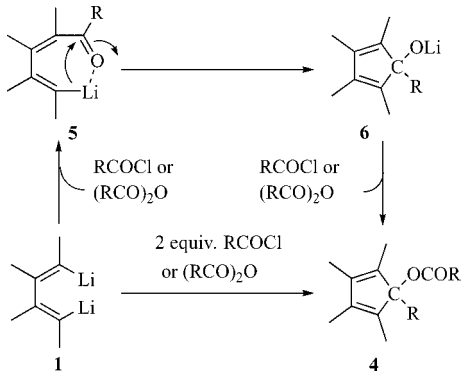
Figure 1. X-ray structure of **4b** (CCDC-606926).







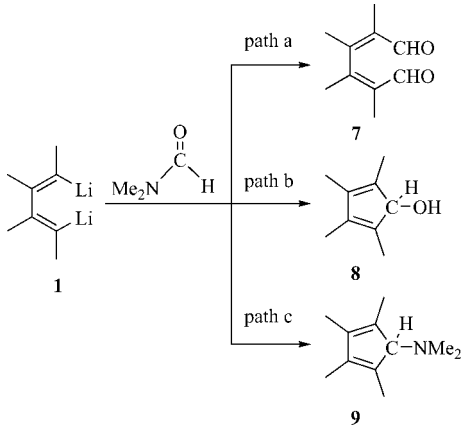
Scheme 3. Reactions between 1,4-dilithio-1,3-dienes **1** and anhydrides.



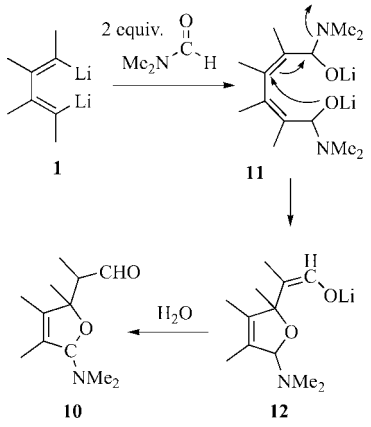
Scheme 4. A proposed mechanism.

Reactions between Lithiobutadiene Derivatives and DMF, Affording Multiply Substituted Stereodefined Dienedials

N,*N*-Dimethylformamide (DMF) and other formic acid derivatives are well known as very important carbonyl sources for the introduction of carbon–oxygen double bonds into target molecules:[17] reactions between DMF and organolithium reagents, for example, have been a useful method for the preparation of aldehydes and ketones.[18] For reactions between 1,4-dilithio-1,3-dienes and DMF, three types of possible routes might be expected (Scheme 5).[11]



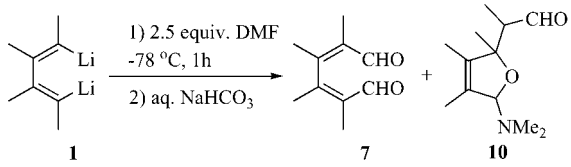
Scheme 5. Expected products from reactions between **1** and DMF.

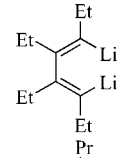
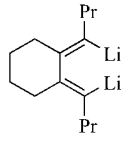
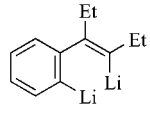
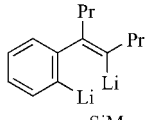
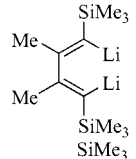
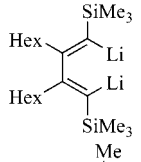
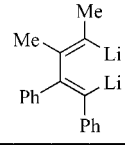


Scheme 6. Proposed reaction mechanism for the formation of **10**.

As we have reported in our preliminary communication,[11] however, the unexpected 2,5-dihydrofuran derivatives **10** (Scheme 6) were also obtained in addition to the expected diene-dials **7**, while no formation of the other two expected products **8** and **9** was observed. Results are given in Table 2. Both alkyl-substituted lithium reagents **1d** and **1e** reacted with DMF to afford both **7** and **10**, with compounds **7** as the major products. Interestingly, the aryl-vinyl dilithium reagents **1f** and **1g** afforded the expected dials **7c** and **7d** as the sole products in 83% and 77% isolated yields, respectively, while the trimethylsilyl-substituted lithium reagents **1h** or **1i** and the lithium reagent **1j**, with phenyl substituents, gave only the 2,5-dihydrofuran derivatives **10** in moderate isolated yields. Scheme 6 gives a proposed reaction mechanism for the formation of 2,5-dihydrofuran derivatives **10** from 1,4-dilithio-1,3-dienes and DMF.

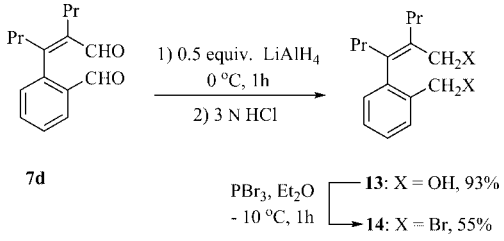
Table 2. Formation of **7** and/or **10** from **1** and DMF.



1		Isol. yield of **7** (%)	Isol. yield of **10** (%)
	**1d**	**7a**, 61	**10a**, 10[a]
	**1e**	**7b**, 44	**10b**, 32[b]
	**1f**	**7c**, 83	—
	**1g**	**7d**, 77	—
	**1h**	—	**10c**, 39[b]
	**1i**	—	**10d**, 45[b]
	**1j**	—	**10e**, 55[a]

[a] Two isomers in 3:2 ratio. [b] Single product.

Treatment of 1,6-dials **7** with different organometallic reagents efficiently afforded the corresponding 1,6-diols **13**.[11] As a representative result, the preparation of **13** from **7d** and lithium aluminium hydride is shown in Scheme 7. 1,6-Diols of this type have been utilized to prepare many complex structures:[7–9] treatment of 1,6-diol **13** with PBr_3, for instance, resulted in derivative of allyl bromide **14** in moderate isolated yield (Scheme 7). Structures such as the dibromide **14** are important synthons, able to take part in, for example, the formation of some seven-membered ring systems difficult to prepare by other means.[19]



Scheme 7. Demonstration of the usefulness of the obtained 1,6-dials.

As well as DMF, we also treated these 1,4-dilithio-1,3-dienes with other amides such as Me_2NCOMe and Me_2NCOPh, expecting the formation of 2,4-diene-1,6-diones **2**, which are also very important compounds. However, these reactions afforded mixtures of unknown products, along with small amounts of monoacylated conjugated dienones.

Conclusions

In summary, we have developed an alternative method for the preparation of multiply substituted cyclopentadienes through reactions between 1,4-dilithio-1,3-dienes and two molecules of acyl chlorides or anhydrides. Cyclopentadienes of this type, which are otherwise difficult to prepare, might be expected to have applications as building units for conjugated organic materials. Depending on the substitution patterns of the butadienyl skeletons, we have achieved the synthesis of multiply substituted 2,4-diene-1,6-dials and/or 2,5-dihydrofuran derivatives by treatment of 1,4-dilithio-1,3-dienes with DMF. Under the reaction conditions used here, mixtures of products were obtained from reactions of 1,4-dilithio-1,3-dienes with esters such as $PhCO_2Me$, $PhCO_2Et$ and AcOEt and with amides other than DMF, such as Me_2NCOMe and Me_2NCOPh.

Experimental Section

General Methods: All reactions were conducted under slightly positive pressures of dry, prepurified nitrogen with use of standard Schlenk line techniques when appropriate. Unless otherwise noted, all starting materials were commercially available and were used without further purification. Diethyl ether and tetrahydrofuran were heated at reflux and distilled from sodium/benzophenone ketyl under nitrogen. 1,4-Dihalo-1,3-butadiene compounds were prepared according to the literature.[10a] ^1H and ^{13}C NMR spectra were recorded at 300 and 75.4 MHz, respectively, in $CDCl_3$ unless stated otherwise. HR-MS were recorded with a ZAB-HS instrument (1–2000u, 1000–10000, 10–10 C ug^{-1}.)

A Typical Procedure for the Synthesis of Cyclopentadiene Derivatives 4 through the Reactions between the Dilithio-1,3-dienes 1 and Acyl Chlorides: *t*BuLi (4.0 mmol, 1.5 M in pentane) was added at –78 °C to a solution of the 1,4-diiodo-1,3-butadiene compound in Et_2O (10 mL, 1.0 mmol; for **4e** the corresponding dibromide in THF was used). After this reaction mixture had been stirred at –78 °C for 1 h, the acyl chloride (2.2 mmol) was added. The reaction mixture was maintained at –78 °C for 0.5 h and then at room temperature for 0.5 h, quenched with water, and extracted with Et_2O. The extract was washed with brine and dried with $MgSO_4$, the solvent was then evaporated in vacuo, and the residue was then purified by column chromatography (silica gel, dichloromethane/hexane, 1:4) to afford the title products **4**.

Compound 4a: Colorless crystals, 80% yield (447 mg). M.p. 197.4–199.1 °C. ^1H NMR (300 MHz, $CDCl_3$, Me_4Si, 25 °C): δ = –0.42 (s, 18 H, CH_3), 7.46–8.07 (m, 16 H, CH), 8.17 (d, J = 8.1 Hz, 2 H, CH), 8.65–8.70 (m, 2 H, CH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si, 25 °C): δ = –0.37 (6 × CH_3), 101.49 (1 × quat. C), 125.30 (2 × CH), 126.82 (1 × CH), 126.88 (2 × CH), 127.30 (4 × CH), 128.40 (2 × CH), 128.63 (2 × CH), 129.24 (4 × CH), 129.58 (2 × CH), 131.45 (1 × quat. C), 132.68 (1 × CH), 137.27 (1 × quat. C), 137.44 (2 × quat. C), 152.38 (2 × quat. C), 157.59 (2 × quat. C), 163.50 (1 × quat. C) ppm. IR (neat): ν = 1730 cm^{-1} (C=O). HRMS calcd. for $C_{36}H_{38}O_2Si_2$: 558.2410; found: 558.2411. Elemental analysis for $C_{36}H_{38}O_2Si_2$ (558.86): calcd. C 77.37, H 6.85; found: C 77.41, H 6.89.

Compound 4b: Colorless crystals, 79% yield (464 mg). M.p. 166.3–167.8 °C. ^1H NMR (300 MHz, $CDCl_3$, Me_4Si, 25 °C): δ = –0.42 (s, 18 H, CH_3), 2.39 (s, 3 H, CH_3), 2.46 (s, 3 H, CH_3), 7.00–8.16 (m, 10 H, CH), 7.19 (d, J = 6.0 Hz, 2 H, CH), 7.33 (d, J = 6.0 Hz, 2 H, CH), 7.61 (d, J = 6.0 Hz, 2 H, CH), 8.13 (d, J = 6.0 Hz, 2 H, CH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si, 25 °C): δ = –0.32 (6 × CH_3), 21.11 (1 × CH_3), 21.69 (1 × CH_3), 101.38 (1 × quat. C), 125.22 (2 × CH), 126.80 (2 × CH), 127.27 (4 × CH), 128.84 (1 × quat. C), 129.10 (2 × CH), 129.28 (4 × CH), 129.34 (2 × CH), 129.63 (2 × CH), 134.04 (1 × quat. C), 136.26 (1 × quat. C), 137.58 (2 × quat. C), 143.23 (1 × quat. C), 152.46 (2 × quat. C), 157.19 (2 × quat. C), 163.66 (1 × quat. C) ppm. IR (neat): ν = 1729 cm^{-1} (C=O). HRMS calcd. for $C_{38}H_{42}O_2Si_2$: 586.2723; found: 586.2729. Elemental analysis for $C_{38}H_{42}O_2Si_2$ (586.91): calcd. C 77.76, H 7.21; found C 77.78, H 7.11.

CCDC-606926 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Compound 4c: Colorless crystals, 78% yield (509 mg). M.p. 181.6–183.2 °C. ^1H NMR (300 MHz, $CDCl_3$, Me_4Si, 25 °C): δ = –0.53 (s, 18 H, CH_3), 7.10–7.29 (m, 10 H, CH), 7.43–7.71 (m, 6 H, CH), 7.85–7.89 (m, 2 H, CH), 7.94 (d, J = 6.0 Hz, 1 H, CH), 8.09 (d, J = 6.0 Hz, 1 H, CH), 8.46 (d, J = 4.0 Hz, 1 H, CH), 8.53 (d, J = 4.0 Hz, 1 H, CH), 8.81–8.88 (m, 1 H, CH), 8.96 (d, J = 4.0 Hz, 1 H, CH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si, 25 °C): δ = –0.47 (6 × CH_3), 102.38 (1 × quat. C), 124.70 (1 × CH), 125.10 (1 × CH), 125.23 (1 × CH), 125.35 (1 × CH), 125.41 (1 × CH), 125.83 (1 × CH), 125.97 (1 × CH), 126.28 (1 × CH), 127.10 (4 × CH), 127.42 (4 × CH), 127.82 (1 × CH), 128.58 (1 × CH), 128.85 (2 × CH), 128.99 (1 × CH), 129.00 (1 × CH), 129.06 (1 × CH), 129.24 (1 × quat. C), 129.73 (1 × quat. C), 131.50 (1 × quat. C), 132.75 (1 × CH), 133.62 (1 × quat. C), 134.12 (1 × quat. C), 134.22 (1 × quat. C), 137.72 (2 × quat. C), 150.45 (2 × quat. C), 161.07

(2 × quat. C), 163.50 (1 × quat. C) ppm. IR (neat): ν = 1712 cm^{-1} (C=O). HRMS calcd. for $C_{44}H_{42}O_2Si_2$: 658.2723; found: 658.2726. Elemental analysis for $C_{44}H_{42}O_2Si_2$ (658.97): calcd. C 80.20, H 6.42; found C 80.10, H 6.56.

Compound 4d: Colorless crystals, 62% yield (442 mg). M.p. 215.4–216.9 °C. ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si, 25 °C): δ = –0.34 (s, 18 H, CH_3), 7.08–7.19 (m, 10 H, CH), 7.33–7.53 (m, 6 H, CH), 7.53–7.65 (m, 6 H, CH), 7.77 (d, *J* = 6.0 Hz, 2 H, CH), 7.83 (d, *J* = 6.0 Hz, 2 H, CH), 8.34 (d, *J* = 6.0 Hz, 2 H, CH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si, 25 °C): δ = –0.24 (6 × CH_3), 101.48 (1 × quat. C), 125.79 (2 × CH), 126.90 (2 × CH), 126.92 (2 × CH), 127.00 (2 × CH), 127.27 (2 × CH), 127.32 (4 × CH), 127.34 (4 × CH), 127.37 (2 × CH), 128.13 (1 × CH), 128.80 (2 × CH), 128.95 (2 × CH), 129.25 (2 × CH), 130.12 (2 × CH), 136.41 (1 × quat. C), 137.44 (2 × quat. C), 139.49 (1 × quat. C), 140.08 (1 × quat. C), 140.63 (1 × quat. C), 145.45 (1 × quat. C), 152.35 (2 × quat. C), 157.68 (2 × quat. C), 163.44 (1 × quat. C) ppm. IR (neat): ν = 1728 cm^{-1} (C=O). HRMS calcd. for $C_{48}H_{46}O_2Si_2$: 710.3036; found: 710.3035. Elemental analysis for $C_{44}H_{42}O_2Si_2$ (711.04): calcd. C 81.08, H 6.52; found C 80.78, H 6.67.

Compound 4e: Colorless crystals, 68% yield (301 mg). M.p.169.8–171.0 °C. ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si, 25 °C): δ = 2.25 (s, 3 H, CH_3), 2.38 (s, 3 H, CH_3), 7.03 (s, 2 H, CH), 6.98–7.49 (m, 14 H, CH), 7.62 (d, *J* = 6.0 Hz, 2 H, CH), 7.01 (d, *J* = 4.0 Hz, 2 H, CH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si, 25 °C): δ = 21.03 (1 × CH_3), 21.65 (1 × CH_3), 90.01 (1 × quat. C), 124.44 (2 × CH), 125.60 (4 × CH), 126.77 (2 × CH), 127.18 (2 × CH), 127.79 (1 × quat. C), 128.29 (4 × CH), 129.20 (2 × CH), 129.54 (2 × CH), 129.72 (2 × CH), 132.75 (1 × quat. C), 134.21 (1 × quat. C), 136.95 (1 × quat. C), 143.66 (2 × quat. C), 151.37 (2 × quat. C), 162.84 (1 × quat. C) ppm. IR (neat): ν = 1731 cm^{-1} (C=O). HRMS calcd. for $C_{32}H_{26}O_2$: 442.1933; found: 442.1930. Elemental analysis for $C_{32}H_{26}O_2$ (442.55): calcd. C 86.85, H 5.92; found C 86.73, H 5.97.

A Typical Procedure for the Synthesis of Cyclopentadiene Derivatives 4 through the Reactions between the Dilithio-1,3-dienes 1 and Acyl Anhydrides: *t*BuLi (4.0 mmol, 1.5 M in pentane) was added at –78 °C to a solution of the 1,4-diiodo-1,3-butadiene compound in Et_2O (10 mL, 1.0 mmol). This reaction mixture was stirred at –78 °C for 1 h and HMPA (4.4 mmol) was then added. After 20 min, the acid anhydride (2.1 mmol) was added, and the reaction mixture was allowed to warm to room temperature and kept for 1 h. The above reaction mixture was quenched with water and extracted with Et_2O, the extract was washed with brine and dried with $MgSO_4$, the solvent was then evaporated in vacuo, and the residue was then purified by column chromatography (silica gel, dichloromethane/hexane, 1:4) to afford the title products **4**.

Compound 4a: 88% yield (506 mg).

Compound 4f: Colorless oil, 83% yield (358 mg). ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si, 25 °C): δ = 0.66 (t, *J* = 7.2 Hz, 6 H, CH_3), 1.00 (t, *J* = 7.5 Hz, 6 H, CH_3), 1.48–1.61 (m, 2 H, CH_2), 1.83–2.04 (m, 2 H, CH_2), 2.19–2.32 (m, 2 H, CH_2), 7.20–7.60 (m, 3 H, CH), 8.13–8.16 (m, 2 H, CH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si, 25 °C): δ = 14.73 (2 × CH_3), 14.96 (2 × CH_3), 21.86 (2 × CH_2), 23.30 (2 × CH_2), 28.33 (4 × CH_2), 95.00 (1 × quat. C), 125.21 (2 × CH), 126.95 (1 × CH), 128.43 (2 × CH), 128.67 (2 × CH), 129.76 (2 × CH), 131.70 (1 × quat. C), 132.76 (1 × CH), 139.48 (1 × quat. C), 142.04 (2 × quat. C), 142.61 (2 × quat. C), 163.36 (1 × quat. C) ppm. IR (neat): ν = 1733 cm^{-1} (C=O). HRMS calcd. for $C_{30}H_{38}O_2$: 430.2872; found: 430.2870.

Compound 4g: Colorless oil, 78% yield (284 mg). ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si, 25 °C): δ = 0.81–0.96 (m, 18 H, CH_3), 1.27–1.73 (m, 12 H, CH_2), 1.90–2.22 (m, 12 H, CH_2) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si, 25 °C): δ = 13.82 (1 × CH_3), 14.18 (1 × CH_3), 14.50 (2 × CH_3), 14.97 (1 × CH_2), 15.02 (2 × CH_3), 18.35 (1 × CH_2), 21.72 (2 × CH_2), 23.15 (2 × CH_2), 27.91 (2 × CH_2), 28.07 (2 × CH_2), 36.40 (1 × CH_2), 36.99 (1 × CH_2), 93.47 (1 × quat. C), 137.46 (2 × quat. C), 141.09 (2 × quat. C), 170.49 (1 × quat. C) ppm. IR (neat): ν = 1746 cm^{-1} (C=O). HRMS calcd. for $C_{24}H_{42}O_2$: 362.3185; found: 362.3188.

A Typical Procedure for the Synthesis of 1,6-Dials 7 or 2,5-Dihydrofurans 10 through the Reactions between the Dilithio-1,3-dienes 1 and DMF: *t*BuLi (4.0 mmol, 1.5 M in pentane) was added at –78 °C to a solution of the 1,4-diiodo-1,3-butadiene compound (1.0 mmol) in Et_2O (10 mL). After this reaction mixture had been stirred at –78 °C for 1 h, DMF (2.5 mmol) was added. After having been stirred at –78 °C for a further 1 h, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ and extracted with Et_2O. The extract was washed with water and brine and dried with $MgSO_4$, the solvent was then evaporated in vacuo, and the residue was purified by column chromatography (silica gel, Et_2O/hexane 1:30) to afford the product **7** or **10** as a colorless liquid.

Compound 7a: Colorless oil, 61% yield (136 mg). ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si, 25 °C): δ = 1.01–1.09 (m, 12 H), 2.26–2.49 (m, 6 H), 2.66–2.79 (m, 2 H), 9.59 (s, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si, 25 °C): δ = 11.77 (2 × CH_3), 13.73 (2 × CH_3), 18.49 (2 × CH_2), 25.69 (2 × CH_2), 143.49 (2 × quat. C), 157.36 (2 × quat. C), 192.33 (2 × CH) ppm. IR (neat): ν = 1673 cm^{-1} (C=O). HRMS calcd. for $C_{14}H_{22}O_2$: 222.1620; found: 222.1611.

Compound 7b: Colorless oil, 44% yield (111 mg). ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si, 25 °C): δ = 0.94 (t, *J* = 7.2 Hz, 6 H), 1.27–1.50 (m, 4 H), 1.65–1.80 (m, 2 H), 2.00–2.39 (m, 8 H), 3.00–3.08 (m, 2 H), 9.61 (s, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si, 25 °C): δ = 14.29 (2 × CH_3), 22.72 (2 × CH_2), 26.98 (2 × CH_2), 28.50 (2 × CH_2), 35.29 (2 × CH_2), 139.94 (2 × quat. C), 158.09 (2 × quat. C), 191.56 (2 × CH) ppm. IR (neat): ν = 1673 cm^{-1} (C=O). HRMS calcd. for $C_{16}H_{24}O_2$: 248.1776; found: 248.1784.

Compound 7c: Colorless oil, 83% yield (180 mg). ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si, 25 °C): δ = 1.00 (t, *J* = 7.5 Hz, 3 H), 1.11 (t, *J* = 7.5 Hz, 3 H), 2.36–2.61 (m, 3 H), 2.76–2.92 (m, 1 H), 7.17–7.25 (m, 1 H), 7.50–7.66 (m, 2 H), 7.95–8.02 (m, 1 H), 9.23 (s, 1 H), 10.05 (s, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si, 25 °C): δ = 11.85 (1 × CH_3), 13.71 (1 × CH_3), 18.30 (1 × CH_2), 29.75 (1 × CH_2), 128.56 (1 × CH), 130.24 (1 × CH), 130.80 (1 × CH), 133.52 (1 × CH), 134.17 (1 × quat. C), 141.37 (1 × quat. C), 141.44 (1 × quat. C), 159.83 (1 × quat. C), 190.98 (1 × CH), 192.61 (1 × CH) ppm. IR (neat): ν = 1673 cm^{-1}, 1698 cm^{-1} (C=O). HRMS calcd. for $C_{14}H_{16}O_2$: 216.1150; found: 216.1171.

Compound 7d: Colorless oil, 77% yield (188 mg). ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si, 25 °C): δ = 0.94 (t, *J* = 7.5 Hz, 3 H), 1.01 (t, *J* = 7.5 Hz, 3 H), 1.24–1.60 (m, 4 H), 2.28–2.59 (m, 3 H), 2.70–2.85 (m, 1 H), 7.14–7.24 (m, 1 H), 7.46–7.68 (m, 2 H), 7.93–8.03 (m, 1 H), 9.25 (s, 1 H), 10.06 (s, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si, 25 °C): δ = 14.20 (1 × CH_3), 14.36 (1 × CH_3), 20.82 (1 × CH_2), 22.45 (1 × CH_2), 27.12 (1 × CH_2), 39.05 (1 × CH_2), 128.53 (1 × CH), 130.19 (1 × CH), 130.82 (1 × CH), 133.48 (1 × CH), 134.02 (1 × quat. C), 140.37 (1 × quat. C), 141.86 (1 × quat. C), 158.92 (1 × quat. C), 190.98 (1 × CH), 192.83 (1 × CH) ppm. IR (neat): ν = 1673 cm^{-1}, 1698 cm^{-1} (C=O). HRMS calcd. for $C_{16}H_{20}O_2$: 244.1463; found: 244.1475.

Compound 10a: Colorless oil, 10% yield (28 mg, two isomers in 3:2 ratio). ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si, 25 °C): δ = 065–1.19

(s, 12 H), 1.46–1.99 (m, 6 H), 2.01–2.13 (m, 2 H), 2.29 (s, 3.6 H), 2.31 (s, 2.4 H), 5.28 (s, 0.6 H), 5.37 (s, 0.4 H), 9.55 (d, J = 4.6 Hz, 0.4 H), 9.68 (d, J = 4.0 Hz, 0.6 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si, 25 °C): δ = 7.50 (1×CH_3), 8.29 (1×CH_3), 12.49 (1×CH_3), 12.54 (1×CH_3), 12.59 (1×CH_3), 12.82 (1×CH_3), 13.59 (1×CH_3), 13.92 (1×CH_3), 17.65 (1×CH_2), 17.70 (1×CH_2), 18.28 (1×CH_2), 18.38 (1×CH_2), 18.58 (1×CH_2), 18.63 (1×CH_2), 29.14 (1×CH_2), 29.85 (1×CH_2), 39.52 (1×CH_3), 39.61 (2×CH_3), 61.51 (1×CH), 62.06 (1×CH), 91.34 (1×quat. C), 91.41 (1×quat. C), 101.22 (1×quat. C), 101.72 (1×quat. C), 136.33 (1×quat. C), 136.78 (1×quat. C), 138.93 (1×quat. C), 140.49 (1×quat. C), 204.44 (1×CH), 204.49 (1×CH) ppm. HRMS calcd. for $C_{16}H_{29}NO_2$: 267.2198; found: 267.2196.

Compound 10b: Colorless oil, 32% yield (91 mg). ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si, 25 °C): δ = 0.84 (t, J = 7.5 Hz, 3 H), 0.92 (t, J = 7.5 Hz, 3 H), 1.10–1.76 (m, 10 H), 1.78–2.05 (m, 5 H), 2.20–2.29 (m, 1 H), 2.29 (s, 6 H), 2.44–2.60 (m, 1 H), 5.31 (s, 1 H),9.38 (d, J = 4.8 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si, 25 °C): δ = 14.03 (1×CH_3), 14.19 (1×CH_3), 20.98 (1×CH_2), 21.31 (1×CH_2), 23.26 (1×CH_2), 24.06 (1×CH_2), 26.37 (1×CH_2), 26.77 (1×CH_2), 26.92 (1×CH_2), 35.75 (1×CH_2), 39.40 (2×CH_3), 55.66 (1×CH), 87.69 (1×quat. C), 102.84 (1×quat. C), 129.54 (1×quat. C), 139.42 (1×quat. C), 205.04 (1×CH) ppm.

Compound 10c: Colorless oil, 39% yield (128 mg). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 0.00 (s, 9 H), 0.05 (s, 9 H), 1.17 (s, 3 H), 1.51 (s, 3 H), 2.11 (s, 6 H), 5.34 (s, 1 H), 9.10 (d, J = 6.3 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = –0.65 (3×CH_3), 0.00 (3×CH_3), 12.35 (1×CH_3), 26.37 (1×CH_3), 39.67 (2×CH_3), 57.49 (1×CH), 90.11 (1×quat. C), 106.10 (1×quat. C), 131.24 (1×quat. C), 153.58 (1×quat. C), 204.13 (1×CH) ppm. IR (neat): ν = 1699 cm^{-1} (C=O). HRMS calcd. for $C_{16}H_{33}NO_2Si_2$: 327.2050; found: 327.2043.

Compound 10d: Colorless oil, 45% yield (208 mg). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 0.00 (s, 18 H), 0.66–0.78 (m, 7 H), 0.99–1.29 (m, 15 H), 1.49–1.72 (m, 4 H), 2.10 (s, 6 H), 2.30–2.50 (m, 1 H), 5.32 (s, 1 H), 9.70–9.74 (m, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 0.00 (6×CH_3), 14.74 (1×CH_3), 14.79 (1×CH_3), 23.31 (1×CH_2), 23.35 (1×CH_2), 24.12 (1×CH_2), 27.92 (1×CH_2), 30.01 (1×CH_2), 30.82 (1×CH_2), 31.99 (1×CH_2), 32.27 (1×CH_2), 32.55 (1×CH_2) 39.46 (1×CH_2), 40.34 (2×CH_3), 53.16 (1×CH), 91.54 (1×quat. C), 107.71 (1×quat. C), 134.11 (1×quat. C), 156.13 (1×quat. C), 203.78 (1×CH) ppm. IR (neat): ν = 1723 cm^{-1} (C=O).

Compound 10e: Colorless oil, 55% (185 mg, two isomers in 3:2 ratio). ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si, 25 °C): δ = 1.11 (d, J = 7.2 Hz, 1.3 H), 1.17 (d, J = 7.2 Hz, 1.7 H), 1.60 (s, 1.7 H), 1.61 (s, 1.3 H), 2.37 (s, 3.6 H), 2.38 (s, 2.4 H), 2.43–2.52 (m, 1 H), 5.91 (s, 0.6 H), 6.03 (s, 0.4 H), 6.99–7.36 (m, 10 H), 9.63 (d, J = 2.7 Hz, 0.6 H), 9.82 (d, J = 3.9 Hz, 0.4 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si, 25 °C): δ = 9.34 (1×CH_3), 9.58 (1×CH_3), 24.65 (1×CH_3), 25.71 (1×CH_3), 39.26 (2×CH_3), 39.27 (2×CH_3), 53.81 (1×CH), 54.18 (1×CH), 89.82 (1×quat. C), 90.06 (1×quat. C), 102.15 (1×quat. C), 103.02 (1×quat. C), 127.47 (1×CH), 127.49 (1×CH), 127.87 (1×CH), 127.89 (1×CH), 127.97 (1×CH), 128.02 (1×CH), 128.59 (1×CH), 128.60 (1×CH), 128.71 (1×CH), 128.72 (1×CH), 128.96 (1×CH), 129.39 (1×CH), 132.93 (1×CH_2), 133.09 (1×CH_2), 134.50 (1×quat. C), 134.60 (1×quat. C), 135.55 (1×quat. C), 136.17 (1×quat. C), 142.23 (1×quat. C), 143.12 (1×quat. C), 204.51 (1×CH), 205.47 (1×CH) ppm. IR (neat): ν = 1720 cm^{-1} (C=O). HRMS calcd. for $C_{22}H_{25}NO_2$: 335.1885; found: 335.1870.

Synthesis of 1,6-Diols 13 by Treatment of Compounds 7 with Organometallic Reagents: $LiAlH_4$ (0.5 mmol) was added at –10 °C to a solution of **7** (1.0 mmol) in Et_2O (10 mL). After having been stirred at the same temperature for 1 h, this reaction mixture was quenched with H_2SO_4 (6 M) and then extracted with Et_2O. The extract was washed with water and brine and dried with Na_2SO_4, the solvent was then evaporated in vacuo, and the residue was purified by column chromatography (silica gel, Et_2O/hexane 1:3) to afford the product **13** as a colorless solid, 93% yield (231 mg). M.p. 69–70 °C. ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si, 25 °C): δ = 0.85 (t, J = 7.2 Hz, 3 H), 0.97 (t, J = 7.2 Hz, 3 H), 1.11–1.38 (m, 2 H), 1.41–1.62 (m, 2 H), 2.03–2.40 (m, 4 H), 3.58 (s, 2 H), 4.10 (br., 1 H), 4.19–4.52 (m, 2 H), 4.73 (br., 1 H), 6.76–6.99 (m, 1 H), 7.08–7.26 (m, 2 H), 7.28–7.50 (m, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si, 25 °C): δ = 14.23 (1×CH_3), 14.26 (1×CH_3), 20.87 (1×CH_2), 22.09 (1×CH_2), 31.69 (1×CH_2), 36.61 (1×CH_2), 61.83 (1×CH_2), 62.13 (1×CH_2), 126.80 (1×CH), 127.32 (1×CH), 129.19 (1×CH), 129.86 (1×CH), 136.59 (1×quat. C), 137.94 (1×quat. C), 138.01 (1×quat. C), 141.68 (1×quat. C) ppm. HRMS calcd. for $[C_{16}H_{24}O_2Na]^+$: 271.1668; found: 271.1667.

Synthesis of Dibromide 14 from 13 and Phosphorus Tribromide: Phosphorus tribromide (2.0 mmol) was added at –10 °C to a solution of **13** (1.0 mmol) in Et_2O (10 mL). After having been stirred at the same temperature for 1 h, this reaction mixture was quenched with water and extracted with hexane. The extract was dried with Na_2SO_4 after having been washed in turn with saturated aqueous $NaHCO_3$, water, and brine. The solvent was then evaporated in vacuo and the residue was purified by column chromatography (silica gel, hexane) to afford the product **14** as a colorless oil, 55% yield (206 mg). ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si, 25 °C): δ = 0.90 (t, J = 7.5 Hz, 3 H), 1.03 (t, J = 7.5 Hz, 3 H), 1.20–1.71 (m, 4 H), 2.02–2.20 (m, 1 H), 2.26–2.62 (m, 3 H), 3.59–3.85 (m, 2 H), 4.42 (s, 1 H), 6.91–7.59 (m, 4 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si, 25 °C): δ = 14.12 (1×CH_3), 14.23 (1×CH_3), 21.10 (1×CH_2), 21.86 (1×CH_2), 31.48 (1×CH_2), 31.57 (1×CH_2), 35.95 (1×CH_2), 36.18 (1×CH_2), 127.87 (1×CH), 128.36 (1×CH), 129.05 (1×CH), 130.99 (1×CH), 134.39 (1×quat. C), 134.64 (1×quat. C), 140.47 (1×quat. C), 141.20 (1×quat. C). HRMS calcd. for $C_{16}H_{22}Br_2$: 372.0088; found: 372.0090.

Supporting Information (see also the footnote on the first page of this article): Copies of ^{1}H NMR and ^{13}C NMR spectra of all new compounds.

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