Pergamon

SCIENCE DIRECT®

Tetrahedron 59 (2003) 3779–3786

TETRAHEDRON

Reaction of aluminacyclopentadienes with aldehydes affording cyclopentadiene derivatives

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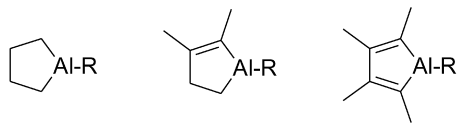
Received 4 December 2002; revised 6 March 2003; accepted 17 March 2003

Abstract—Aluminacyclopentadienes, prepared in situ from the reaction of $AlCl_3$ and 1,4-dilithio-1,3-dienes at room temperature, reacted with aldehydes at room temperature to afford cyclopentadiene derivatives including tetrahydroindenes in good to excellent yields. Both aromatic and aliphatic aldehydes undergo this reaction.

1. Introduction

In recent years, preparative methods and synthetic applications of metallacyclic compounds of transition metals have attracted much attention which continues to grow since many important transition-metal-mediated processes are assumed to proceed via metallacyclic intermediates.[1,2] On the contrary, little advancement in the preparative methods and synthetic applications of metallacyclic compounds of main group metals such as aluminum has been achieved. Two major reasons could be responsible for this situation: (1) the reaction chemistry of metallacyclic compounds of main group metals is generally thought to be not as rich as that of the transition metals; and (2) there is a lack of preparative methods.

Aluminacycles, including alumina-cyclopentanes (**1**, Fig. 1), -cyclopentenes (**2**, Fig. 1) and -pentadienes (**3**, Fig. 1) have been known for decades.[3–7] In 1962, Eisch and Kaska prepared for the first time 1,2,3-triphenyl-benzaluminole, via the addition and cyclization reactions of arylaluminum compounds.[3] Except iodination and hydrolysis, the reaction chemistry of these aluminoles had not been studied. In 1977, Hoberg and Krause-Going reported the formation of pentaphenylaluminacyclopentadienes by the reaction of 1,4-dilithio-1,2,3,4-tetraphenylbutadiene with Cl_2AlPh in Et_2O.[4] The structure of this compound was characterized by X-ray single-crystal analysis.[4b] This aluminacyclopentadiene was immediately used as a ligand to prepare new transition metal complexes.[4b,5] Preparations of alumina-cyclopentanes **1** and aluminacyclopentenes **2** using the Zr-catalyzed carboalumination of alkenes or alkynes were reported by Negishi,[6] Dzhemilev,[7] and others.



1 2 3

Figure 1. 1: aluminacyclopentane; **2**: aluminacyclopentene; **3**: aluminacyclopentadiene; R=alkyl or aryl groups such as Et, Ph.

Synthetic applications of such aluminacyclopentanes and aluminacyclopentenes for cyclic organic compounds have also been reported.[6,7] However, although aluminacyclopentadienes **3** had been prepared for a long time,[3,4] their reaction chemistry, especially their applications in organic synthesis had not been investigated. Recently, we reported a one-pot formation of cyclopentadiene derivatives from two molecules of alkynes and one molecule of aldehyde, via a deoxygenative cycloaddition of the aldehyde with the alkynes mediated by zirconocene and $AlCl_3$.[8] An alumina-cyclopentadiene was assumed to be a possible intermediate. As part of our continued interest in the discovery and development of synthetically useful organometallic reagents of main group metals,[9–14] we investigated the reaction of a wide range of aluminacyclopentadienes with various substrates.

2. Results and discussion

As mentioned above, Hoberg and Krause-Going reported

Keywords: aluminacyclopentadiene; cyclopentadiene; 1,4-dilithio-1,3-diene; aldehyde; $AlCl_3$.

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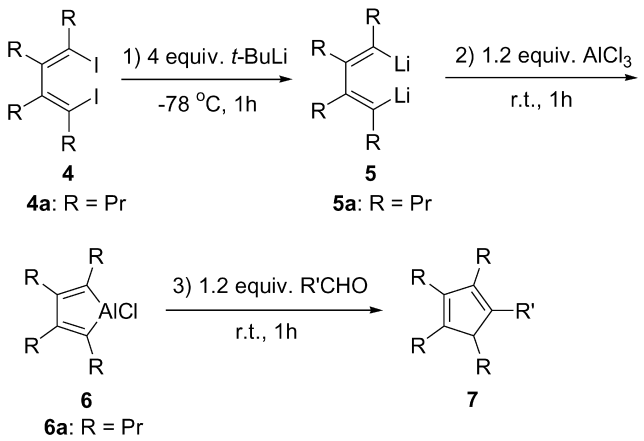
0040–4020/03/$ - see front matter
doi:10.1016/S0040-4020(03)00522-2



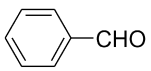
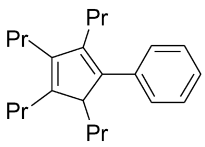
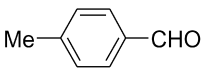
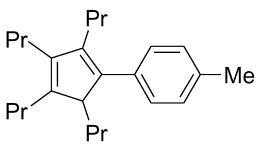
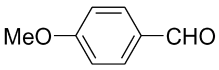
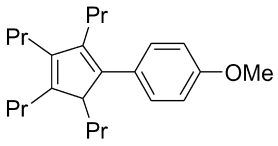
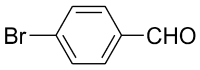
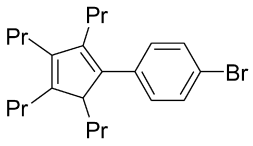
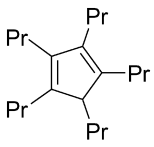
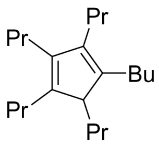
Scheme 1.

the single-crystal structural determination of pentaphenylaluminacyclopentadiene, and the application of this aluminacyclopentadiene as a ligand to prepare transition metal complexes.[4,5] This compound was prepared by the reaction of 1,4-dilithio-1,2,3,4-tetraphenyl-butadiene with Cl_2AlPh in Et_2O.[4] In fact, a variety of main group metalloles have been prepared by using 1,4-dilithio-1,3-dienes as 1,4-dianion precursors,[15,16] especially since 1,4-diiodo-1,3-dienes **4**, from which 1,4-dilithio-1,3-dienes **5** are usually generated in situ, became easily available.[16,17] In this laboratory, 1,4-diiodo-1,3-dienes **4** were prepared mainly by the CuCl-mediated iodolysis of zirconacyclopentadienes.[16] Lithiation of 1,4-diiodo-1,3-dienes **4** can be easily achieved to generate the corresponding 1,4-dilithio-1,3-dienes **5** in quantitative yields.

2.1. Reaction of aluminacyclopentadienes with aldehydes affording cyclopentadiene derivatives

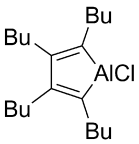
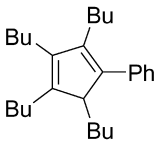
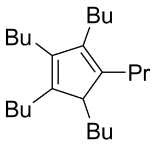
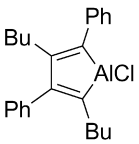
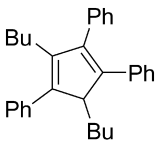
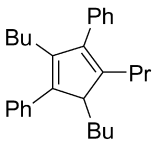
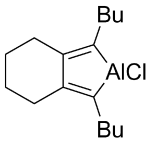
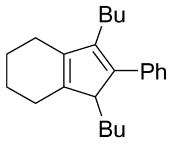
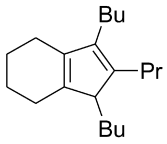
As shown in Scheme 1, treatment of 1,4-dilithio-1,3-dienes **5** with $AlCl_3$ afforded chloro-aluminacyclopentadienes **6**, a different kind aluminole from compounds **3** which have no halides on Al. Reaction of **6** with aldehydes afforded multiply-substituted cyclopentadienes **7**.[8,10] Deoxygenation of carbonyl groups took place in these reactions. Although the reaction of dilithio compounds **5** with aldehydes gave the same products **7**,[10a] further investigation indicated that the reaction course of **6** is different from that of **5** (vide infra). Listed in Table 1 are the results obtained from the

Table 1. Formation of cyclopentadiene derivatives **7** by the reaction of 1-chloro-2,3,4,5-aluminacyclopentadiene **6a** with aldehydes

Aldehyde	Product **7**[a]		Yield of **7** (%)[b]
		**7a**[c]	73 (50)
		**7b**[d]	76 (62)
		**7c**[e]	92 (71)
		**7d**[d]	94 (80)
PrCHO		**7e**[f]	90 (65)
BuCHO		**7f**[c]	67 (44)

[a] The structure for the major isomer is given in the cases of mixtures.
[b] GC yields. Isolated yields are given in parentheses. In the cases of double bond positional isomers, combined yields are given.
[c] Three isomers in 2:1:1 ratio.
[d] Three isomers in 3:1:1 ratio.
[e] Three isomers in 5:3:2 ratio.
[f] Two isomers in 1:1 ratio. One of the isomers has an exocyclic double bond.

Table 2. More examples of cyclopentadiene derivatives obtained from a variety of aluminacyclopentadienes and aldehydes

Alumina-cyclopentadiene		Aldehyde	Cyclopentadiene product[a]		Yield of product (%)[b]
	**6b**	PhCHO		**8a**[c]	85 (60)
6b		PrCHO		**8b**[d]	77 (54)
	**6c**	PhCHO		**9a**[e]	86 (61)
6c		PrCHO		**9b**[f]	78 (52)
	**6d**	PhCHO		**10a**[g]	96 (91)
6d		PrCHO		**10b**[e]	85 (63)

[a] The structure for the major isomer is given in the cases of mixtures.
[b] GC yields. Isolated yields are given in parentheses. In the cases of double bond positional isomers, combined yields are given.
[c] Three isomers in 3:1:1 ratio.
[d] Four isomers in 5:2:2:1 ratio.
[e] Two isomers in 2:1 ratio.
[f] Three isomers in 2:1:1 ratio.
[g] Five isomers in 4:2:2:1:1 ratio.

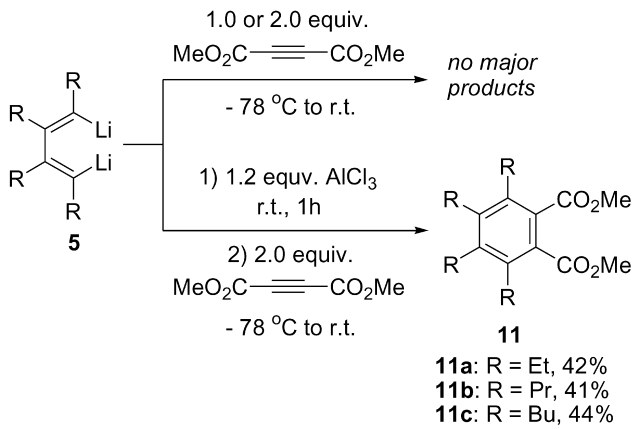
reaction of 1-chloro-2,3,4,5-tetrapropylaluminacyclopentadiene **6a** with various aldehydes. Double bond isomerization in the cyclopentadienyl skeletons took place easily, especially under reaction conditions and work-up procedures reported herein, to afford a mixture of cyclopentadiene derivatives as products; the structure for the major isomer is given in the table. Both aromatic and aliphatic aldehydes could be used in these reactions. Aromatic aldehydes with either electron-donating or electron-withdrawing groups could afford cyclopentadiene derivatives in high yields. More examples of cyclopentadiene derivatives obtained from different aluminacyclopentadienes and aldehydes are given in Table 2. Tetrahydroindene derivatives could be also prepared by this method.

2.2. Demonstration of formation of aluminacyclopentadienes

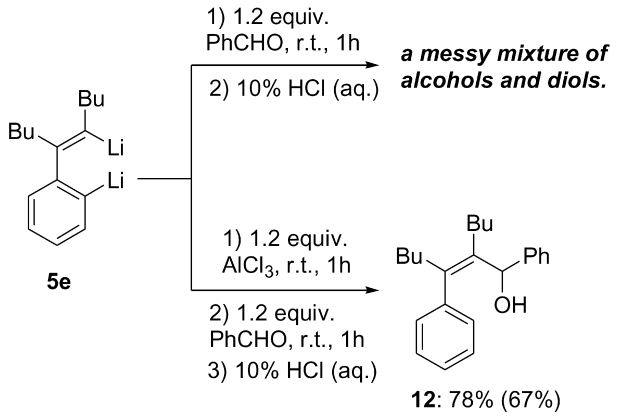
As we have reported, reactions of dilithio compounds **5** with aldehydes afforded cyclopentadiene derivatives.[10a] The reactions reported herein afforded the same products, although the ratio of double bond positional isomers varied in some cases. The question that needs to be addressed is whether the cyclopentadiene product was formed from the reaction of aldehydes with dilithio compounds **5** or with aluminacyclopentadienes **6**. In order to answer this question and to further study the reaction of aluminacyclopentadienes, the following experiments were carried out.

Firstly, the reaction of **5** with $AlCl_3$ was observed by NMR since a change in the ^{13}C NMR spectrum was expected upon the conversion of dilithio compound **5** to aluminacyclopentadiene **6**. Indeed, a change in the ^{13}C NMR spectrum was clearly observed before and after the addition of $AlCl_3$ to dilithio compound **5**.

Secondly, the reaction of dilithio compounds **5** with dimethylacetylene dicarboxylate (DMAD) afforded a messy mixture without any major products (Scheme 2). However, interestingly, after treatment of dilithio compounds **5** with $AlCl_3$ at room temperature for 1 h, the addition of DMAD to the reaction mixture gave benzene derivatives in moderate isolated yields.[18]



Scheme 2.

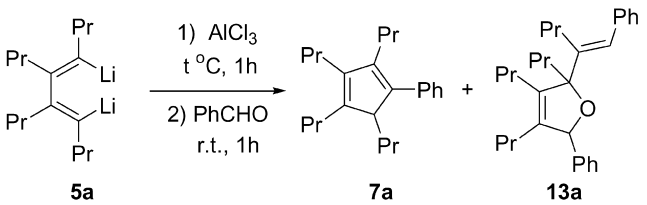


Scheme 3.

Thirdly, the reaction of dilithio compound **5e** with benzaldehyde afforded a messy mixture of alcohols and diols after hydrolysis. Interestingly, as shown in Scheme 3, a single product, alcohol **12** was obtained in high yield when the dilithio compound **5e** was treated with $AlCl_3$ before the addition of benzaldehydes to the reaction mixture.

Fourthly, we have recently reported that 1,4-dilithiobutadienes **5** reacted with ketones to form cyclopentadiene derivatives,[10a] while 1,4-dilithiobutadienes **5** reacted with nitriles to afford pyridine derivatives.[14] However, after 1,4-dilithiobutadiene derivatives were treated with 1.2 equiv. of $AlCl_3$ at room temperature for 1 h, no reactions were observed when ketones or nitriles were added to the reaction mixtures.

Fifthly, as shown in Tables 1 and 2, cyclopentadiene derivatives were formed in high yields and no other products were obtained. These results indicated that the reactive intermediates were not dilithio compounds, since the reaction of dilithio compounds with 2 equiv. of aldehydes at room temperature led to the formation of 2,5-dihydrofuran derivatives.[10b] To further investigate this point, reactions shown in Scheme 4 were carried out and the results are listed in Table 3. When the reaction of dilithio compound **5a** with $AlCl_3$ was carried out at −78°C, the addition of aldehydes to the reaction mixtures afforded 2,5-dihydrofuran derivative **13a** as the major product. These results indicated that aluminacyclopentadienes could not be



Scheme 4.

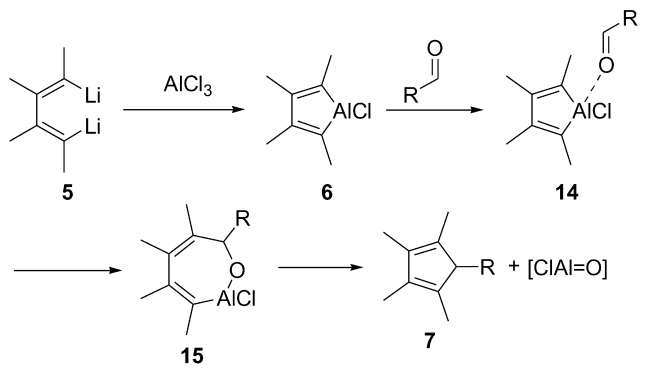
Table 3. Influence of reaction conditions on the formation of cyclopentadienes

$AlCl_3$ (equiv.)	T (°C)[a]	PhCHO (equiv.)	Yield of **7a** (%)[b]	Yield of **13a** (%)
0	–	2.0	<3	57
0.5	rt	1.2	40	20
1.0	rt	1.2	78	0
2.0	rt	1.2	84	0
1.0	−78	1.2	43	41
1.0	−78	2.0	33	64

Reaction procedures are given in Scheme 4, with 1 equiv. of **5a**.
[a] Reaction temperature for the treatment of dilithio compound **5a** with $AlCl_3$ as given in Scheme 4.
[b] GC yields.

formed when the temperature was too low. When one or more equivalents of $AlCl_3$ were added at room temperature, these reactions gave only cyclopentadiene derivative **7a** as the product and no formation of **13a** was observed. Similarly, when the reaction of aluminacyclopentadiene **6** with benzaldehydes was carried out at −78°C, no formation of **13a** was observed while **7a** was obtained in moderate yield.

A proposed reaction mechanism is given in Scheme 5.[8] The reaction of dilithio compounds **5** with 1 equiv. of $AlCl_3$ affords aluminacyclopentadienes **6**.[4,5] The formation of complex **14** is followed by the insertion of the carbonyl groups of aldehydes into one of the Al–C bonds, affording oxa-aluminacycles **15**,[19] which finally gives cyclopentadiene derivatives **7**.



Scheme 5.

3. Conclusion

The preparation and reactions of aluminacyclopentanes and aluminacyclopentenes have been studied in recent years.[6,7] In this project, we investigated the preparation and reactions of a wide variety of aluminacyclopentadiene derivatives.

Our results demonstrate that aluminacyclopentadienes, which are the most likely intermediates, have interesting and synthetically useful reactivities. More applications of such compounds containing Cl_nAl-C bonds in organic synthesis can be expected.

4. Experimental

4.1. General methods

All reactions were conducted under a slight positive pressure of dry, prepurified nitrogen using standard Schlenk line techniques when appropriate. Unless otherwise noted, all starting materials were commercially available and were used without further purification. Diethyl ether was refluxed and distilled from sodium/ benzophenone ketyl under a nitrogen atmosphere. $AlCl_3$ was freshly sublimed before use.

^1H and ^{13}C NMR spectra were record at 300 and 75.4 MHz, respectively, in $CDCl_3$ unless stated otherwise. GC yields were determined using suitable hydrocarbons as internal standards. 1,4-Diiodo-1,3-diene derivatives were synthesized by the reported procedure.[17]

4.2. Typical procedure for the preparation of cyclopentadiene derivatives from corresponding dilithium compounds

To a diethyl ether (5 mL) solution of 1,4-dilithio-1,3-butadiene (1 mmol) at −78°C was added $AlCl_3$ (1.2 mmol). After the reaction mixture was warmed to room temperature and stirred for 1 h, aldehyde (1.2 mmol) was added. Then the mixture was stirred for 1 h at room temperature. The above reaction mixture was quenched with 3N HCl and extracted with ether. The extract was washed with aqueous $NaHCO_3$, water, and brine and dried over $MgSO_4$. The solvent was then evaporated in vacuo to give a residue, which was purified by column chromatography (silica gel, hexane) to afford purified cyclopentadiene.

4.2.1. 1-Phenyl-2,3,4,5-tetrapropyl-1,3-cyclopentadiene (7a). Pale yellow liquid, isolated yield 50% (155 mg), GC yield 71%. Three isomers (2:1:1). IR (neat): 3063, 3030, 2966, 2925, 2873, 1704, 1493, 1456, 1378, 1074, 761, 702 cm^{-1}; ^1H NMR ($CDCl_3$, Me_4Si) for the mixture: δ 0.60–0.99 (m, 14H), 1.39–1.55 (m, 8H), 2.11–2.37 (m, 6H), 3.04 (t, J=4.5 Hz, 0.2H), 3.41 (t, J=6.4 Hz, 0.6H), 3.71 (s, 1.2H), 7.10–7.38 (m, 5H); ^{13}C NMR ($CDCl_3$, Me_4Si) for the mixture: δ 13.93, 14.20, 14.25, 14.37, 14.45, 14.48, 14.70, 16.13, 16.51, 22.78, 23.74, 23.87, 24.00, 27.77, 27.85, 27.94, 28.70, 28.92, 28.97, 29.06, 29.11, 30.47, 30.56, 51.31, 52.61, 59.49, 125.38, 125.85, 125.99, 127.23, 127.74, 128.03, 128.25, 128.31, 128.44, 129.34, 137.91, 140.21, 140.60, 141.72, 142.46, 144.24, 144.33. These NMR data are consistent with the reported data.[8]

4.2.2. 1-(4-Methylphenyl)-2,3,4,5-tetrapropyl-1,3-cyclopentadiene (7b). Pale yellow liquid, isolated yield 62% (201 mg), GC yield 76%. Three isomers (3:1:1). IR (neat): 2958, 2871, 1703, 1510, 1457, 1377, 1109, 815 cm^{-1}; ^1H NMR ($CDCl_3$, Me_4Si) for the mixture: δ 0.62–1.09 (m, 14H), 1.27–1.52 (m, 8H), 2.08–2.45 (m, 6H), 3.04 (t, J=4.5 Hz, 0.2H), 3.40 (t, J=4.8 Hz, 0.6H), 3.79 (s, 0.2H), 6.80–7.17 (m, 4H); ^{13}C NMR ($CDCl_3$, Me_4Si) for the major isomer: δ 4.49 (3 CH_3), 14.70 (CH_3), 16.09, 21.11, 21.14 (CH_3), 23.76, 24.01, 27.86, 28.75, 29.11, 30.62, 52.53, 128.30, 128.48, 128.79, 129.04, 129.20, 140.59, 141.96, 143.97; HRMS m/z calcd for $C_{24}H_{36}$: 324.2817, found: 324.2822.

4.2.3. 1-(4-Methoxyphenyl)-2,3,4,5-tetrapropyl-1,3-cyclopentadiene (7c). Pale yellow liquid, isolated yield 71% (243 mg), GC yield 92%. Three isomers (5:3:2). IR (neat): 2957, 1609, 1583, 1509, 1464, 1377, 1246, 1175, 1105, 1041, 832, 736, 573 cm^{-1}; ^1H NMR ($CDCl_3$, Me_4Si) for the mixture: δ 0.53–0.96 (m, 14H), 1.30–1.45 (m, 8H), 2.02–2.28 (m, 6H), 2.94 (t, J=4.2 Hz, 0.3H), 3.27 (t, J=4.5 Hz, 0.5H), 3.48 (s, 0.2H), 3.73 (s, 3H), 6.69–7.07 (m, 4H); ^{13}C NMR ($CDCl_3$, Me_4Si) for the mixture: δ 13.95, 14.17, 14.21, 14.25, 14.35, 14.43, 14.45, 14.48, 14.69, 16.10, 16.52, 22.81, 23.73, 23.87, 23.97, 24.05, 27.82, 27.87, 27.94, 28.72, 28.91, 28.98, 29.10, 30.47, 30.68, 51.23, 52.66, 55.07, 113.19, 113.51, 113.70, 113.73, 129.43, 130.33, 130.57, 139.88, 140.55, 141.32, 141.43, 141.48, 143.60, 143.93, 157.52; HRMS m/z calcd for $C_{24}H_{36}O$: 340.2766, found: 340.2761.

4.2.4. 1-(4-Bromophenyl)-2,3,4,5-tetrapropyl-1,3-cyclopentadiene (7d). Pale yellow liquid, isolated yield 80% (311 mg), GC yield 94%. Three isomers (3:1:1). IR (neat): 2960, 2360, 1896, 1709, 1573, 1464, 1377, 1073, 1010, 829, 737, 572, 508 cm^{-1}; ^1H NMR ($CDCl_3$, Me_4Si) for the mixture: δ 0.62–1.05 (m, 14H), 1.41–1.70 (m, 8H), 2.06–2.39 (m, 6H), 3.01 (t, J=4.8 Hz, 0.2H), 3.36 (t, J=4.2 Hz, 0.6H), 3.75 (s, 0.2H), 6.93–7.46 (m, 4H); ^{13}C NMR ($CDCl_3$, Me_4Si) for the major isomer: δ 14.44 ($3CH_3$), 14.66 (CH_3), 16.12, 23.56, 23.95, 24.01, 27.77, 28.65, 29.06, 30.48, 52.54, 129.98, 130.96, 131.05, 131.19, 131.45, 140.68, 143.29, 144.86; HRMS m/z calcd for $C_{23}H_{33}Br$ 388.1766, found 388.1766.

4.2.5. 1,2,3,4,5-Pentapropylcyclopentadiene (7e). Pale yellow liquid, isolated yield 65% (179 mg), GC yield 90%. Two isomers (1:1). IR (neat): 2957, 2930, 2871, 1650, 1464, 1375, 1090 cm^{-1}; ^1H NMR ($CDCl_3$, Me_4Si) for the mixture: δ 0.79–0.94 (m, 17H), 1.29–1.59 (m, 10H), 2.03–2.30 (m, 8H), 2.86 (t, J=6.6 Hz, 0.5H); 5.06 (t, J=7.5 Hz, 0.5H); ^{13}C NMR ($CDCl_3$, Me_4Si) for the mixture: δ 14.31, 14.36, 14.46, 14.56, 14.57, 14.71, 15.06, 16.42, 19.98, 20.40, 21.32, 22.20, 22.21, 23.85, 24.07, 26.76, 27.91, 29.01, 29.18, 30.44, 36.07, 38.65, 44.62, 50.30, 50.97, 117.57, 136.61, 139.69, 141.47, 146.17, 150.07. These NMR data are consistent with the reported data.[8]

4.2.6. 1-Butyl-2,3,4,5-tetrapropyl-1,3-cyclopentadiene (7f). Pale yellow liquid, isolated yield 44% (128 mg), GC yield 67%. Three isomers (2:1:1). IR (neat): 2959, 2361, 1700, 1464, 1378, 1088 cm^{-1}; ^1H NMR ($CDCl_3$, Me_4Si) for the mixture: δ 0.72–1.07 (m, 17H), 1.30–1.59 (m, 12H), 2.01–2.41 (m, 8H), 2.86 (t, J=3.9 Hz, 1H); ^{13}C NMR ($CDCl_3$, Me_4Si) for the mixture: δ 13.95, 14.07, 14.10, 14.13, 14.16, 14.27, 14.29, 14.35, 14.44, 14.56, 14.69, 15.03, 16.38, 16.40, 19.96, 20.35, 20.36, 21.31, 22.19, 22.22, 23.05, 23.08, 23.11, 23.18, 23.25, 23.64, 23.83,

24.06, 25.19, 25.54, 26.55, 26.75, 27.62, 27.90, 28.96, 29.00, 29.14, 29.17, 30.39, 30.40, 33.00, 33.24, 36.06, 38.59, 38.62, 44.59, 44.61, 50.26, 50.77, 50.96, 115.69, 139.46, 19.67, 139.69, 139.72, 141.16, 141.41, 141.47, 141.62; HRMS *m/z* calcd for $C_{21}H_{38}$: 290.2974, found: 290.2975.

4.2.7. 1-Phenyl-2,3,4,5-tetrabutyl-1,3-cyclopentadiene (8a). Pale yellow liquid, isolated yield 60% (219 mg), GC yield 85%. Three isomers (3:1:1). IR (neat): 2957, 1704, 1600, 1492, 1458, 1378, 1071, 756, 700 cm^{-1}; ^1H NMR ($CDCl_3$, Me_4Si) for the mixture: δ 0.66–1.07 (m, 16H), 1.22–1.55 (m, 14H), 2.16–2.42 (m, 8H), 3.06 (t, J=4.2 Hz, 0.2H), 3.43 (t, J=3.6 Hz, 0.6H), 3.82 (s, 0.2H), 7.13–7.36 (m, 5H); ^{13}C NMR ($CDCl_3$, Me_4Si) for the major: δ 13.92, 14.02, 14.10 (2 CH_3), 22.79, 22.91, 23.07 (2 CH_2), 24.80, 25.43, 26.30, 26.64, 27.76, 32.67, 33.07, 33.21, 52.42, 125.33, 128.00, 128.45, 137.86, 140.63, 141.44, 142.60, 144.28; HRMS *m/z* calcd for $C_{27}H_{42}$: 366.3287, found: 366.3283.

4.2.8. 1-Propyl-2,3,4,5-tetrabutyl-1,3-cyclopentadiene (8b). Pale yellow liquid, isolated yield 54% (179 mg), GC yield 77%. Four isomers (5:2:2:1). IR (neat): 2959, 2873, 1702, 1460, 1379, 1103 cm^{-1}; ^1H NMR ($CDCl_3$, Me_4Si) for the mixture: δ 0.78–0.97 (m, 19H), 1.18–1.1.62 (m, 14H), 2.05–2.40 (m, 8H), 2.60 (t, J=7.5 Hz, 0.5H); 2.84 (t, J=7.2 Hz, 0.2H), 5.09 (dt, J=7.2 Hz, J=1.8 Hz, 0.2H), 5.33 (t, J=7.2 Hz, 0.1H); ^{13}C NMR ($CDCl_3$, Me_4Si) for the mixture: δ 13.95, 13.98, 14.06, 14.09, 14.14, 14.47, 14.58, 14.71, 16.40, 19.89, 20.29, 22.49, 22.67, 22.81, 22.89, 22.93, 23.01, 23.04, 23.08, 23.17, 23.24, 23.63, 24.07, 24.47, 5.20, 25.55, 26.52, 26.77, 27.06, 27.62, 27.93, 28.99, 29.10, 29.41, 30.35, 30.40, 31.00, 31.33, 32.34, 32.97, 33.23, 33.35, 34.13, 35.80, 36.10, 38.55, 44.62, 44.77, 50.31, 50.44, 50.85, 51.03, 115.60, 125.96, 135.30, 136.73, 136.89, 19.70, 139.73, 139.94, 146.04, 141.34, 141.37, 150.75; HRMS *m/z* calcd for $C_{24}H_{44}$: 332.3443, found: 332.3442.

4.2.9. 1,3,5-Triphenyl-2,4-dibutyl-1,3-cyclopentadiene (9a). Pale yellow liquid, isolated yield 61% (247 mg), GC yield 86%. Two isomers (2:1). IR (neat): 2958, 2871, 1703, 1598, 1492, 1445, 1378, 1071, 910, 699 cm^{-1}; ^1H NMR ($CDCl_3$, Me_4Si) for the mixture: δ 0.51–1.53 (m, 14H), 2.14–2.55 (m, 4H), 4.17 (t, J=4.8 Hz, 0.7H), 4.51 (t, J=3.3 Hz, 0.3H), 7.02–7.41 (m, 15H); ^{13}C NMR ($CDCl_3$, Me_4Si) for the major: δ 22.54 (2 CH_3), 22.58, 24.56, 25.90, 28.35, 31.33 (2 CH_2), 54.14, 126.12, 126.65, 127.84, 127.89, 127.98, 128.15, 128.20, 128.25, 128.40, 128.47, 128.57, 128.60, 128.83, 128.88, 129.39, 129.68; HRMS *m/z* calcd for $C_{31}H_{34}$: 406.2661, found: 406.2664.

4.2.10. 1,3-Diphenyl-2,5-dibutyl-4-propyl-1,3-cyclopentadiene (9b). Pale yellow liquid, isolated yield 52% (193 mg), GC yield 78%. Three isomers (2:1:1). IR (neat): 2961, 2361, 1717, 1598, 1492, 1449, 1071, 753, 701 cm^{-1}; ^1H NMR ($CDCl_3$, Me_4Si) for the mixture: δ 0.52–1.43 (m, 19H), 2.15–2.33 (m, 6H), 3.60 (t, J=3.9 Hz, 0.6H), 3.93 (t, J=3.9 Hz, 0.2H), 3.98 (t, J=3.9 Hz, 0.2H), 7.21–7.40 (m, 10H); ^{13}C NMR ($CDCl_3$, Me_4Si) for the mixture: δ 13.61, 13.74, 13.81, 13.86, 13.95, 13.99, 14.11, 14.24, 14.29, 14.46, 14.51, 16.33, 22.55, 22.62, 22.66, 22.75, 22.95, 23.03, 23.74, 24.00, 24.68, 25.01, 26.11, 26.16, 26.63, 26.81, 27.95, 28.00, 28.54, 29.01, 29.23, 30.69, 31.48, 31.52, 31.61, 32.65, 32.98, 33.11, 52.92, 54.49, 59.90, 125.69, 125.90, 126.16, 126.31, 126.37, 127.89, 128.16, 128.30, 128.42, 128.49, 128.65, 129.32, 129.48, 129.81, 137.69, 142.94, 143.08; HRMS *m/z* calcd for $C_{28}H_{36}$: 372.2817, found: 372.2803.

4.2.11. 1,3-Dibutyl-2-phenyl-4,5,6,7-tetrahydroindene (10a). Pale yellow liquid, isolated yield 91% (280 mg), GC yield 96%. Five isomers (4:2:2:1:1). IR (neat): 2956, 2925, 2861, 1701, 1646, 1456, 1377, 1089, 745 cm^{-1}; ^1H NMR ($CDCl_3$, Me_4Si) for the mixture: δ 0.67–0.91 (m, 8H), 1.05–1.48 (m, 4H), 1.63–1.74 (m,.8H), 2.14–2.16 (m, 6H), 3.31 (s, 0.2H), 3.42 (s, 0.2H), 3.56 (t, J=5.2 Hz, 0.4H), 5.12 (t, J=7.8 Hz, 0.1H), 5.41 (t, J=7.8 Hz, 0.1H), 7.11–7.32 (m, 5H); ^{13}C NMR($CDCl_3$, Me_4Si) for the mixture: δ 13.63, 13.76, 13.95, 14.07, 14.09, 22.09, 22.41, 22.72, 22.87, 22.91, 22.96, 23.03, 23.08, 23.22, 23.27, 23.65, 24.38, 25.12, 25.38, 25.72, 26.11, 26.41, 27.90, 28.85, 29.05, 29.77, 30.77, 32.34, 33.59, 36.11, 50.58, 52.03, 54.00, 57.89, 58.82, 114.13, 116.66, 125.37, 125.41, 125.83, 127.16, 127.70, 128.05, 128.10, 128.23, 128.26, 128.49, 129.09, 138.99, 142.04, 142.36; HRMS *m/z* calcd for $C_{23}H_{32}$: 308.2504, found: 308.2497.

4.2.12. 1,3-Dibutyl-2-propyl-4,5,6,7-tetrahydroindene (10b). Pale yellow liquid, isolated yield 63% (173 mg), GC yield 85%. Two isomers (2:1). IR (neat): 2957, 2870, 1702, 1599, 1492, 1458, 1378, 1032, 762, 701 cm^{-1}; ^1H NMR ($CDCl_3$, Me_4Si) for the mixture: δ 0.81–0.95 (m, 13H), 1.17–1.66 (m, 14H), 2.02–2.17 (m, 6H), 5.00 (t, J=7.2 Hz, 0.7H); 5.27 (t, J=3.0 Hz, 0.3H); ^{13}C NMR ($CDCl_3$, Me_4Si) for the major isomer: δ 14.07, 14.14, 14.49, 19.97, 21.90, 22.75, 23.15, 23.20, 23.28, 23.65, 25.12, 29.36, 30.93, 33.51, 38.52, 45.37 (CH), 114.57, 134.64, 144.99, 150.78; HRMS *m/z* calcd for $C_{20}H_{34}$: 274.2661, found: 274.2659.

4.2.13. Alcohol (12). Colorless crystals (mp: 83°C), isolated yield 67% (216 mg), GC yield 78%. ^1H NMR ($CDCl_3$, Me_4Si) 0.80–0.97 (m, 6H), 1.17–1.34 (m, 10H), 1.59 (br, 1H), 1.95–2.40 (m, 2H), 5.34 (s, 1H), 7.17–7.36 (m, 10H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 13.78, 13.98, 22.86, 23.41, 27.16, 30.15, 33.21, 34.24, 73.85, 125.73, 126.45, 126.66, 127.94, 128.21, 128.73, 137.17, 141.20, 142.59, 143.10; HRMS *m/z* calcd for $C_{23}H_{30}O$: 322.2297, found: 322.2289.

4.3. Typical procedure for the preparation of benzene derivatives from reactions of aluminacyclopentadienes with dimethylacetylene dicarboxylate (DMAD)

To a diethyl ether (5 mL) solution of 1,4-dilithio-1,3-butadiene (1 mmol) at −78°C was added $AlCl_3$ (1.2 mmol). The reaction mixture was warmed to room temperature and stirred for 1 h. The reaction mixture was then again cooled down to −78°C and was added dimethylacetylene dicarboxylate (DMAD) (2 mmol). The reaction mixture was then warmed to room temperature and stirred for 2 h. The reaction mixture was quenched with 3N HCl and extracted with ether. The extract was washed with aqueous $NaHCO_3$, water, and brine and dried over $MgSO_4$. The solvent was then evaporated in vacuo to give a residue, which was

purified by column chromatography (silica gel) to afford benzene derivatives.

4.3.1. Dimethyl 3,4,5,6-tetraethylbenzene-1,2-dicarboxylate (11a). Colorless liquid, isolated yield 42% (128 mg). IR (neat): 2958, 1729, 1436, 1379, 1291, 1206, 1085, 1058, 1020, 979, 954, 904, 828, 783, 737, 654, 596 cm^{-1}; ^1H NMR ($CDCl_3$, Me_4Si) δ 1.15 (t, J=7.6 Hz, 6H), 1.19 (t, J=7.6 Hz, 6H), 2.64–2.75 (m, 8H), 3.84 (s, 6H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 15.49, 15.98, 22.07, 23.54, 52.16, 130.46, 138.13, 143.25, 169.74. These NMR data are consistent with the reported data.[18]

4.3.2. Dimethyl 3,4,5,6-tetrapropylbenzene-1,2-dicarboxylate (11b). Colorless crystals (mp: 86°C), isolated yield 41% (148 mg). ^1H NMR ($CDCl_3$, Me_4Si) δ 0.96 (t, J=7.2 Hz, 6H), 1.51 (t, J=7.2 Hz, 6H), 1.75–1.80 (m, 8H), 2.16–2.20 (m, 8H), 3.86 (s, 6H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 14.65, 22.57 (2 CH_2), 23.69, 26.96, 32.13, 52.14, 129.67, 136.94, 136.61, 169.72.

4.3.3. Dimethyl 3,4,5,6-tetrabutylbenzene-1,2-dicarboxylate (11c). Colorless liquid, isolated yield 44% (184 mg). IR (neat): 2957, 1734, 1563, 1438, 1379, 1295, 1198, 1102, 1075, 1035, 999, 917, 843, 731, 592 cm^{-1}; ^1H NMR ($CDCl_3$, Me_4Si) δ 0.67–0.94 (m, 12H), 1.30–1.53 (m, 16H), 2.34–2.58 (m, 4H), 3.83 (s, 6H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 13.67, 13.69, 23.17, 23.33, 29.03, 30.09, 33.31, 33.81, 51.96, 130.31, 136.85, 142.07, 169.67.

Acknowledgements

This work was partially supported by the Natural Science Foundation of China (29825105, 20172003, 20232010) and the Major State Basic Research Development Program (G2000077502-D). Cheung Kong Scholars Programme and Qiu Shi Science & Technologies Foundation are gratefully acknowledged.

References

1. (a) Vollhardt, K. P. C. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 539. (b) Schore, N. E. *Chem. Rev.* **1988**, *88*, 1081. (c) Lautens, M.; Klute, W.; Tam, W. *Chem. Rev.* **1996**, *96*, 49. (d) Ojima, I.; Tzamarioudaki, M.; Li, Z.; Donovan, R. J. *Chem. Rev.* **1996**, *96*, 635. (e) Fruhauf, H.-W. *Chem. Rev.* **1997**, *97*, 523. (f) Grubbs, R. H.; Chang, S. *Tetrahedron* **1998**, *54*, 4413. (g) Saito, S.; Yamamoto, Y. *Chem. Rev.* **2000**, *100*, 2901.
2. (a) Negishi, E. *Acc. Chem. Res.* **1987**, *20*, 65. (b) Buchwald, S. L.; Nielsen, R. B. *Chem. Rev.* **1988**, *88*, 1047. (c) Negishi, E.; Takahashi, T. *Acc. Chem. Res.* **1994**, *27*, 124. (d) Ohff, A.; Pulst, S.; Lefeber, C.; Peulecke, N.; Arndt, P.; Burkalov, V. V.; Rosenthal, U. *Synlett* **1996**, 111. (e) Takahashi, T.; Xi, Z.; Hara, R. *Trends Organomet. Chem.* **1997**, *2*, 117. (f) Takahashi, T.; Kotora, M.; Hara, R.; Xi, Z. *Bull. Chem. Soc. Jpn* **1999**, *72*, 2591. (g) Takahashi, T. *Pure Appl. Chem.* **2001**, *73*, 271.
3. (a) Eisch, J. J.; Kaska, W. C. *J. Am. Chem. Soc.* **1962**, *84*, 1501. (b) Eisch, J. J.; Kaska, W. C. *J. Am. Chem. Soc.* **1966**, *88*, 2976.
4. (a) Hoberg, H.; Krause-Going, R. *J. Organomet. Chem.* **1977**, *127*, C29. (b) Kruger, C.; Sekutowski, J. C.; Hoberg, H.; Krause-Going, R. *J. Organomet. Chem.* **1977**, *141*, 141.
5. (a) Hoberg, H.; Gotor, V.; Milchereit, A.; Kruger, C.; Sekutowski, J. C. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 539. (b) Hoberg, H.; Krause-Going, R.; Kruger, C.; Sekutowski, J. C. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 183.
6. (a) Takahashi, T.; Seki, T.; Nitto, Y.; Saburi, M.; Rousset, C. J.; Negishi, E. *J. Am. Chem. Soc.* **1991**, *113*, 6266. (b) Negishi, E.; Kondakov, D. Y.; Choueiry, D.; Kasai, K.; Takahashi, T. *J. Am. Chem. Soc.* **1996**, *118*, 9577. (c) Negishi, E.; Montchamp, J. L.; Anastasia, L.; Elizarov, A.; Choueiry, D. *Tetrahedron Lett.* **1998**, *39*, 2503.
7. (a) Dzhemilev, U. M.; Ibragimov, A. G.; Zolotarev, A. P. *Mendeleev Commun.* **1992**, 135. (b) Dzhemilev, U. M.; Ibragimov, A. G.; Zolotarev, A. P. *Mendeleev Commun.* **1992**, 28. (c) Dzhemilev, U. M.; Ibragimov, A. G.; Morozov, A. B. *Mendeleev Commun.* **1992**, 26. (d) Dzhemilev, U. M.; Ibragimov, A. G. *J. Organomet. Chem.* **1994**, *466*, 1. (e) Dzhemilev, U. M.; Ibragimov, A. G.; Azhgaliev, M. N.; Zolotarev, A. P.; Muslukhov, R. R. *Russ. Chem. Bull.* **1994**, *43*, 252. (f) Khalilov, L. M.; Parfenova, L. V.; Rusakov, S. V.; Ibragimov, A. G.; Dzhemilev, U. M. *Russ. Chem. Bull.* **2000**, *49*, 2051. (g) Dzhemilev, U. M.; Ibragimov, A. G.; Khafizova, L. O.; Ramazanov, I. R.; Yalalova, D. F.; Tolstikov, G. A. *J. Organomet. Chem.* **2001**, *636*, 76.
8. (a) Xi, Z.; Li, P. *Angew. Chem., Int. Ed. Engl.* **2000**, *39*, 2950. (b) Zhao, C.; Li, P.; Cao, X.; Xi, Z. *Chem. Eur. J.* **2002**, *8*, 4292.
9. Xi, Z.; Song, Q. *J. Org. Chem.* **2000**, *65*, 9157.
10. (a) Xi, Z.; Song, Q.; Chen, J.; Guan, H.; Li, P. *Angew. Chem., Int. Ed. Engl.* **2001**, *40*, 1913. (b) Chen, J.; Song, Q.; Li, P.; Guan, H.; Jin, X.; Xi, Z. *Org. Lett.* **2002**, *4*, 2269.
11. Xi, Z.; Li, P.; Song, Q.; Chen, J.; Chin, *J. Org. Chem. (in Chinese)* **2001**, *21*, 824.
12. Chen, J.; Song, Q.; Xi, Z. *Tetrahedron Lett.* **2002**, *43*, 3533.
13. Song, Q.; Chen, J.; Jin, X.; Xi, Z. *J. Am. Chem. Soc.* **2001**, *123*, 10419.
14. Chen, J.; Song, Q.; Wang, C.; Xi, Z. *J. Am. Chem. Soc.* **2002**, *124*, 6238.
15. For applications of 1,4-dilithio-1,3-dienes as 1,4-dianion precursors for main group metalloles, see: (a) Dubac, J.; Laporterie, A.; Manuel, G. *Chem. Rev.* **1990**, *90*, 215, and references cited therein. (b) Ashe, A. J., III.; Kampf, J. W.; Al-Taweel, S. M. *J. Am. Chem. Soc.* **1992**, *114*, 372. (c) Ashe, A. J., III.; Al-Ahmad, S.; Pilotek, S.; Puranik, D. B.; Elschenbroich, C.; Behrendt, A. *Organometallics* **1995**, *14*, 2689. (d) Bankwitz, U.; Sohn, H.; Powell, D. R.; West, R. *J. Organomet. Chem.* **1995**, *499*, C7. (e) Freeman, W. P.; Tilley, T. D.; Liable-Sands, L. M.; Rheingold, A. L. *J. Am. Chem. Soc.* **1996**, *118*, 10457. (f) Yamaguchi, S.; Jin, R.; Tamao, K. *J. Organomet. Chem.* **1998**, *559*, 73.
16. Xi, C.; Huo, S.; Afifi, T. H.; Hara, R.; Takahashi, T. *Tetrahedron Lett.* **1997**, *38*, 4099.
17. For preparative methods for 1,4-diiodo-1,3-diene derivatives, see: (a) Negishi, E.; Cederbaum, F. E.; Takahashi, T. *Tetrahedron Lett.* **1986**, *27*, 2829. (b) Negishi, E.; Holmes, S. J.; Tour, J. M.; Miller, J. A.; Cederbaum, F. K.; Swanson, D. R.; Takahashi, T. *J. Am. Chem. Soc.* **1989**, *111*, 3336. (c) Buchwald, S. L.; Nielsen, R. B. *J. Am. Chem. Soc.* **1989**, *111*, 2870. (d) Hill, J. E.; Balaich, G.; Fanwick, P. E.; Rothwell, I. P. *Organometallics* **1993**, *12*, 2911.

(e) Yamaguchi, S.; Jin, R.; Tamao, K.; Sato, F. *J. Org. Chem.* **1998**, *63*, 10060.

18. Takahashi, T.; Xi, Z.; Yamazaki, A.; Liu, Y.; Nakajima, K.; Kotora, M. *J. Am. Chem. Soc.* **1998**, *120*, 1672.

19. (a) Santelli, M.; Pons, J. M. *Lewis Acids and Selectivity in Organic Synthesis*; CRC: Tokyo, 1996. (b) In *Lewis Acids in Organic Synthesis*; Yamamoto, H., Ed.; Wiley-VCH: Weinheim, 2000.