Lewis Acid Mediated Reactions of Zirconacyclopentadienes with Aldehydes: One-Pot Synthetic Route to Indene and Cyclopentadiene Derivatives from Aldehydes and Benzyne or Alkynes

Changjia Zhao, Pixu Li, Xiaoyu Cao, and Zhenfeng Xi*[a]

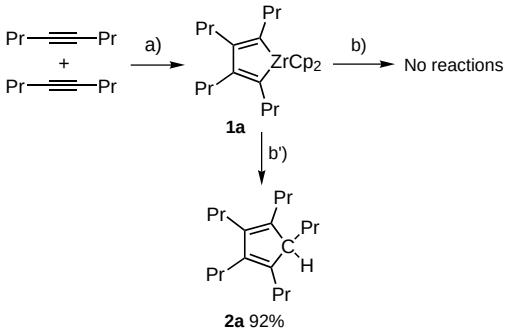
Abstract: One-pot procedures for the preparation of highly substituted indenes, tetrahydroindenes, and cyclopentadienes have been developed by using a combination of zirconocene-mediated C–C-bond-forming reactions with Lewis acid mediated activation of carbonyl groups. The carbonyl groups of aldehydes were deoxygenated in the reaction and behaved formally as a one-carbon unit. A variety of Lewis acids were checked and showed different reactivities in this reaction.

Keywords: aldehydes · cyclopentadienes · Lewis acids · synthetic methods · zirconium

Introduction

Synthetic methodologies involving multicomponent systems have attracted increasing interest.[1] Classical Lewis acids such as $AlCl_3$, BF_3, $TiCl_4$, and $SnCl_4$ have been widely used in organic synthesis.[2] Indeed, some of the most remarkable advances in organic synthesis methodology have been developed with the aid of Lewis acids. On the other hand, transition-metal-mediated C–C-bond-forming reactions have become another most powerful tool in organic synthesis.[3, 4] In this context, an effective combination of these two powerful protocols or an efficient cooperation of organometallic compounds with Lewis acids, especially with the above mentioned most often encountered classical ones, should open a new route to useful synthetic methodologies.[1, 5, 6]

Recently, we applied this strategy by adding $AlCl_3$ to reaction mixtures of zirconacyclopentadienes with aldehydes;[7] cyclopentadiene derivatives were formed in one-pot reactions from two molecules of alkyne and one molecule of aldehyde, by means of deoxygenative cycloaddition of the aldehyde with the alkynes.[8] As demonstrated in Scheme 1, tetrapropylzirconacyclopentadiene (**1a**),[9] formed in situ in quantitative yield using Negishi's method, does not react with aldehydes.[4] Addition of $AlCl_3$, the most common classical Lewis acid, to the above mixture of **1a** with PrCHO caused an immediate reaction, affording cyclopentadiene **2a** in 92% yield. Tilley and co-workers have recently demonstrated that Lewis acids can dramatically improve the yields of *N*-phenylpyrroles from the insertion intermediates of PhNO into zirconacyclopentadienes.[5a] Reaction of zirconacyclopentadienes with diethyl ketomalonate in the presence of $BiCl_3$ to form six-membered oxacyclohexadienes was recently reported by Takahashi and co-workers.[5d] These novel reactions demonstrate that the combination of transition-metal-mediated C–C-bond-forming reactions with Lewis acid mediated organic transformation in one pot can result in new and useful synthetic methodologies. In this full investigation, we report 1) effects of various Lewis acids on the reactions of zirconacyclopentadienes with aldehydes; BF_3 was found to be about as effective as $AlCl_3$, while other Lewis acids such as $TiCl_4$, $SnCl_4$, $FeCl_3$, and WCl_6 polymerize zirconacyclopentadienes or cyclopentadienes; 2) mechanistic aspects; 3) one-pot preparation of cyclopentadiene derivatives from two alkynes and one aldehyde; 4) one-pot preparation of indene



Scheme 1. $AlCl_3$-mediated reactions of zirconacyclopentadienes with aldehydes. a) Negishi reagent [Cp_2ZrBu_2]; b) PrCHO; b′) PrCHO + $AlCl_3$.

[a] Prof. Dr. Z. Xi, C. Zhao, P. Li, X. Cao
Key Laboratory of Bioorganic Chemistry
and Molecular Engineering of Ministry of Education
College of Chemistry and Molecular Engineering
Peking University, Beijing 100871 (China)
Fax: (+86) 10-62751708
E-mail: zfxi@pku.edu.cn

Supporting information for this article is available on the WWW under http://www.chemeurj.org or from the author. Copies of ^1H and ^{13}C NMR spectra for new compounds.

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derivatives from one molecule of in situ generated benzyne, one normal alkyne, and one aldehyde.

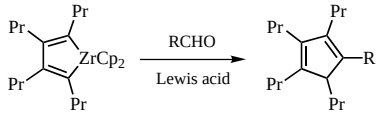
Results and Discussion

Effects of different Lewis acids on the reactions of zirconacyclopentadienes with aldehydes: We previously found that $AlCl_3$ was effective for the deoxygenative cycloaddition of aldehydes with zirconacyclopentadienes.[7] The quality of $AlCl_3$ has a very remarkable effect on the formation of cyclopentadienes; freshly sublimed $AlCl_3$ should be used. To investigate the scope of this reaction and to find more convenient Lewis acids, we experimented with various Lewis acids. The results are summarized in Table 1.

In addition to $AlCl_3$, other Lewis acids such as $AlBr_3$, $AlEtCl_2$, BF_3, and $Sc(CF_3SO_3)_3$ are also effective for the above reactions, generally resulting in relatively lower yields of cyclopentadiene derivatives. When $AlCl_3$ was used, two equivalents of $AlCl_3$ were found to be best for high-yield formation of cyclopentadiene derivatives; a lower temperature ($-30\,^{\circ}C$) should be used in the case of aliphatic aldehydes to ensure clean and high-yield formation of products, whereas room temperature is suitable for aromatic aldehydes to afford products in high yields. In contrast, when BF_3 is used the reaction temperature should be higher. One equivalent of BF_3 is enough to afford the product in a good yield in case of aromatic aldehydes, whilst at least two equivalents of BF_3 should be used for aliphatic aldehydes. Only aldehydes could be used for the aforementioned reactions; ketones did not undergo the above reactions under reaction conditions used here.

Some Lewis acids were found to polymerize zirconacyclopentadienes both in the presence and in the absence of aldehydes even at $-78\,^{\circ}C$. Treatment of zirconacyclopentadienes in the absence of aldehydes with $SnCl_4$, $FeCl_3$, and WCl_6 caused a fast disappearance of zirconacyclopentadienes; in the presence of aldehydes, no formation of the desired cyclopentadiene derivatives was observed, although some of aldehydes disappeared. $TiCl_4$ did not polymerize zirconacyclopentadienes at $-78\,^{\circ}C$, however it did polymerize the products, cyclopentadiene derivatives, even at low temperatures. Formation of cyclopentadienes was observed at the beginning. However as time passed, the zirconacyclopentadienes disappeared; the cyclopentadiene derivatives did not increase but eventually disappeared.

Table 1. Effects of various Lewis acids on the deoxygenative cyclization of aldehydes with zirconacyclopentadienes.



1a **2a**: R = Pr **2b**: R = Ph

Entry	Lewis acids	Equivalents	Conditions for PrCHO T [°C]	t [h]	Yield [%] of **2a**[a]	Conditions for PhCHO T [°C]	t [h]	Yield [%] of **2b**[a]
1	$AlCl_3$	0.5	−30	6	8	RT	3	13
2	$AlCl_3$	1	−30	3	47	RT	3	65
3	$AlCl_3$	2	−30	1	92 (88)	RT	1	89 (65)
4	$AlBr_3$	2	−30	1	94	RT	1	76
5	$AlBr_3$	2	RT	1	75	50	1	54
6	$AlEtCl_2$	2	RT	1	55	RT	1	71
7	BF_3	0.5	70	3	trace	80	3	16
8	BF_3	1	70	3	19	80	3	76
9	BF_3	2	RT	3	57	RT	3	51
10	BF_3	2	70	3	64			
11	BF_3	4	70	3	73			
12	$ZnCl_2$	2	RT	3	trace	RT	3	trace
13	$ZnCl_2$	2	70	3	trace	50	3	10
14	$Sc(CF_3SO_3)_3$	0.5	RT	1	12	RT	1	13
15	$Sc(CF_3SO_3)_3$	1	RT	1	54	RT	1	21

[a] GC yields. Yields of isolated products are given in parentheses.

Abstract in Chinese:

将二茂锆促进的碳-碳键形成反应与路易斯酸促进的羰基活化结合起来，从两分子同种或不同的炔烃和一分子醛一锅煮地合成了多取代茚、四氢合茚或环戊二烯衍生物。在该反应中，醛羰基上的碳-氧双键被切断，醛羰基的碳作为一个碳单元与两个碳-碳三键环化形成了环戊二烯骨架。试验了多种路易斯酸在锆杂环戊二烯与醛反应中的作用，发现不同的路易斯酸在不同的反应体系中效果不同。

Aspects of reaction mechanisms: In a previous communication[7] we proposed that transmetallation of zirconacyclopentadienes to aluminacyclopentadienes is a critical step for the formation of cyclopentadienes.[10] However, further investigation shows that many other Lewis acids, which cannot undergo transmetalation, also promote the above reactions as $AlCl_3$ does. Therefore, although we cannot exclude the transmetallation step in case of $AlCl_3$, a different reaction mechanism is assumed to be more likely for other Lewis acids. It is known that isonitrile[11] and nitrosobenzene[5a] can undergo insertion reactions into the Zr–C bond of zirconacycles, including zirconacyclopentadienes, to form seven-membered zirconacycles, which have different NMR data from those of the parent zirconacyclopentadienes. In our reaction, the ^1H NMR chemical shift of the Cp ligands in zirconacyclopentadienes did not change at all after treatment with benzaldehyde for 1 h at room temperature, which indicates that no insertion takes place in the reaction mixtures. Therefore, the reaction mechanism must be different from those for the Lewis acid mediated reaction of zirconacyclopentadienes with nitrosobenzene proposed by Tilley and co-workers or with diethyl ketomalonate proposed by Takahashi and co-workers.[5]

As given in Scheme 2, two pathways are proposed for reactions of the aldehyde–Lewis acid adduct with zirconacyclopentadienes **1**.[2a] The transmetalation path shown in path a affords **2′**, such as aluminacyclopentadienes, followed by insertion of the carbonyl group into the Al–C bond to form the oxo aluminum species **3**.[5] Path b in Scheme 2 forms the oxazirconacyles **5**, which finally afford cyclopentadienes **2** along with the adduct **6** of zirconocene oxide with Lewis acid.

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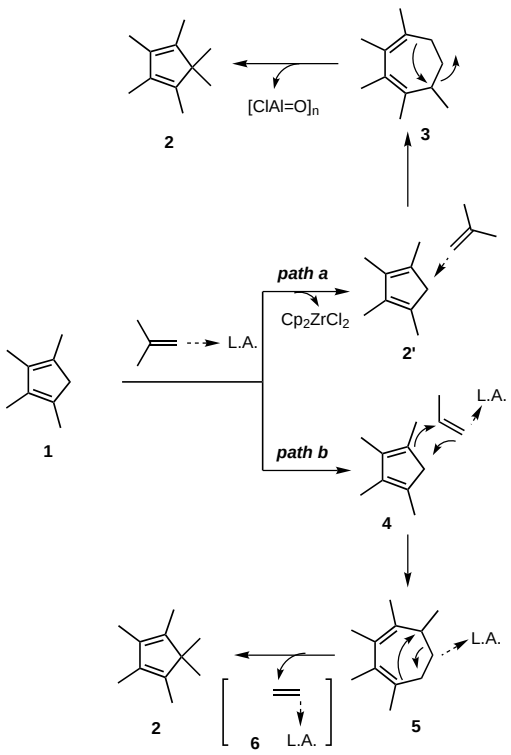
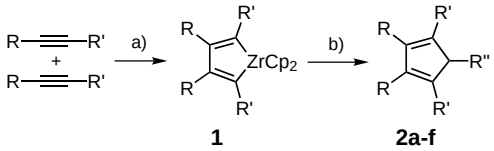


Scheme 2. Proposed reaction mechanisms.

One-pot synthesis of cyclopentadiene derivatives: Cyclopentadiene derivatives are very important compounds.[12] Synthetically useful preparation methods for highly substituted cyclopentadienes are thus in demand.[12] The reaction reported here represents a general and convenient route to highly substituted cyclopentadienes (Scheme 3), by means of a

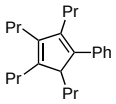
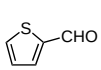
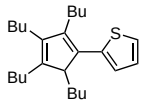
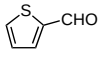
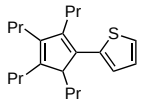
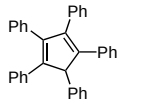
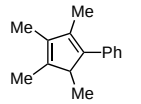


Scheme 3. One-pot synthesis of cyclopentadiene derivatives from two molecules of alkyne and one aldehyde. a) $[Cp_2ZrBu_2]$, $-78\,^{\circ}C$ to room temperature, 1 h; b) two equivalents of aldehyde and two equivalents of $AlCl_3$, room temperature, 1 h for aromatic aldehydes; $-30\,^{\circ}C$, 1 h for aliphatic aldehydes; two equivalents of aldehyde and two equivalents of BF_3, $70\,^{\circ}C$, 3 h.

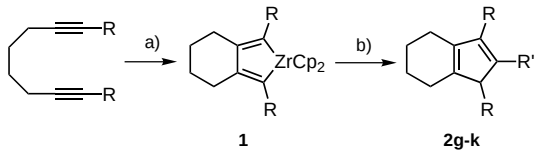
successful combination of zirconocene-mediated C–C-bond-forming reactions with Lewis acid mediated organic transformations. In this reaction, an aldehyde behaves formally as a C_1 unit.[13] Results are shown in Table 2. Both BF_3 and $AlCl_3$ demonstrate high abilities to mediate the reaction. Aromatic as well as aliphatic aldehydes could be used to prepare cyclopentadienes with various substituents.

One-pot synthesis of tetrahydroindene derivatives: Similarly, the above reaction can be also used for the preparation of tetrahydroindene derivatives when a diyne is used

Table 2. One-pot synthesis of cyclopentadiene derivatives from two molecules of alkyne and one aldehyde, mediated by Lewis acids and zirconocene.[a]

Entry	Alkyne	Aldehyde	Lewis acid	Product	Yield [%][b]
1			$AlCl_3$		92 (88)
		PrCHO		**2a**	
2			BF_3		64 (45)
3			$AlCl_3$		89 (65)
		PhCHO		 **2b**	
4			BF_3		84 (62)
5			$AlCl_3$		85 (60)
				 **2c**	
6			BF_3		91 (76)
7			$AlCl_3$		86 (67)
				 **2d**[c]	
8			BF_3		95
9			$AlCl_3$		(47)
		PhCHO		 **2e**	
10			BF_3		(44)
11			$AlCl_3$		(45)
		PhCHO		 **2f**	
12			BF_3		(30)

[a] Reaction conditions are given in Scheme 3. [b] GC yields. Yields of isolated products are given in parentheses. [c] Two isomers in 10:1.



Scheme 4. One-pot synthesis of tetrahydroindene derivatives from one diyne and one aldehyde. a) $[Cp_2ZrBu_2]$, $-78\,^{\circ}C$ to room temperatures, 1 h; b) two equivalents of aldehyde and two equivalents of $AlCl_3$, room temperature, 1 h for aromatic aldehydes; $-30\,^{\circ}C$, 1 h for aliphatic aldehydes; two equivalents of aldehyde and two equivalents of BF_3, $70\,^{\circ}C$, 3 h.

(Scheme 4). Results are given in Table 3. Tetrahydroindene derivatives **2g**, **2i**, and **2j** were formed as the only products. In the case of **2k**, a mixture of three double bond positional isomers in a ratio of 10:7:7 was obtained; a mixture of two isomers in a ratio of 3:1 was obtained for **2h**. Structures for the major isomers are given in Table 3.

One-pot synthesis of indene derivatives: The development of synthetically useful methods for substituted indenes has attracted much attention.[12a, 14] After we successfully devel-

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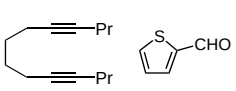
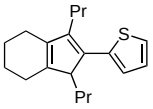
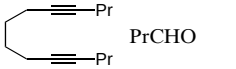
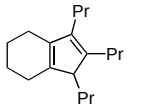
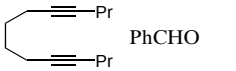
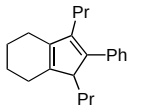
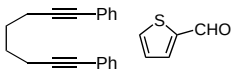
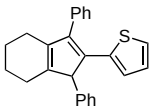
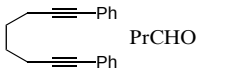
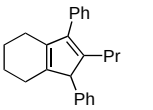
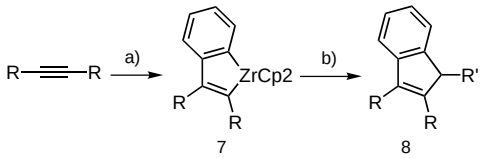
Table 3. One-pot synthesis of tetrahydroindene derivatives from one diyne and one aldehyde, mediated by Lewis acids and zirconocene.[a]

Entry	Diyne	Aldehyde	Lewis acid	Product	Yield [%][b]
1			$AlCl_3$	 **2g**	95 (66)
2			BF_3		92
3		PrCHO	$AlCl_3$	 **2h**[c]	85 (65)
4			BF_3		90
5		PhCHO	$AlCl_3$	 **2i**	89 (70)
6			BF_3		79 (59)
7			$AlCl_3$	 **2j**	45 (33)
8			BF_3		65
9		PrCHO	$AlCl_3$	 **2k**[d]	90 (72)
10			BF_3		69

[a] Reaction conditions are given in Scheme 4. [b] GC yields. Yields of isolated products are given in parentheses. [c] A mixture of two isomers in 3:1. [d] A mixture of three isomers in 10:7:7.

oped the above one-pot preparation of cyclopentadiene derivatives, we applied this strategy to the preparation of substituted indenes. Treatment of $[Cp_2ZrPh_2]$ with an alkyne affords zirconaindene **7**.[15] Addition of a Lewis acid and an aldehyde to the reaction mixture gave substituted indenes in good yields, as we expected (Scheme 5). This is the first



Scheme 5. One-pot synthesis of indene derivatives from one benzyne, one normal alkyne, and one aldehyde. a) $[Cp_2ZrPh_2]$, 100 °C in toluene for 9 h; b) two equivalents of aldehydes and two equivalents of $AlCl_3$, room temperature, 1 h for aromatic aldehydes; −30 °C, 1 h for aliphatic aldehydes; two equivalents of aldehyde and two equivalents of BF_3, 70 °C, 3 h.

example of a one-pot preparation of indene derivatives from one benzyne, one alkyne, and one aldehyde. Results are given in Table 4. It is interesting to compare the efficiencies of the Lewis acids. For the preparation of cyclopentadienes and tetrahydronindenes $AlCl_3$ and BF_3 show similar efficiency, affording the products in similar yields. However, for the preparation of indene derivatives, although the reason is not clear, better yields in many cases were obtained when BF_3 was used.

Conclusion

New methods for the preparations of highly substituted indenes, tetrahydroindenes, and cyclopentadienes have been developed. This success indicates that the combination of transition-metal-mediated C–C-bond-forming reactions with Lewis acid mediated organic transformation is a powerful and attractive tool for the development of novel and synthetically useful methodologies. In addition, this reaction is the first example of a one-pot preparation of cyclopentadienes from three components by deoxygenation of the C=O double bond of aldehydes.

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. Diynes were prepared by using conventional methods. Zirconocene dichloride was obtained from Nichia. Boron trifluoride diethyl etherate ($BF_3 \cdot Et_2O$) was purchased from Aldrich, *n*BuLi and PhLi from Kanto Chemicals. Toluene was refluxed and distilled from sodium benzophenone ketyl under a nitrogen atmosphere. Aluminum chloride ($AlCl_3$) was used after sublimation.

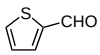
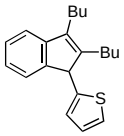
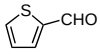
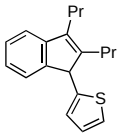
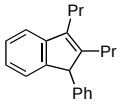
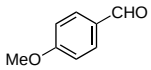
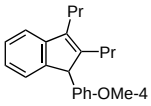
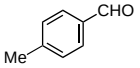
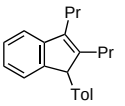
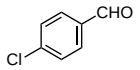
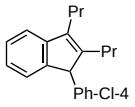
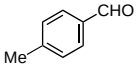
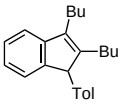
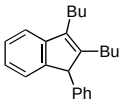
^1H and ^{13}C NMR spectra were recorded on a JEOL-300MHz spectrometer. IR spectra were recorded as neat liquids. GLC analysis was performed on a gas chromatograph (Shimadzu 14B) equipped with a flame ionization detector and a capillary column (CBP1-M25–25). GLC yields were determined using suitable hydrocarbons as internal standards. IR spectra were recorded on a Bruker Vector 22 FT-IR spectrometer.

General procedure for the preparation of cyclopentadienes (2a–f): A monoyne (4.0 mmol) was added into a toluene solution of $[Cp_2ZrBu_2]$ (Negishi reagent),[9] prepared in situ from $[Cp_2ZrCl_2]$ (2.0 mmol, 0.58 g) and *n*BuLi (4.0 mmol, 2.6 mL, 1.60 M hexane solution) in toluene (15 mL) at −78 °C. The reaction mixture was then stirred at room temperature for 1 h to afford zirconacyclopentadiene. An aldehyde (4.0 mmol) and $AlCl_3$ (4.0 mmol, 0.54 g), $BF_3 \cdot Et_2O$ (4.0 mmol), or other Lewis acids were added to this solution. When $AlCl_3$ was used, for aromatic aldehydes the reaction mixture was stirred at room temperature for 1 h; for aliphatic aldehydes the reaction mixture was stirred at −30 °C for 1 h. When BF_3 was used, the reaction mixture was stirred at 70 °C for 3 h for both aliphatic and aromatic aldehydes. Hydrolysis with 3 N HCl followed by normal work up and column chromatography afforded the products.

1,2,3,4,5-Pentapropylcyclopentadiene (2a): Colorless liquid. $AlCl_3$: yield 86 % (474 mg), GC yield 92 %; BF_3: yield 45 % (249 mg), GC yield 64 %; ^1H NMR ($CDCl_3$, Me_4Si): $\delta = 0.79–0.94$ (m, 17H), 1.29–1.59 (m, 10H), 2.03–2.30 (m, 8H), 2.86 ppm (t, $J = 6.6$ Hz, 1H); ^{13}C NMR ($CDCl_3$, Me_4Si): $\delta = 14.32, 14.41, 14.68, 16.41, 23.87, 24.10, 27.93, 29.01, 30.46, 50.95$ (CH), 139.73, 141.43 ppm; HRMS calcd for $C_{20}H_{36}$ 276.2817, found 276.2820; IR (neat): $\tilde{\nu} = 2957, 2930, 2871, 1650, 1464, 1375, 1090\ cm^{-1}$.

1-Phenyl-2,3,4,5-tetrapropyl-1,3-cyclopentadiene (2b): Colorless liquid. $AlCl_3$: yield 65 % (404 mg), GC yield 89 %; BF_3: yield 62 % (385 mg), GC yield 84 %; ^1H NMR ($CDCl_3$, Me_4Si): $\delta = 0.77–1.02$ (m, 14H), 1.30–1.62 (m, 8H), 2.02–2.44 (m, 6H), 3.61 (t, $J = 6.4$ Hz, 1H), 7.10–7.38 ppm (m, 5H); ^{13}C NMR ($CDCl_3$, Me_4Si): $\delta = 14.50$ ($3CH_3$), 14.58 (CH_3), 16.18 (CH_2), 23.70, 23.96, 24.05, 27.86, 28.69, 29.12, 30.57, 52.69 (CH), 125.38, 128.02, 128.46, 137.96, 140.61, 141.76, 142.45, 144.33 ppm; HRMS calcd for $C_{23}H_{34}$ 310.2661, found 310.2656; IR (neat): $\tilde{\nu} = 3063, 3030, 2966, 2925, 2873, 1704, 1493, 1456, 1378, 1074, 761, 702\ cm^{-1}$.

Table 4. One-pot synthesis of indene derivatives from one benzyne, one normal alkyne, and one aldehyde, mediated by Lewis acids and zirconocene.[a]

Entry	Alkyne	Aldehyde	Lewis acid	Product		Yield [%][b]
1			$AlCl_3$		**8a**	67 (38)
2			BF_3			72 (63)
3			$AlCl_3$		**8b**	60 (48)
4			BF_3			66 (55)
5		PhCHO	$AlCl_3$		**8c**	60 (42)
6			BF_3			87 (60)
7			$AlCl_3$		**8d**	52 (39)
8			BF_3			60
9			$AlCl_3$		**8e**	57 (44)
10			BF_3			80 (56)
11			$AlCl_3$		**8f**	47 (39)
12			BF_3			71 (51)
13			$AlCl_3$		**8g**	64 (45)
14			BF_3			90 (68)
15		PhCHO	$AlCl_3$		**8h**	50 (34)
16			BF_3			72 (52)

[a] Reaction conditions are given in Scheme 5. [b] GC yields. Yields of isolated products are given in parentheses.

1-Thienyl-2,3,4,5-tetrabutyl-1,3-cyclopentadiene (2c): Colorless liquid. $AlCl_3$: yield 60% (446 mg), GC yield 85%; BF_3: yield 76% (565 mg), GC yield 91%; ^{1}H NMR ($CDCl_3$, Me_4Si): $\delta = 0.68-0.95$ (m, 12H), 1.02–1.77 (m, 14H), 2.05–2.50 (m, 4H), 3.34 (t, $J = 4.2$ Hz, 1H), 6.84 (d, $J = 3.3$ Hz, 1H), 7.00–7.02 (m, 1H), 7.16 ppm (d, $J = 5.1$ Hz, 1H); ^{13}C NMR ($CDCl_3$, Me_4Si): $\delta = 13.95$, 13.99, 14.02, 14.09, 22.98, 23.02, 23.04, 23.21, 24.63, 25.31, 26.65, 26.87, 29.02, 32.00, 32.95, 52.92, 122.69, 123.26, 126.88, 134.16, 140.01, 140.92, 143.95, 144.76 ppm; HRMS calcd for $C_{25}H_{40}S$ 372.2851, found 372.2855; IR (neat): $\tilde{\nu} = 3071$, 2966, 2929, 2859, 1464, 1378, 1224, 1102, 847, 819, 687 cm^{-1}.

1-Thienyl-2,3,4,5-tetrapropyl-1,3-cyclopentadiene (2d): Colorless liquid. Two double bond positional isomers in a ratio of 10:1. In the case of $AlCl_3$: GC yield 86%, yield 67% (423 mg). In the case of BF_3: GC yield 95%. NMR data is given for the major isomer. ^{1}H NMR ($CDCl_3$, Me_4Si): $\delta = 0.66-1.03$ (m, 12H), 1.16–1.77 (m, 8H), 2.07–2.50 (m, 8H), 3.34 (t, $J = 4.2$ Hz, 1H), 6.84 (d, $J = 3$ Hz, 1H), 7.00–7.03 (m, 1H), 7.16 ppm (d, $J = 4.8$ Hz, 1H); ^{13}C NMR ($CDCl_3$, Me_4Si): $\delta = 14.41$, 14.45, 14.49, 14.54, 15.9, 23.22, 23.84, 23.91, 27.73, 29.10, 129.18, 31.80, 53.07, 122.76, 123.32, 126.91, 134.41, 139.99, 140.89, 143.83, 144.82 ppm; HRMS calcd. for $C_{21}H_{32}S$ 316.2225, found 316.2236; IR (neat): $\tilde{\nu} = 3079$, 2958, 2925, 2861, 1712, 1509, 1464, 1377, 1089, 845, 817, 743, 689 cm^{-1}.

1,2,3,4,5-Pentaphenylcyclopentadiene (2e):[16] Colorless crystals. $AlCl_3$: yield 47% (420 mg); BF_3: yield 44% (394 mg); m.p. 255–257 °C; ^{1}H NMR ($CDCl_3$, Me_4Si): $\delta = 5.0$ (s, 1H), 6.82–7.20 ppm (m, 25H); ^{13}C NMR (C_6D_6, Me_4Si): $\delta = 63.15$ (CH), 126.56, 126.73, 126.86, 127.64, 127.85, 128.57, 128.65, 129.26, 130.30, 136.08, 136.43, 144.16, 147.03 ppm. These data are in agreement with those previously reported.[16]

1-Phenyl-2,3,4,5-tetramethyl-1,3-cyclopentadiene (2f): Colorless liquid. $AlCl_3$: yield 45% (178 mg); BF_3: yield 30% (119 mg); ^{1}H NMR ($CDCl_3$, Me_4Si): $\delta = 1.02$ (d, $J = 7.4$ Hz, 3H), 1.82 (s, 3H), 1.94 (s, 3H), 2.04 (s, 3H), 3.20 (m, 1H), 7.15–7.50 ppm (m, 5H); ^{13}C NMR ($CDCl_3$, Me_4Si): $\delta = 11.10$, 11.89, 12.68, 14.75, 50.05 (CH), 125.37, 128.07, 128.35, 134.99, 137.09, 140.67, 142.68 ppm; HRMS calcd for $C_{15}H_{18}$ 198.1409, found 198.1410; IR (neat): $\tilde{\nu} = 3055$, 2966, 2928, 1716, 1447, 1377, 1072, 760, 701 cm^{-1}.

General procedure for the preparation of tetrahydroindenes (2g–k): A diyne (2.0 mmol) was added to the toluene solution of [Cp_2ZrBu_2] (Negishi reagent),[9] prepared in situ from [Cp_2ZrCl_2] (2.0 mmol, 0.58 g) and *n*BuLi (4.0 mmol, 2.6 mL, 1.60 M hexane solution) in toluene (15 mL) at −78 °C. The reaction mixture was then stirred at room temperature for 1 h to afford zirconacyclopentadiene. An aldehyde (4.0 mmol) and $AlCl_3$ (4.0 mmol, 0.54 g) or $BF_3 \cdot Et_2O$ (4.0 mmol) were added to this solution. When $AlCl_3$ was used, for aromatic aldehydes the reaction mixture was stirred at room temperature for 1 h; for aliphatic aldehydes the reaction mixture was stirred at −30 °C for 1 h. When BF_3 was used, the reaction mixture was stirred at 70 °C for 3 h for both aliphatic and aromatic aldehydes. Hydrolysis with 3 N HCl followed by normal work up and column chromatography afforded the products.

1,3-Dipropyl-2-thienyl-4,5,6,7-tetrahydroindene (2g): Colorless liquid. $AlCl_3$: yield 66% (377 mg), GC yield 95%; BF_3: GC yield 92%; ^{1}H NMR ($CDCl_3$, Me_4Si): $\delta = 0.72$ (t, $J = 7.2$ Hz, 3H), 0.99 (t, $J = 7.2$ Hz, 3H), 1.26–1.70 (m, 10H), 2.25–2.54 (m, 6H), 3.24 (t, $J = 4.2$ Hz, 1H), 6.84 (d, $J = 3.3$ Hz, 1H), 7.00–7.03 (m, 1H), 7.17 ppm (d, $J = 4.8$ Hz, 1H); ^{13} C NMR ($CDCl_3$, Me_4Si): $\delta = 14.30$, 14.45, 16.65, 22.80, 22.94, 23.05, 23.10, 24.29, 28.73, 31.71, 54.55, 122.68, 123.28, 126.81, 134.07, 139.05, 139.80, 142.65,

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142.86 ppm; HRMS calcd for $C_{19}H_{26}S$ 286.1755, found 286.1762; IR (neat): $\tilde{\nu}$ = 3079, 2958, 2930, 1714, 1456, 1377, 1042, 846, 693 cm^{-1}.

1,2,3-Tripropyl-4,5,6,7-tetrahydroindene (2h): Colorless liquid. A mixture of two double bond positional isomers in a ratio of 3:1. $AlCl_3$: combined yield 65% (320 mg), GC yield 85%; BF_3: GC yield 90%; data are given for the major isomer. ^{13}C NMR ($CDCl_3$, Me_4Si): δ = 14.28, 14.37, 14.42, 15.01, 24.08, 24.14, 24.20, 27.53, 27.90, 28.47, 28.72, 30.43, 52.48, 138.16, 139.03, 139.55, 141.27 ppm; HRMS calcd for $C_{18}H_{30}$ 246.2348, found 246.2354; IR (neat): $\tilde{\nu}$ = 2957, 2925, 2861, 1699, 1646, 1463, 1377, 1089, 745 cm^{-1}.

1,3-Dipropyl-2-phenyl-4,5,6,7-tetrahydroindene (2i): Colorless liquid. $AlCl_3$: yield 70% (392 mg), GC yield 89%; BF_3: yield 59% (330 mg), GC yield 79%. ^{1}H NMR ($CDCl_3$, Me_4Si): δ = 0.64–0.94 (m, 8H), 1.44–1.62 (m, 8H), 2.27–2.35 (m, 6H), 3.31 (t, J = 5.2 Hz, 1H), 7.14–7.34 ppm (m, 5H); ^{13}C NMR ($CDCl_3$, Me_4Si): δ = 14.38, 14.45, 16.98, 23.21 (2CH_2), 23.25, 23.36, 24.34, 28.48, 30.62, 54.08 (CH), 125.41, 128.04, 128.44, 137.71, 138.91, 141.47, 141.85, 142.32 ppm; HRMS calcd for $C_{21}H_{28}$ 280.2191, found 280.2187; IR (neat): $\tilde{\nu}$ = 3063, 3022, 2958, 2870, 1711, 1599, 1492, 1454, 1377, 1032, 762, 701 cm^{-1}.

1,3-Diphenyl-2-thienyl-4,5,6,7-tetrahydroindene (2j): Colorless liquid. $AlCl_3$: yield 33% (234 mg), GC yield 45%; BF_3: GC yield 65%; ^{1}H NMR ($CDCl_3$, Me_4Si): δ = 1.29 (t, J = 7.2 Hz, 2H), 1.41–2.33 (m, 6H), 4.31 (s, 1H), 6.64–7.34 ppm (m, 13H); ^{13}C NMR ($CDCl_3$, Me_4Si): δ = 22.86, 23.37, 26.26, 29.70, 54.96, 123.30, 124.31, 125.51, 125.97, 126.02, 126.28, 126.39, 127.49, 128.06, 128.32, 128.66, 128.86, 129.36, 136.05, 140.08, 142.36 ppm; HRMS calcd for $C_{25}H_{22}S$ 354.1442, found 354.1409; IR (neat): $\tilde{\nu}$ = 3063, 3024, 2926, 2861, 1644, 1594, 1490, 1443, 1315, 1071, 1028, 698 cm^{-1}.

1,3-Diphenyl-2-propyl-4,5,6,7-tetrahydroindene (2k): Colorless liquid. A mixture of three double bond positional isomers in a ratio of 10:7:7. $AlCl_3$: combined yield 72% (452 mg), GC yield 90%; BF_3: GC yield 69%; ^{1}H NMR ($CDCl_3$, Me_4Si):δ = 0.47–0.88 (m, 3H), 1.10–1.26 (m, 2H), 1.43–2.62 (m, 10H), 3.92–4.04 (m, 1H), 7.18–7.37 ppm (m, 10H); ^{13}C NMR ($CDCl_3$, Me_4Si):δ = 14.06, 14.14, 14.33, 16.37, 22.40, 23.17, 23.52, 23.89, 24.10, 25.71, 25.76, 26.28, 26.74, 28.66, 28.99, 29.08, 29.98, 31.70, 32.58, 52.98, 53.75, 60.68, 124.16, 125.68, 126.17, 126.37, 127.94, 127.98, 128.05, 128.13, 128.21, 128.29, 128.41, 128.53, 129.09, 129.22, 129.47, 136.95, 137.35, 138.17, 139.63, 139.71, 141.39, 142.11, 142.56, 142.84, 146.22, 146.60 ppm; HRMS calcd for $C_{24}H_{26}$ 314.2035, found 314.2029; IR (neat): $\tilde{\nu}$ = 3056, 3025, 2966, 2925, 2870, 1714, 1597, 1492, 1445, 1377, 1071, 1028, 914, 752, 699 cm^{-1}.

General procedure for the preparation of indenes (8a–h): A monoyne (2.0 mmol) was added to a solution of [Cp_2ZrPh_2] in toluene,[15] prepared in situ from [Cp_2ZrCl_2] (2.0 mmol, 0.58 g) and PhLi (2.0 mmol, 2.0 mL, 1.0 M cyclohexane-diethyl ether) in toluene (15 mL) at −78 °C. The reaction mixture was then stirred at 100 °C for 9 h to afford zirconaindene. The solution was cooled to room temperature and an aldehyde (4.0 mmol) and $AlCl_3$ (4.0 mmol, 0.54 g) or $BF_3 \cdot Et_2O$ (4.0 mmol) were added. When $AlCl_3$ was used, for aromatic aldehydes the reaction mixture was stirred at room temperature for 1 h; for aliphatic aldehydes the reaction mixture was stirred at −30 °C for 1 h. When BF_3 was used, the reaction mixture was stirred at 70 °C for 3 h for both aliphatic and aromatic aldehydes. Hydrolysis with 3 N HCl followed by normal work up and column chromatography afforded the products.

1-(2-Thienyl)-2,3-dibutylindene (8a): Colorless liquid. $AlCl_3$: yield 38% (239 mg), GC yield 67%; BF_3: yield 63% (403 mg), GC yield 72%; ^{1}H NMR ($CDCl_3$, Me_4Si): δ = 0.85 (t, J = 6.9 Hz, 3H), 0.92 (t, J = 6.9 Hz, 3H), 1.26–1.59 (m, 8H), 2.12–2.54 (m, 4H), 4.7 (s, 1H), 6.87–7.24 ppm (m, 7H); ^{13}C NMR ($CDCl_3$, Me_4Si): δ = 13.96, 14.06, 22.70, 22.83, 25.12, 26.26, 31.08, 32.10, 51.41, 118.69, 123.51, 123.80, 124.37, 125.21, 126.60, 126.82, 137.62, 143.25, 145.13, 146.03, 147.22 ppm; HRMS calcd for $C_{21}H_{26}$ 310.1775, found 310.1758; IR (neat): $\tilde{\nu}$ = 3067, 3021, 2956, 2925, 2858, 1602, 1456, 1378, 1230, 1111, 1038, 852, 821, 753, 694 cm^{-1}.

1-(2-Thienyl)-2,3-dipropylindene (8b): Colorless liquid. $AlCl_3$: yield 48% (269 mg), GC yield 60%; BF_3: yield 55% (310 mg), GC yield 66%; ^{1}H NMR ($CDCl_3$, Me_4Si): δ = 1.06 (t, J = 7.2 Hz, 3H), 1.15 (t, J = 7.2 Hz, 3H), 1.43–1.85 (m, 4H), 2.28–2.64 (m, 2H), 2.70 (t, J = 7.2 Hz, 2H), 4.90 (s, 1H), 7.05–7.45 ppm (m, 7H); ^{13}C NMR ($CDCl_3$, Me_4Si): δ = 14.16, 22.05, 23.07, 27.30, 28.64, 51.39, 118.71, 123.50, 123.80, 124.39, 125.19, 126.57, 126.81, 137.56, 143.22, 145.05, 146.05, 147.19 ppm; HRMS calcd for $C_{19}H_{22}S$ 282.1442, found 282.1446; IR (neat): $\tilde{\nu}$ = 3067, 3021, 2958, 2930, 2870, 1600, 1459, 1377, 1230, 1074, 1037, 851, 819, 739, 696 cm^{-1}.

1-Phenyl-2,3-dipropylindene (8c): Colorless liquid. $AlCl_3$: yield 42% (232 mg), GC yield 60%; BF_3: yield 60% (326 mg), GC yield 87%; ^{1}H NMR ($CDCl_3$, Me_4Si): δ = 0.86 (t, J = 7.2 Hz, 3H), 1.00 (t, J = 7.2 Hz, 3H), 1.26–1.52 (m, 2H), 1.60–1.70 (m, 2H), 1.94–2.04 (m, 1H), 2.34–2.44 (m, 1H), 2.56 (t, J = 7.2 Hz, 2H), 4.39 (s, 1H), 6.97–7.29 ppm (m, 9H); ^{13}C NMR ($CDCl_3$, Me_4Si): δ = 14.17, 14.31, 22.24, 23.11, 27.40, 28.76, 56.84, 118.55, 123.60, 124.24, 126.45, 126.50, 128.23, 128.56, 137.74, 140.55, 145.77, 147.06, 148.39 ppm; HRMS calcd for $C_{21}H_{24}$ 276.1878, found 276.1878; IR (neat): $\tilde{\nu}$ = 3063, 3024, 2958, 2877, 1943, 1898, 1803, 1715, 1600, 1493, 1458, 1377, 1180, 1154, 1072, 1030, 934, 752, 699 cm^{-1}.

1-(4-Methoxyphenyl)-2,3-dipropylindene (8d): Colorless liquid. $AlCl_3$: yield 39% (238 mg), GC yield 52%; BF_3: GC yield 60%; ^{1}H NMR ($CDCl_3$, Me_4Si): δ = 0.89 (t, J = 7.2 Hz, 3H), 1.02 (t, J = 7.2 Hz, 3H), 1.36–1.72 (m, 4H), 1.97–2.46 (m, 2H), 2.57 (t, J = 7.2 Hz, 2H), 3.76 (s, 3H), 4.37 (s, 1H), 6.80 (d, J = 8.4 Hz, 2H), 6.92 (d, J = 8.4 Hz, 2H), 7.03–7.31 ppm (m, 4H); ^{13}C NMR ($CDCl_3$, Me_4Si): δ = 14.15, 14.27, 22.21, 23.08, 27.37, 28.73, 55.09, 56.05, 113.98, 118.48, 123.50, 124.18, 126.35, 129.13, 132.37, 137.40, 145.66, 147.24, 148.61, 158.27 ppm; HRMS calcd for $C_{22}H_{26}O$ 306.1984, found 306.1976; IR (neat): $\tilde{\nu}$ = 3071, 2957, 2870, 1609, 1510, 1463, 1301, 1248, 1175, 1107, 1037, 821, 761, 701, 652 cm^{-1}.

1-(4-Methylphenyl)-2,3-dipropylindene (8e): Colorless liquid. $AlCl_3$: yield 44% (254 mg), GC yield 57%; BF_3: yield 56% (325 mg), GC yield 80%; ^{1}H NMR ($CDCl_3$, Me_4Si): δ = 0.86 (t, J = 7.2 Hz, 3H), 1.00 (t, J = 7.2 Hz, 3H), 1.32–1.70 (m, 4H), 1.95–2.04 (m, 1H), 2.28 (s, 3H), 2.32–2.44 (m, 1H), 2.55 (t, J = 7.5 Hz, 2H), 4.36 (s, 1H), 6.87 (d, J = 7.8 Hz, 2H), 7.02–7.11 (m, 4H), 7.19–7.28 ppm (m, 2H); ^{13}C NMR ($CDCl_3$, Me_4Si): δ = 14.18, 14.31, 21.09, 22.24, 23.12, 27.40, 28.75, 56.46, 118.50, 123.55, 124.21, 126.37, 128.10, 129.30, 135.96, 137.41, 137.55, 145.75, 147.17, 148.55 ppm; HRMS calcd for $C_{22}H_{26}$ 290.2035, found 290.2033; IR (neat): $\tilde{\nu}$ = 3056, 3016, 2959, 2929, 2870, 1593, 1513, 1438, 1326, 1261, 1021, 806, 758, 702, 655 cm^{-1}.

1-(4-Chlorophenyl)-2,3-dipropylindene (8f): Colorless liquid. $AlCl_3$: yield 39% (241 mg), GC yield 47%; BF_3: yield 51% (316 mg), GC yield 71%; ^{1}H NMR ($CDCl_3$, Me_4Si): δ = 0.87 (t, J = 7.2 Hz, 3H), 1.00 (t, J = 7.2 Hz, 3H), 1.26–1.69 (m, 4H), 1.91–2.00 (m, 1H), 2.34–2.44 (m, 1H), 2.55 (t, J = 7.5 Hz, 2H), 4.36 (s, 1H), 6.92 (d, J = 8.4 Hz, 2H), 7.05–7.30 ppm (m, 6H); ^{13}C NMR ($CDCl_3$, Me_4Si): δ = 14.16, 14.31, 22.20, 23.10, 27.37, 28.70, 56.08, 118.70, 123.53, 124.39, 126.67, 128.76, 129.58, 132.17, 138.13, 139.16, 145.70, 146.60, 147.94 ppm; HRMS calcd for $C_{21}H_{23}Cl$ 310.1488, found 310.1474; IR (neat): $\tilde{\nu}$ = 3055, 2959, 2941, 2871, 1708, 1594, 1490, 1439, 1325, 1090, 1015, 813, 758, 702, 653 cm^{-1}.

1-(4-Methylphenyl)-2,3-dibutyl indene (8g): Colorless liquid. $AlCl_3$: yield 45% (286 mg), GC yield 64%; BF_3: yield 68% (432 mg), GC yield 90%; ^{1}H NMR ($CDCl_3$, Me_4Si): δ = 0.86 (t, J = 7.2 Hz, 3H), 0.96 (t, J = 7.2 Hz, 3H), 1.26–1.58 (m, 8H), 1.97–2.40 (m, 2H), 2.29 (s, 3H), 2.56 (t, J = 7.5 Hz, 2H), 4.36 (s, 1H), 6.87 (d, J = 7.8 Hz, 2H), 7.03–7.26 ppm (m, 6H); ^{13}C NMR ($CDCl_3$, Me_4Si): δ = 13.99, 14.09, 21.10, 22.68, 22.95, 25.15, 26.33, 31.28, 32.15, 56.43, 118.46, 123.54, 124.18, 126.36, 128.10, 129.28, 135.96, 137.41, 137.57, 145.78, 147.12, 148.54 ppm; HRMS calcd for $C_{24}H_{30}$ 318.2348, found 318.2343; IR (neat): $\tilde{\nu}$ = 3030, 2957, 2925, 2871, 1712, 1596, 1513, 1455, 1326, 1179, 1009, 758, 702 cm^{-1}.

1-Phenyl-2,3-dibutylindene (8h): Colorless liquid. $AlCl_3$: yield 34% (205 mg) GC yield 50%; BF_3: yield 52% (316 mg), GC yield 72%; ^{1}H NMR ($CDCl_3$, Me_4Si): δ = 1.00–1.14 (m, 6H), 1.42–2.59 (m, 10H), 2.72 (t, J = 7.5 Hz 2H), 4.54 (s, 1H), 7.12–7.42 ppm (m, 9H); ^{13}C NMR ($CDCl_3$, Me_4Si): δ = 13.95, 14.08, 22.66, 22.94, 25.14, 26.35, 31.27, 32.12, 56.84, 118.49, 123.58, 124.21, 126.44, 126.48, 128.22, 128.54, 137.76, 140.54, 145.77, 146.97, 148.36 ppm; HRMS calcd for $C_{23}H_{28}$ 304.2191, found 304.2199; IR (neat): $\tilde{\nu}$ = 3062, 3024, 2958, 2858, 1600, 1493, 1455, 1378, 1180, 1072, 1021, 751, 699 cm^{-1}.

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  0947-6539/02/0818-4297 $ 20.00+.50/0

[1] a) E. Negishi, F. Liu in Metal-catalyzed Cross-coupling Reactions (Eds.: F. Diederich, P. J. Stang), Wiley-VCH, Weinheim, **1997**, Chapter 1; b) P. A. Wender, *Chem. Rev.* **1996**, *96*, 1.

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

[3] a) K. P. C. Vollhardt, *Angew. Chem.* **1984**, *96*, 525; *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 539; b) N. E. Schore, *Chem. Rev.* **1988**, *88*, 1081; c) I. Ojima, M. Tzamarioudaki, Z. Y. Li, R. J. Donovan, *Chem. Rev.* **1996**, *96*, 635; b) M. Lautens, W. Klute, W. Tam, *Chem. Rev.* **1996**, *96*, 49.

[4] a) M. Kotora, Z. Xi, T. Takahashi, *J. Synth. Org. Chem. Jpn.* **1997**, *55*, 958; b) T. Takahashi, Z. Xi, M. Kotora, *Recent Research Developments in Pure & Applied Chemistry* **1998**, *2*, 170; c) T. Takahashi, M. Kotora, R. Hara, Z. Xi, *Bull. Chem. Soc. Jpn.* **1999**, *72*, 2591.

[5] a) M. Nakamoto, T. D. Tilley, *Organometallics* **2001**, *20*, 5515; b) M. C. Suh, B. Jiang, T. D. Tilley, *Angew. Chem.* **2000**, *112*, 2992; *Angew. Chem. Int. Ed.* **2000**, *39*, 2870; c) B. Jiang, T. D. Tilley, *J. Am. Chem. Soc.* **1999**, *121*, 9744; d) T. Takahashi, Y. Li, T. Ito, F. Xu, K. Nakajima, Y. Liu, *J. Am. Chem. Soc.* **2002**, *124*, 1144.

[6] a) E. Negishi, N. Okukado, A. O. King, D. E. van Horn, B. J. Spiegel, *J. Am. Chem. Soc.* **1978**, *100*, 2254; b) D. E. van Horn, L. F. Valente, M. J. Idacavage, E. Negishi, *J. Organomet. Chem.* **1978**, *156*, C20; c) E. Negishi, T. Takahashi, S. Baba, D. E. van Horn, N. Okukado, *J. Am. Chem. Soc.* **1987**, *109*, 2393; d) K. Suzuki, T. Hasegawa, T. Imai, H. Maeta, S. Ohba, *Tetrahedron* **1995**, *51*, 4483; e) G. J. Gordon, T. Luker, M. W. Tuckett, R. J. Whitby, *Tetrahedron* **2000**, *56*, 2113; see also: f) S. A. Hitchcock, D. R. Mayhugh, G. S. Gregory, *Tetrahedron Lett.* **1995**, *36*, 9085; g) T. Kamikawa, Y. Uozumi, T. Hayashi, *Tetrahedron Lett.* **1996**, *37*, 3161.

[7] Z. Xi, P. Li, *Angew. Chem.* **2000**, *112*, 3057; *Angew. Chem. Int. Ed.* **2000**, *39*, 2950.

[8] a) A. Yamamoto, *Adv. Organomet. Chem.* **1992**, *34*, 111; b) Y. S. Lin, A. Yamamoto in *Topics in Organometallic Chemistry, Vol. 3* (Ed.: S. Murai), Springer, Berlin, **1999**, pp. 161.

[9] E. Negishi, F. E. Cederbaum, T. Takahashi, *Tetrahedron Lett.* **1986**, *27*, 2829.

[10] a) E. Negishi, D. Y. Kondakov, D. Choueiry, K. Kasai, T. Takahashi, *J. Am. Chem. Soc.* **1996**, *118*, 9577; b) C. Kruger, J. C. Sekutowski, H. Hoberg, R. Krausegoing, *J. Organomet. Chem.* **1977**, *141*, 141; c) H. Hoberg, R. Krausegoing, C. Kruger, J. C. Sekutowski, *Angew. Chem.* **1977**, *89*, 179; *Angew. Chem. Int. Ed. Engl.* **1977**, *16*, 183; d) J. J. Eisch, W. C. Kaska, *J. Am. Chem. Soc.* **1966**, *83*, 2976; e) H. Ishikawa, W. A. Noyes, *J. Am. Chem. Soc.* **1962**, *84*, 1501.

[11] a) E. Negishi, D. R. Swanson, S. R. Miller, *Tetrahedron Lett.* **1988**, *29*, 1631; b) S. L. Buchwald, R. B. Nielsen, *Chem. Rev.* **1988**, *88*, 1047; c) K. Aoyagi, K. Kasai, D. Y. Kondakov, R. Hara, N. Suzuki, T. Takahashi, *Inorg. Chem. Acta*, **1994**, *220*, 319; d) T. Takahashi, F. Y. Tsai, Y. Li, K. Nakajima, *Organometallics* **2001**, *20*, 4122.

[12] a) J. Okuda, *Top. Curr. Chem.* **1991**, *160*, 97; b) R. L. Halterman, *Chem. Rev.* **1992**, *92*, 965; c) B. Y. Lee, H. Moon, Y. K. Chung, N. Jeong, *J. Am. Chem. Soc.* **1994**, *116*, 2162; c) T. Takahashi, Z. Xi, M. Kotora, C. Xi, K. Nakajima, *Tetrahedron Lett.* **1996**, *37*, 7521; d) Z. Xi, Q. Song, J. Chen, H. Guan, P. Li, *Angew. Chem.* **2001**, *113*, 1967; *Angew. Chem. Int. Ed.* **2001**, *40*, 1913.

[13] Several compounds have been used as one-carbon unit equvalents. For CO, see: a) T. Takahashi, S. Huo, R. Hara, Y. Noguchi, K. Nakajima, W. Sun, *J. Am. Chem. Soc.* **1999**, *121*, 1094; b) T. Takahashi, Z. Xi, Y. Nishihara, K. Kasai, S. Huo, E. Negishi, *Tetrahedron* **1997**, *53*, 9123; for RCN, see: c) J. M. Davis, R. J. Whitby, A. J. Chamiec, *Tetrahedron Lett.* **1992**, *33*, 5655; for terminal alkynes, see: d) T. Takahashi, W. Sun, C. Xi, M. Kotora, *Chem. Commun.* **1997**, 2079; for RCOCl, see: e) T. Takahashi, Z. Xi, M. Kotora, C. Xi, K. Nakajima, *Tetrahedron Lett.* **1996**, *37*, 7521.

[14] a) E. Yoshikawa, K. V. Radhakrishnan, Y. Yamamoto, *J. Am. Chem. Soc.* **2000**, *122*, 7280; b) M. F. Semmelhack, S. Ho, D. Cohen, M. Steigerwald, M. C. Lee, G. Lee, A. M. Gilbert, W. D. Wulff, R. G. Ball, *J. Am. Chem. Soc.* **1994**, *116*, 7108; c) P. G. Gassman, J. A. Ray, P. G. Wenthold, J. W. Mickelson, *J. Org. Chem.* **1991**, *56*, 5143; d) A. Padwa, T. J. Blacklock, R. Loza, *J. Org. Chem.* **1982**, *47*, 3712; e) W. G. Miller, C. U. Pittman Jr., *J. Org. Chem.* **1972**, *37*, 1545.

[15] S. L. Buchwald, B. T. Watson, J. C. Hoffman, *J. Am. Chem. Soc.* **1986**, *108*, 7411.

[16] J. W. Chambers, A. J. Baskar, S. G. Bott, J. L. Atwood, M. D. Rausch, *Organometallics* **1986**, *5*, 1635.

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