Available online at www.sciencedirect.com
SCIENCE DIRECT
Tetrahedron 62 (2006) 6295–6302
Tetrahedron

Metallo-phosphorylation of alkenes: a highly regioselective reaction of zirconocene–alkene complexes with chlorophosphate

Chunbo Lai,[a] Chanjuan Xi,[a,b,*] Weixuan Chen[a] and Ruimao Hua[a]

[a]*Key Laboratory for Bioorganic Phosphorus Chemistry and Chemical Biology (Ministry of Education), Department of Chemistry, Tsinghua University, Beijing 100084, China*
[b]*State Key Laboratory of Elemento-Organic Chemistry, Nankai University, Tianjin 300071, China*

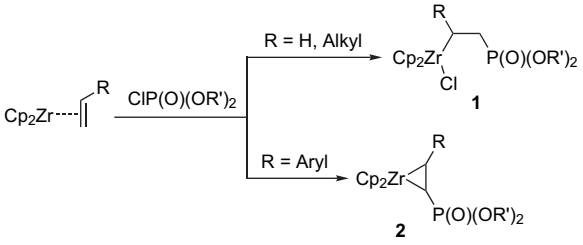
Received 27 January 2006; revised 12 April 2006; accepted 17 April 2006
Available online 8 May 2006

Abstract—Zirconocene–alkene complexes $Cp_2Zr(CH_2{=}CHR)$ reacted with chlorophosphate to form zircono-ethylphosphonate with high regioselectivity, which is versatile and could be converted into various functionalized organophosphonates.

1. Introduction

Phosphorylation of unsaturated substrates is an attractive reaction for the synthesis of organophosphonates $RP(O)(OR')_2$ that are useful intermediates in organic synthesis.[1] Particularly interesting and challenging in the reaction are the simultaneous introduction of phosphonate and other functional groups to multiple carbon–carbon bonds.[2] The metallo-phosphorylation is especially interesting, as it is a more versatile and elegant synthetic elaboration, although hydrophosphinylation of alkenes,[3] and hydrophosphorylation of alkenes,[4] and hydrophosphorylation of allenes[5] have been reported.

Zirconocene–alkene complexes have been attractive compounds in organic synthesis since they can be easily prepared by several methods such as (1) addition of alkenes to Cp_2ZrBu_2 (Negishi reagent),[6] (2) a β-hydrogen abstraction and an elimination of alkanes from zirconocenedialkyls,[7] (3) addition of alkenes to $Cp_2Zr(PMe_3)_2$,[8] and (4) replacement of alkenes in zirconocene–alkene complexes $Cp_2Zr(alkene)(PR_3)$.[9] A number of reactions of zirconocene–alkene complexes with unsaturated substrates such as alkenes[10] or aldehydes or ketones[11] have been studied. Recently, we reported a metallo-phosphorylation of ethylene based on the reaction of zirconocene–ethylene complex $Cp_2Zr(CH_2{=}CH_2)$ with chlorophosphate.[12] In the course of further investigations, we found a highly regioselective reaction of zirconocene–alkene complexes $Cp_2Zr(CH_2{=}CHR)$ with chlorophosphate to form zircono-ethylphosphonate **1** or three-membered zirconacycle **2** (Scheme 1). This result is useful for the preparation of variously functionalized organophosphonates $RP(O)(OR')_2$.



Scheme 1.

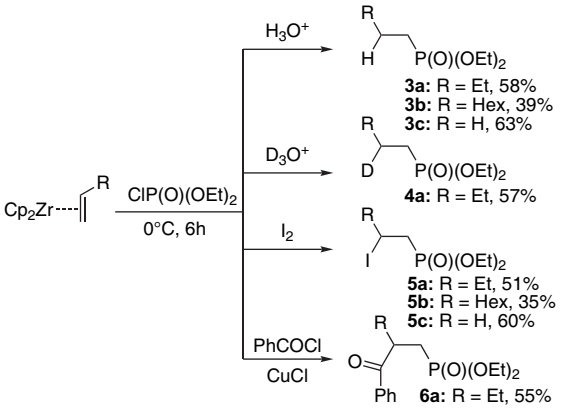
2. Results and discussion

To a solution of zirconocene–butene complex $Cp_2Zr(CH_2{=}CHEt)$,[6] generated by the reaction of Cp_2ZrCl_2 with 2 equiv of *n*-BuLi in THF, was added 1 equiv of diethyl chlorophosphate. The reaction mixture was kept at 0 °C for 6 h, and then it was quenched with 3 N HCl. Purification of crude product was carried out by column chromatography on silica gel. Diethyl butylphosphonate **3a** was exclusively obtained in ^{31}P NMR yield of 65% (isolated yield 58%) with excellent regioselectivity. Deuteriolysis and iodinolysis of the reaction mixture afforded deuterated compound **4a** in 57% yield with 95% deuterium incorporation and iodinated product **5a** in 51% yield, respectively (Scheme 2). The formation of **4a** and **5a** indicated that zirconium-containing complex **1a**

Keywords: Organophosphonate; Alkenes; Metallo-phosphorylation; Regioselectivity; Zirconocene–alkene.
* Corresponding author. Tel.: +86 10 62782695; fax: +86 10 62618239; e-mail: cjxi@tsinghua.edu.cn

0040–4020/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tet.2006.04.048

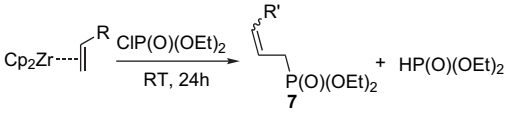
(R=Et) was formed as an intermediate. Moreover, addition of acyl chloride to the reaction mixture in the presence of CuCl afforded compound **6a** in 55% isolated yield, in which a new carbon–carbon bond was formed.



Scheme 2.

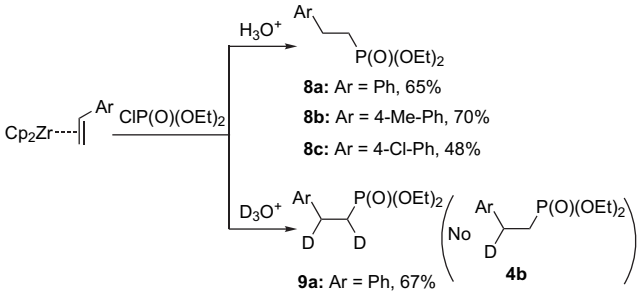
Similar types of products **3b**, **5b**, **3c**, and **5c** were obtained for reaction of zirconocene–octene complex $Cp_2Zr(CH_2{=}CHHex)$ or zirconocene–ethylene $Cp_2Zr(CH_2{=}CH_2)$[13] and chlorophosphate.

Moreover, when the reaction mixture of zirconocene–butene or zirconocene–octene complex with chlorophosphate was warmed to room temperature and kept for 24 h (Scheme 3), allylphosphonate **7** was obtained. This result further confirmed that the intermediate **1** was formed when reaction mixture was kept at 0 °C. Then, a β-hydrogen abstraction and elimination of Cp_2ZrHCl afforded allylphosphonate **7** slowly after the reaction mixture was warmed to room temperature. It was noteworthy that in this case $HP(O)(OEt)_2$ was obtained as indicated by ^{31}P NMR.



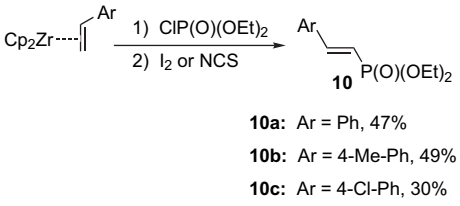
Scheme 3.

To extend the scope of the title reaction, we tested $Cp_2Zr(CH_2{=}CHAr)$ and chlorophosphonate under optimized reaction conditions (Scheme 4). Treatment of zirconocene–styrene complex, generated by addition of styrene to Negishi reagent[6] with diethyl chlorophosphonate at 5 °C for 14 h afforded diethyl 2-phenylethylphosphonate **8a** in 65% yield after hydrolysis. To our surprise, deuteriolysis of reaction mixture instead of hydrolysis afforded diethyl 1,2-deuterium-2-phenyl-ethylphosphonate **9a** in 67% yield with 85% deuterium incorporation. No formation of **4b** was observed. This result showed that the product of the reaction $Cp_2Zr(CH_2{=}CHPh)$ with chlorophosphate before hydrolysis contained two Zr–C bonds. It was noteworthy that in this case only small amount of product **8a** was observed.



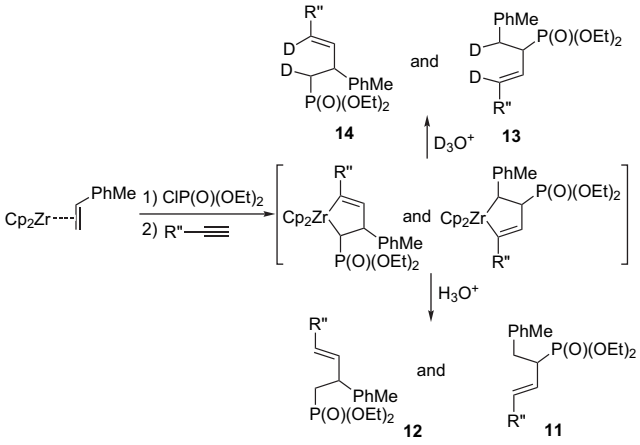
Scheme 4.

It is interesting to note that treatment of the reaction mixture of $Cp_2Zr(CH_2{=}CHAr)$ and chlorophosphate with iodine or NCS afforded diethyl *E*-2-arylethenylphosphonate in moderate yields (Scheme 5). No formation of halogenated organophosphonates was observed.



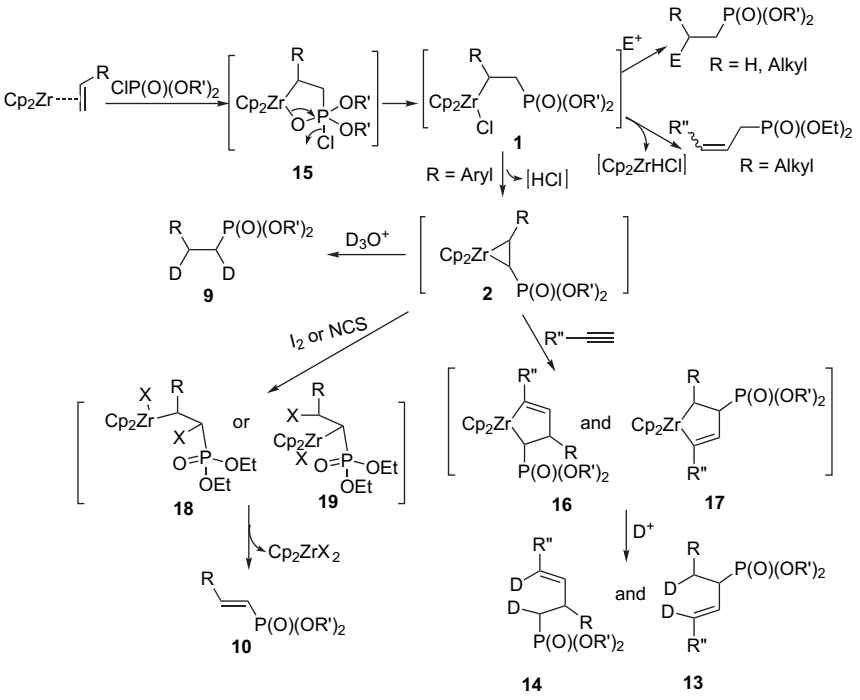
Scheme 5.

To further confirm the reaction intermediate, the reaction of $Cp_2Zr(CH_2{=}CHC_6H_4Me)$ and chlorophosphonate was carried out at 5 °C for 6 h and followed by addition of alkyne. The compounds **11** and **12** or **13** and **14** were formed after hydrolysis (or deuteriolysis) of the reaction mixture (Scheme 6).



Scheme 6.

On the basis of the results obtained above, a plausible reaction mechanism was shown in Scheme 7. In the first step, the zirconocene–alkene complex reacted with chlorophosphonate to form five-membered zirconacycle **15**. Then, elimination of chloride ion from zirconacycle took place to form zircono-ethylphosphonate **1**, which could be converted into



Scheme 7.

functionalized ethylphosphonate derivatives by coupling with various electrophiles when substituted R is hydrogen or alkyl groups. When R is aryl group, the conjugative effect of aryl group and electron-withdrawing effect of phosphate group favor β-H elimination to form intermediate **2**, which can be confirmed by further deuteriolysis to form compound **9** or coupling with terminal alkyne to produce compound **13** and **14** after deuteriolysis. The intermediate **2** could react with I_2 or NCS to form intermediate **18** or **19**, which would easily eliminate Cp_2ZrX_2 to form compound **10**.

3. Conclusion

In summary, we developed a versatile reaction to synthesize various functionalized organophosphonates $RP(O)(OR')_2$ via highly regioselective metallo-phosphorylation of alkenes. A detailed study on the reaction process is also presented.

4. Experimental

4.1. General

All manipulations were conducted in pre-dried Schlenk tube and under nitrogen with a slightly positive pressure. The reaction progress was monitored by ^{31}P NMR. The ^{31}P NMR yield of the products was obtained in proportion to the integral area of corresponding products. Unless otherwise noted, all starting materials were commercially available and were used without further purification. Tetrahydrofuran (THF) was refluxed and freshly distilled from dark purple solutions of sodium and benzophenone under a nitrogen atmosphere. ^1H NMR and ^{13}C NMR spectra were recorded on JOEL 300 NMR spectrometer with TMS as internal standard. ^{31}P NMR spectra were recorded on Bruker AC 200 NMR spectrometer at 81 MHz under ^1H decoupled conditions using 85% H_3PO_4 (δ_P=0) as an internal standard. Mass spectra were obtained using a Bruker Esquire iontrap mass spectrometer in positive ion mode.

4.2. A procedure for the reaction of $Cp_2Zr(CH_2{=}CHCH_2CH_3)$ with chlorophosphate: preparation of 2-zircono-*n*-butylphosphonate

To a solution of dibutylzirconocene, generated by the reaction of Cp_2ZrCl_2 with 2 equiv of BuLi (1.5 mL, 1.6 M in hexane solution) in THF was added 1.0 mmol diethyl chlorophosphate (144.6 μL) at −78 °C. The reaction mixture was warmed to 0–5 °C and stirred at the same temperature for 6 h (^{31}P NMR yield in 65%). ^{31}P NMR (81 MHz, THF, 85% H_3PO_4) δ 36.8 ppm.

4.2.1. Preparation of diethyl *n*-butylphosphonate (3a).[14] The resulting mixture of 2-zircono-*n*-butylphosphonate was treated with 3 N HCl. Product was extracted with ethyl acetate and the organic extract was dried over $MgSO_4$. Removal of the solvent and subsequent purification by column chromatography on silica gel (ethyl acetate/petroleum ether=3/1) afforded 113 mg of the title compound as a colorless liquid (isolated yield 58%). ^1H NMR (300 MHz, $CDCl_3$, Me_4Si) δ 0.85 (t, $^3J_{HH}$=7.2 Hz, 3H), 1.25 (t, $^3J_{HH}$=6.9 Hz, 6H), 1.30–1.37 (m, 2H), 1.50–1.56 (m, 2H), 1.58–1.72 (m, 2H), 4.01–4.06 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si) δ 13.4, 16.3 (d, $^3J_{PC}$=5.7 Hz), 23.9 (d, $^3J_{PC}$=17.2 Hz), 24.3, 25.2 (d, $^1J_{PC}$=142.7 Hz), 61.2 (d, $^2J_{PC}$=6.5 Hz); ^{31}P NMR (81 MHz, $CDCl_3$, 85% H_3PO_4) δ 33.5. Positive ion ESI-MS, *m/z*=217.0 ($M+Na^+$). HRMS calcd for $C_8H_{19}O_3P$, 194.1072; found, 194.1075.

4.2.2. Preparation of diethyl 2-deuterium-*n*-butylphosphonate (4a). The reaction was carried out in a similar way to that described above using 20% DCl instead of 3 N HCl

to quench the reaction mixture and stirred for 3 h at room temperature (isolated yield: 57%). ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si) δ 0.92 (t, $^3J_{HH}$=7.2 Hz, 3H), 1.33 (t, $^3J_{HH}$=6.9 Hz, 6H), 1.37–1.42 (m, 2H), 1.48–1.62 (m, 1H), 1.72 (dd, $^3J_{HH}$=7.5 Hz, $^2J_{PH}$=18.0 Hz, 2H), 4.02–4.16 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si) δ 13.4, 16.4 (d, $^3J_{PC}$=5.7 Hz), 23.5 (d, $^3J_{PC}$=17.2 Hz), 23.7–24.2 (m), 25.2 (d, $^1J_{PC}$=139.8 Hz), 61.3 (d, $^2J_{PC}$=6.5 Hz); ^{31}P NMR (81 MHz, $CDCl_3$, 85% H_3PO_4) δ 33.6. Positive ion ESI-MS, *m*/*z*=196.0 (M+H$^+$), 217.9 (M+Na$^+$). HRMS calcd for $C_8H_{18}DO_3P$, 195.1135; found, 195.1139.

4.2.3. Preparation of diethyl 2-iodo-*n*-butylphosphonate (5a).[15] The reaction was carried out in a similar way to that described above using I_2 (1.0 mmol, 254 mg) instead of 3 N HCl and the reaction mixture was stirred for 6 h at room temperature. The resulting mixture was treated with 3 N HCl and $Na_2S_2O_3$ solution. Product was extracted with ethyl acetate and the organic extract was dried over $MgSO_4$. Removal of the solvent and subsequent purification by column chromatography on silica gel (ethyl acetate/petroleum ether=3/1) afforded 163 mg of the title compound as yellow oil (yield 51%). ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si) δ 1.04 (t, 3H, $^3J_{HH}$=7.0 Hz), 1.34 (t, $^3J_{HH}$=6.9 Hz, 6H), 1.72–2.00 (m, 2H), 2.50–2.70 (m, 2H), 4.01–4.14 (m, 4H), 4.30–4.40 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si) δ 14.0, 16.3 (d, $^3J_{PC}$=5.7 Hz), 27.9, 33.8 (d, $^3J_{PC}$=5.0 Hz), 38.4 (d, $^1J_{PC}$=130.3 Hz), 61.5 (d, $^2J_{PC}$=6.5 Hz), 61.7 (d, $^2J_{PC}$=6.5 Hz); ^{31}P NMR (81 MHz, $CDCl_3$, 85% H_3PO_4) δ 27.1. Positive ion ESI-MS: *m*/*z*=321.0 (M+H$^+$). HRMS calcd for $C_8H_{18}IO_3P$, 320.0038; found, 320.0035.

4.2.4. Preparation of diethyl 2-benzoyl-*n*-butylphosphonate (6a). After addition of CuCl (1.0 mmol, 99 mg) to the reaction mixture of zircono-2-butylphosphonate at room temperature, benzoyl chloride (1.0 mmol, 116 μL) was added and the reaction mixture was stirred at 50 °C for 12 h. The resulting mixture was treated with 3 N HCl at room temperature. Product was extracted with ethyl acetate and the organic extract was dried over $MgSO_4$. Removal of the solvent and subsequent purification by column chromatography on silica gel (ethyl acetate/petroleum ether=3/1) yielded 164 mg of the title compound as a colorless solid (yield 55%). ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si) δ 0.87 (t, $^3J_{HH}$=7.2 Hz, 3H), 1.34 (m, 6H), 1.57–1.97 (m, 2H), 2.38–2.52 (m, 1H), 3.44–3.90 (m, 2H) 3.93–4.04 (m, 4H), 7.45–7.60 (m, 3H), 8.00 (d, 2H, $^2J_{HH}$=8.3 Hz); ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si) δ 11.0, 16.2 (d, $^3J_{PC}$=5.7 Hz), 26.6 (d, $^1J_{PC}$=139.9 Hz), 27.1 (d, $^3J_{PC}$=13.6 Hz), 41.4 (d, $^2J_{PC}$=3.6 Hz), 61.5 (d, $^2J_{PC}$=6.5 Hz), 61.7 (d, $^2J_{PC}$=6.5 Hz), 128.3, 128.6, 133.1, 136.7, 202.0 (d, $^3J_{PC}$=5.7 Hz); ^{31}P NMR (81 MHz, $CDCl_3$, 85% H_3PO_4) δ 31.5. Positive ion ESI-MS, *m*/*z*=305.1 (M+Li$^+$), 321.1 (M+Na$^+$). HRMS calcd for $C_{15}H_{23}O_4P$, 298.1334; found, 298.1338.

4.2.5. Preparation of diethyl 2-butenylphosphonate (7a). To a solution of dibutylzirconocene in THF was added 1.4 equiv of diethyl chlorophosphate (217 μL). The reaction mixture was warmed to room temperature and kept at the same temperature for 12 h. The resulting mixture was treated with 3 N HCl. Product was extracted with ethyl acetate and the organic extract was dried over $MgSO_4$. Removing the solvent and subsequent purification by column chromatography on silica gel (ethyl acetate/petroleum ether=2/1) afforded 109.5 mg of the title compound as a colorless liquid (yield 57%, *Z*/*E*=5:1). Major isomer—*diethyl (Z)-2-butenylphosphonate*:[16] ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si) δ 1.34 (m, 6H), 1.67 (dd, $^3J_{HH}$=10.2 Hz, $^4J_{HH}$=0.9 Hz, 3H), 2.62 (dd, $^2J_{PH}$=22.2 Hz, $^3J_{HH}$=7.5 Hz, 2H), 4.06–4.16 (m, 4H), 5.42–5.48 (m, 1H), 5.58–5.71 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si) δ 12.9 (d, $^4J_{PC}$=2.2 Hz), 16.5 (d, $^3J_{PC}$=6.2 Hz), 25.5 (d, $^1J_{PC}$=139.9 Hz), 61.9 (d, $^2J_{PC}$=6.8 Hz), 118.7 (d, $^2J_{PC}$=11.2 Hz), 128.7 (d, $^3J_{PC}$=14.3 Hz); ^{31}P NMR (81 MHz, $CDCl_3$, 85% H_3PO_4) δ 28.3. Positive ion ESI-MS: *m*/*z*=192.8 (M+H$^+$), 214.7 (M+Na$^+$). HRMS calcd for $C_8H_{17}O_3P$, 192.0915; found, 192.0913.

4.3. A procedure for the reaction of $Cp_2Zr(CH_2$=CHHex) with chlorophosphate: preparation of 2-zircono-*n*-octylphosphonate

To a solution of dibutylzirconocene, generated by the reaction of Cp_2ZrCl_2 with 2 equiv of BuLi (1.5 mL, 1.6 M in hexane solution) in THF was added 1.0 equiv of 1-octene (157 μL) at −78 °C. The reaction mixture was warmed to 0–5 °C and stirred at the same temperature for 6 h (^{31}P NMR yield 45%). ^{31}P NMR (81 MHz, THF, 85% H_3PO_4) δ 36.8 ppm.

4.3.1. Preparation of diethyl *n*-octylphosphonate (3b).[17] The resulting mixture of 2-zircono-*n*-octylphosphonate was treated with 3 N HCl. Product was extracted with ethyl acetate and the organic extract was dried over $MgSO_4$. Removing the solvent and subsequent purification by column chromatography on silica gel (ethyl acetate/petroleum ether=3/1) afforded 97 mg of the title compound as a colorless liquid (yield 39%). ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si) δ 0.88 (t, $^3J_{HH}$=6.3 Hz, 3H), 1.26–1.35 (m, 16H), 1.46–1.78 (m, 4H), 4.08–4.13 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si) δ 14.1, 16.5 (d, $^3J_{PC}$=5.7 Hz), 22.4 (d, $^3J_{PC}$=5.0 Hz), 22.6, 25.7 (d, $^1J_{PC}$=139.1 Hz), 29.1 (2C), 30.6 (d, $^3J_{PC}$=17.2 Hz), 31.8, 61.5 (d, $^3J_{PC}$=5.7 Hz); ^{31}P NMR (81 MHz, $CDCl_3$, 85% H_3PO_4) δ 33.7. Positive ion ESI-MS: *m*/*z*=251.2 (M+H$^+$), 273.2 (M+Na$^+$). HRMS calcd for $C_{12}H_{27}O_3P$, 250.1698; found, 250.1695.

4.3.2. Preparation of diethyl 2-iodo-*n*-octylphosphonate (5b). The reaction was carried out in a similar way to that described above using I_2(1.0 mol, 254 mg) instead of 3 N HCl and the reaction mixture was stirred for 6 h at room temperature. The resulting mixture was treated with 3 N HCl and $Na_2S_2O_3$ solution. Product was extracted with ethyl acetate and the organic extract was dried over $MgSO_4$. Removing the solvent and subsequent purification by column chromatography on silica gel (ethyl acetate/petroleum ether=2/1) afforded 132 mg of the title compound as a yellow oil (yield 35%). ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si) δ 0.84 (t, $^3J_{HH}$=8.4 Hz, 3H), 1.25–1.37 (m, 14H), 1.69–1.81 (m, 2H), 2.45–2.68 (m, 2H), 4.08–4.13 (m, 4H), 4.13–4.33 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si) δ 14.1, 16.5 (d, $^3J_{PC}$=5.9 Hz), 22.6, 26.2, 28.3, 29.7, 31.7, 38.9 (d, $^1J_{PC}$=139.1 Hz), 40.7 (d, $^3J_{PC}$=5.7 Hz), 62.0 (d, $^3J_{PC}$=8.2 Hz), 62.1 (d, $^3J_{PC}$=8.2 Hz); ^{31}P NMR (81 MHz,

$CDCl_3$, 85% H_3PO_4) δ 27.1. Positive ion ESI-MS: m/z=377.1 ($M+H^+$), 399.1 ($M+Na^+$). HRMS calcd for $C_{12}H_{26}IO_3P$, 376.0664; found, 376.0668.

4.3.3. Preparation of diethyl 2-octenylphosphonate (7b).[18] To a solution of dibutylzirconocene in THF was added 1.4 equiv of diethyl chlorophosphate (216.9 μL). The reaction mixture was warmed to room temperature and kept at the same temperature for 12 h. The resulting mixture was treated with 3 N HCl. Product was extracted with ethyl acetate and the organic extract was dried over $MgSO_4$. Removing the solvent and subsequent purification by column chromatography on silica gel (ethyl acetate/petroleum ether=2/1) afforded 75 mg of the title compound as a colorless liquid (yield 30%, *Z*/*E*=5:1). Major isomer—*diethyl (Z)-2-octenylphosphonate*: ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si) δ 0.87 (t, $^3J_{HH}$=7.2 Hz, 3H), 1.24–1.60 (m, 12H), 2.03 (m, 2H), 2.59 (dd, $^2J_{PH}$=21.9 Hz, $^3J_{HH}$=7.5 Hz, 2H), 4.00–4.11 (m, 4H), 5.36–5.42 (m, 1H), 5.55–5.61 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si) δ 14.2, 16.5 (d, $^3J_{PC}$=5.0 Hz), 22.6, 25.8 (d, $^1J_{PC}$=139.5 Hz), 27.4, 29.0, 31.6, 61.93 (d, $^2J_{PC}$=5.3 Hz), 117.6 (d, $^2J_{PC}$=10.5 Hz), 134.8 (d, $^3J_{PC}$=14.3 Hz); ^{31}P NMR (81 MHz, $CDCl_3$, 85% H_3PO_4) δ 28.8. Positive ion ESI-MS: m/z=249.2 ($M+H^+$), 271.1 ($M+Na^+$). HRMS calcd for $C_{12}H_{25}O_3P$, 248.1541; found, 248.1545.

4.4. A procedure for the reaction of $Cp_2Zr(CH_2{=}CH_2)$ with chlorophosphate: preparation of 2-zircono-ethylphosphonate

To a solution of diethylzirconocene, generated by the reaction of Cp_2ZrCl_2 with 2 equiv of EtMgBr (2.4 mL, 1 M in ether solution) in THF was added 1 equiv of diethyl chlorophosphate (144.6 μL). The reaction mixture was kept at 5 °C for 24 h or at room temperature for 12 h or at 40 °C for 3 h (^{31}P NMR yield 89%). ^{31}P NMR 34.7 (81 MHz, THF, 85% H_3PO_4).

4.4.1. Preparation of diethyl ethylphosphonate (3c).[19] The reaction mixture of zircono-ethylphosphonate was quenched with 3 N HCl solution and then extracted with ethyl acetate. The extract was washed with water and dried over $MgSO_4$. The solvent was evaporated in vacuo to give a light yellow liquid. Chromatography using a mixture of ethyl acetate and petroleum ether (2:1) as elute provided the product as a colorless liquid 104.6 mg (yield 63%). ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si) δ 1.16 (dt, $^3J_{PH}$=19.8 Hz, $^3J_{HH}$=7.8 Hz, 3H), 1.33 (t, J=7.0 Hz, 6H), 1.72 (q, $^2J_{PH}$=18.3 Hz, $^3J_{HH}$=7.8 Hz, 2H), 4.06–4.11 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si) δ 6.6 (d, $^2J_{PC}$=6.1 Hz), 16.5 (d, $^3J_{PC}$=7.2 Hz), 18.9 (d, $^1J_{PC}$=142.5 Hz), 61.6 (d, $^3J_{PC}$=6.2 Hz); ^{31}P NMR (81 MHz, THF, 85% H_3PO_4) δ 34.7. Positive ion ESI-MS: m/z=167.0 ($M+H^+$).

4.4.2. Preparation of diethyl 2-iodoethylphosphonate (5c).[20] To the reaction mixture of zircono-ethylphosphonate was added 1.2 equiv of I_2 (305 mg) and the reaction mixture was stirred at room temperature for 3 h. The above reaction mixture was quenched with 3 N HCl, and stirred at room temperature for 1 h and then extracted with ethyl acetate. The extract was washed with water and dried over $MgSO_4$. The solvent was evaporated in vacuo to a light brown liquid. Chromatography using a mixture of ethyl acetate and petroleum ether (2:1) as elute provided the product as a colorless liquid 175.2 mg (yield 60%). ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si) δ 1.29 (t, J=6.9 Hz, 6H), 2.31–2.43 (m, 2H), 3.19–3.28 (m, 2H), 4.05–4.10 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si) δ −7.4 (d, $^2J_{PC}$=3.8 Hz), 16.4 (d, $^3J_{PC}$=6.3 Hz), 31.9 (d, $^1J_{PC}$=131.7 Hz), 62.0 (d, $^3J_{PC}$=6.8 Hz); ^{31}P NMR (81 MHz, THF, 85% H_3PO_4) δ 27.0. Positive ion ESI-MS: m/z=292.9 ($M+H^+$).

4.5. A procedure for the reaction of $Cp_2Zr(PhCH{=}CH_2)$ with chlorophosphate: preparation of diethyl 2-phenyl-1,2-zircono-ethylphosphonate

To a solution of dibutylzirconocene in THF was added 1.0 equiv of styrene and stirred for 1 h at room temperature. Chlorophosphate (1 mmol, 144.7 μL) was added to this solution and stirred for 14 h at 0–5 °C (^{31}P NMR yield 58%). ^{31}P NMR (81 MHz, THF, 85% H_3PO_4) δ 49.7 ppm.

4.5.1. Preparation of diethyl 2-phenylethylphosphonate (8a).[21] The resulting mixture of diethyl 2-phenyl-1,2-zircono-ethylphosphonate was treated with 3 N HCl and stirred for 1 h. Product was extracted with ethyl acetate and the organic extract was dried over $MgSO_4$. Removing the solvent and subsequent purification by column chromatography on silica gel (ethyl acetate/petroleum ether=2/1) afforded 157.3 mg of the title compound as a colorless liquid (yield 65%). ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si) δ 1.25–1.38 (m, 6H), 2.00–2.22 (m, 2H), 2.87–2.96 (m, 2H), 4.05–4.13 (m, 4H), 7.19–7.50 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si) δ 16.5 (d, $^3J_{PC}$=6.2 Hz), 27.6 (d, $^1J_{PC}$=139.3 Hz), 28.6 (d, $^2J_{PC}$=4.9 Hz), 61.6 (d, $^2J_{PC}$=6.2 Hz), 126.4, 128.1, 128.6, 140.8 (d, $^3J_{PC}$=15.0 Hz). ^{31}P NMR (81 MHz, $CDCl_3$, 85% H_3PO_4) δ 32.4. Positive ion ESI-MS: m/z=242.8 ($M+H^+$), 264.7 ($M+Na^+$). HRMS calcd for $C_{12}H_{19}O_3P$, 242.1072; found, 242.10726.

4.5.2. Preparation of diethyl 1,2-dideuterium-2-phenylethylphosphonate (9a). The reaction was carried out in a similar way to that described above using 20% DCl instead of 3 N HCl to quench the reaction mixture and stirred for 3 h at 5 °C (yield: 67% with 85% deuterium incorporation). ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si) δ 1.26–1.36 (m, 6H), 2.02–2.12 (m, 1.16H), 2.90–2.96 (m, 1.17H), 4.07–4.13 (m, 4H), 7.20–7.31 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si) δ 16.3 (d, $^3J_{PC}$=5.7 Hz), 27.2 (dt, $^1J_{PC}$=140.2 Hz, $^1J_{DC}$=19.4 Hz), 28.2 (dt, $^2J_{PC}$=4.6 Hz, $^1J_{DC}$=19.7 Hz), 61.4 (d, $^2J_{PC}$=6.5 Hz), 126.1, 127.8, 128.3, 140.7 (d, $^3J_{PC}$=15.8 Hz), ^{31}P NMR (81 MHz, $CDCl_3$, 85% H_3PO_4) δ 31.5. Positive ion ESI-MS: m/z=245.1 ($M+H^+$), 251.1 ($M+Li^+$). HRMS calcd for $C_{12}H_{17}D_2O_3P$, 244.1197; found, 244.1194.

4.5.3. Preparation of diethyl (*E*)-2-phenyl-ethenylphosphonate (10a).[2c,22] The resulting mixture of diethyl 2-phenyl-1,2-zircono-ethylphosphonate was treated with NCS (1 mmol, 133.5 mg) or I_2 (1 mmol, 254 mg) and stirred for 30 min at room temperature. Quenched with 3 N HCl and product was extracted with ethyl acetate and the organic extract was dried over $MgSO_4$. Removal of the solvent and subsequent purification by column chromatography on silica gel (ethyl acetate/petroleum ether=2/1) afforded 113 mg of

the title compound as a colorless liquid (yield 47%). ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si) δ 1.32 (t, $^3J_{HH}$=6.6 Hz, 6H), 4.03–4.16 (m, 4H), 6.28 (t, $^2J_{PH}$=17.4 Hz, $^3J_{HH}$=17.4 Hz, 1H), 7.28–7.58 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si) δ 16.5 (d, $^3J_{PC}$=5.6 Hz), 62.0 (d, $^2J_{PC}$=4.5 Hz), 114.1 (d, $^1J_{PC}$=193.4 Hz), 127.8, 128.9, 130.3, 134.8 (d, $^3J_{PC}$=23.0 Hz), 148.8 (d, $^2J_{PC}$=5.6 Hz); ^{31}P NMR (81 MHz, $CDCl_3$, 85% H_3PO_4) δ 20.2. Positive ion ESI-MS: m/z=241.0 (M+H$^+$), 263.0 (M+Na$^+$). HRMS calcd for $C_{12}H_{17}O_3P$, 240.0915; found, 240.0918.

4.6. A procedure for the reaction of Cp_2Zr(MePhCH=CH_2) with chlorophosphate: preparation of diethyl 2-(4-methylphenyl)-1,2-zircono-ethylphosphonate

To a solution of dibutylzirconocene in THF was added 1.0 equiv of 4-methyl-styrene and stirred for 1 h at room temperature. Chlorophosphate (1 mmol, 144.7 μL) was added to this solution and stirred for 6 h at 5 °C (^{31}P NMR yield 70%). ^{31}P NMR (81 MHz, THF, 85% H_3PO_4) δ 50.1 ppm.

4.6.1. Preparation of diethyl 2-(4-methylphenyl)ethylphosphonate (8b).[23] The resulting mixture of diethyl 2-(4-methylphenyl)-1,2-zircono-ethylphosphonate was treated with 3 N HCl and stirred for 1 h. Then it was carried out in a similar way to that described above to get 179 mg of the title compound as a colorless liquid (yield 70%). ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si) δ 1.32 (m, $^3J_{HH}$=6.9 Hz, 6H), 1.98–2.10 (m, 2H), 2.32 (s, 3H), 2.83–2.92 (m, 2H), 4.10 (t, $^3J_{HH}$=7.0 Hz, 4H), 7.10 (s, 4H); ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si) δ 16.4 (d, $^3J_{PC}$=5.9 Hz), 20.9, 27.6 (d, $^1J_{PC}$=138.4 Hz), 28.0 (d, $^2J_{PC}$=4.3 Hz), 61.5 (d, $^3J_{PC}$=5.7 Hz), 127.8, 129.1, 135.7, 137.8 (d, $^3J_{PC}$= 17.9 Hz) ; ^{31}P NMR (81 MHz, $CDCl_3$, 85% H_3PO_4) δ 31.6. Positive ion ESI-MS: m/z=257.1 (M+H$^+$), 279.0 (M+Na$^+$). HRMS calcd for $C_{13}H_{21}O_3P$, 256.1228; found, 256.1232.

4.6.2. Preparation of diethyl (*E*)-2-(4-methylphenyl) ethenylphosphonate (10b).[24] The resulting mixture of diethyl 2-(4-methylphenyl)-1,2-zircono-ethylphosphonate was treated with NCS (1 mmol, 133.5 mg) or I_2 (1 mmol, 254 mg) and stirred for 30 min at room temperature. Then it was carried out in a similar way to that described above to get 124.5 mg of the title compound as a colorless liquid (yield 49%). ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si) δ 1.25–1.35 (m, 6H), 2.37 (s, 3H), 4.03–4.12 (m, 4H), 6.20 (t, $^2J_{PH}$=17.5 Hz, $^3J_{HH}$=17.5 Hz), 7.18–7.47 (m, 5H), ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si) δ 16.4 (d, $^3J_{PC}$=5.8 Hz, 2C), 21.4, 61.9, 112.6 (d, $^1J_{PC}$=190.4 Hz), 127.7, 129.6, 130.0 (d, $^3J_{PC}$=23.3 Hz), 140.6, 148.8; ^{31}P NMR (81 MHz, $CDCl_3$, 85% H_3PO_4) δ 21.0. Positive ion ESI-MS: m/z=255.2 (M+H$^+$), 277.2 (M+Na$^+$). HRMS calcd for $C_{13}H_{19}O_3P$, 254.1072; found, 254.1075.

4.6.3. Preparation of diethyl 2-(*p*-tolyl)-oct-3-enylphosphonate (12a) and diethyl (4-methyl-benzyl)-hept-2-enylphosphonate (11a). The resulting mixture of diethyl 2-(4-methylphenyl)-1,2-zircono-ethylphosphonate was added 1.0 mmol 1-hexyne and stirred for 3 h at room temperature, then treated with 3 N HCl and stirred for 1 h. The product was extracted with ethyl acetate and the organic extract was dried over $MgSO_4$. Removing the solvent and subsequent purification by column chromatography on silica gel (ethyl acetate/petroleum ether=1/1) afforded 128 mg of the title compounds of the mixture as oil liquid (yield 38%, **12a/11a**=1:2).

4.6.3.1. Diethyl 2-(*p*-tolyl)-oct-3-enylphosphonate (12a). ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si) δ 0.73–0.83 (m, 3H), 1.12–1.24 (m, 4H), 1.25–1.30 (m, 6H), 1.98–2.03 (m, 2H), 2.09–2.26 (m, 2H), 2.26 (s, 3H), 3.50–3.59 (m, 1H), 3.63–4.00 (m, 4H), 5.31–5.59 (m, 2H), 6.94–7.02 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si) δ 13.8, 16.1–16.4 (m), 20.9, 22.1, 31.6, 32.0, 32.5 (d, $^1J_{PC}$=137.9 Hz), 42.4 (d, $^2J_{PC}$=3.0 Hz), 61.2 (d, $^3J_{PC}$=6.8 Hz), 61.3 (d, $^3J_{PC}$=6.8 Hz), 127.2, 129.0, 130.5, 132.9 (d, $^3J_{PC}$=11.3 Hz), 135.8, 141.05 (d, $^3J_{PC}$=9.8 Hz); ^{31}P NMR (81 MHz, $CDCl_3$, 85% H_3PO_4) δ 30.6. Positive ion ESI-MS: m/z=339.3 (M+H$^+$). HRMS calcd for $C_{19}H_{31}O_3P$, 338.2011; found, 338.2009.

4.6.3.2. Diethyl (4-methyl-benzyl)-hept-2-enylphosphonate (11a). ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si) δ 0.73–0.83 (m, 3H), 1.12–1.24 (m, 4H), 1.25–1.30 (m, 6H), 1.98–2.03 (m, 2H), 2.23 (s, 3H), 2.60–2.75 (m, 2H), 3.11–3.18 (m, 1H), 4.06–4.16 (m, 4H), 5.28–5.33 (m, 2H), 6.93–7.02 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si) δ 13.7, 16.1–16.4 (m), 20.9, 21.7, 31.1 (d, $^4J_{PC}$=3.0 Hz), 32.1, 34.5 (d, $^2J_{PC}$=3.0 Hz), 43.6 (d, $^1J_{PC}$=136.6 Hz), 61.7 (d, $^3J_{PC}$=6.8 Hz), 62.1 (d, $^3J_{PC}$=6.8 Hz), 123.5 (d, $^2J_{PC}$= 9.8 Hz), 128.7, 128.9, 135.4, 136.0 (d, $^3J_{PC}$=16.5 Hz), 136.1 (d, $^3J_{PC}$=13.5 Hz); ^{31}P NMR (81 MHz, $CDCl_3$, 85% H_3PO_4) δ 30.0. Positive ion ESI-MS: m/z=339.3 (M+H$^+$).

4.6.4. Preparation of diethyl 4-phenyl-2-(*p*-tolyl)-but-3-enylphosphonate (12b) and diethyl 1-(4-methyl-benzyl)-3-phenyl-allyl-phosphonate (11b). The resulting mixture of diethyl-2-(4-methylphenyl)-1,2-zircono-ethylphosphonate was added 1.0 mmol phenylacetylene and stirred for 3 h at room temperature, then treated with 3 N HCl and stirred for 1 h. The product was extracted with ethyl acetate and the organic extract was dried over $MgSO_4$. Removing the solvent and subsequent purification by column chromatography on silica gel (ethyl acetate/petroleum ether=1/1) afforded 132 mg of the title compounds of the mixture as a colorless solid (yield 37%, **12b/11b**=1:3).

4.6.4.1. Diethyl 1-(4-methyl-benzyl)-3-phenyl-allylphosphonate (11b). ^{1}H NMR ($CDCl_3$, Me_4Si) δ 1.26–1.36 (m, 6H), 2.29 (s, 3H), 2.83–3.00 (m, 2H), 3.22–3.30 (m, 1H), 4.00–4.20 (m, 4H), 6.00–6.13 (m, 1H), 6.27–6.39 (m, 1H) 7.03–7.32 (m, 9H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 16.3–16.6 (m), 21.1, 34.8 (d, $^2J_{PC}$=3.8 Hz), 44.3 (d, $^1J_{PC}$=136.3 Hz), 62.2 (d, $^3J_{PC}$=7.5 Hz), 62.7 (d, $^3J_{PC}$=7.5 Hz), 124.2 (d, $^2J_{PC}$=10.8 Hz), 126.3, 127.6, 128.5, 129.0, 129.2, 134.6 (d, $^3J_{PC}$=14.3 Hz), 135.8, 135.9 (d, $^3J_{PC}$=13.5 Hz), 137.0 (d, $^4J_{PC}$=2.3 Hz); ^{31}P NMR (81 MHz, $CDCl_3$, 85% H_3PO_4) δ 28.9. Positive ion ESI-MS: m/z=359.1 (M+H$^+$), 381.1 (M+Na$^+$). HRMS calcd for $C_{21}H_{27}O_3P$, 358.1698; found, 358.1697.

4.6.5. Preparation of diethyl 1,4-dideuterium-2-(*p*-tolyl)-oct-3-enylphosphonate (14a) and diethyl 3-deuterium-1-(4-methylphenyl-deuterium-methyl)-hept-2-enylphosphonate (13a). The reaction was carried out in a similar way to that

described above using 20% DCl instead of 3 N HCl to quench the reaction mixture and stirred for 3 h at 5 °C (yield 35%, **14a/13a**=1:2).

4.6.5.1. Diethyl 1,4-dideuterium-2-(*p*-tolyl)-oct-3-enylphosphonate (14a). ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si) δ 0.78–0.93 (m, 3H), 1.11–1.24 (m, 4H), 1.26–1.32 (m, 6H), 1.91–2.02 (m, 2H), 2.08–2.22 (m, 1H), 2.29 (s, 3H), 3.66–3.72 (m, 1H), 3.83–4.00 (m, 4H), 5.56 (d, $^3J_{HH}$=6.9 Hz, 1H), 7.02–7.08 (m, 4H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 14.0, 16.1–16.4 (m), 21.1, 22.3, 31.5, 32.2, 33.3–30.9 (m), 42.5, 61.3 (d, $^2J_{PC}$=6.8 Hz), 61.4 (d, $^2J_{PC}$=6.8 Hz), 127.3, 129.3, 130.3 (t, $^1J_{CD}$=18.7 Hz), 133.0 (d, $^3J_{PC}$=11.3 Hz), 136.0, 141.2 (d, $^3J_{PC}$=10.8 Hz); ^{31}P NMR (81 MHz, $CDCl_3$, 85% H_3PO_4) δ 30.5. Positive ion ESI-MS: *m*/*z*=341.4 (M+H$^+$). HRMS calcd for $C_{19}H_{29}D_2O_3P$, 340.2136; found, 340.2139.

4.6.5.2. Diethyl 3-deuterium-1-(4-methylphenyl-deuterium-methyl)-hept-2-enylphosphonate (13a). ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si) δ 0.78–0.93 (m, 3H), 1.11–1.24 (m, 4H), 1.26–1.32 (m, 6H), 1.91–2.02 (m, 2H), 2.28 (s, 3H), 2.62–2.74 (ddd, $^3J_{HH}$=3.1 Hz, $^3J_{HH}$=9.3 Hz, $^2J_{PH}$=20.9 Hz, 1H), 3.12 (d, $^3J_{HH}$=9.6 Hz, 1H), 3.11–3.18 (m, 1H), 4.06–4.14 (m, 4H), 5.24 (t, $^3J_{HH}$=7.5 Hz, $^3J_{PH}$=7.5 Hz, 1H), 6.93–7.02 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si) δ 13.9, 16.3–16.6 (m), 21.1, 21.9, 31.3 (d, $^4J_{PC}$=2.9 Hz), 32.3, 34.3 (t, $^1J_{CD}$=17.9 Hz), 43.6 (d, $^1J_{PC}$=136.3 Hz), 61.8 (d, $^3J_{PC}$=7.5 Hz), 62.3 (d, $^3J_{PC}$=7.5 Hz), 123.6 (d, $^2J_{PC}$=9.8 Hz), 128.9, 129.1, 135.6, 136.2 (d, $^3J_{PC}$=16.5 Hz), 136.5–135.7 (m); ^{31}P NMR (81 MHz, $CDCl_3$, 85% H_3PO_4) δ 29.9. Positive ion ESI-MS: *m*/*z*=341.4 (M+H$^+$).

4.7. A procedure for the reaction of $Cp_2Zr(ClPhCH{=}CH_2)$ with chlorophosphate: preparation of diethyl-2-(4-chlorophenyl)-1,2-zircono-ethylphosphonate

To a solution of dibutylzirconocene in THF was added 1.0 equiv of 4-chloro-styrene and stirred for 1 h at room temperature. Chlorophosphate (1 mmol, 144.7 μL) was added to this solution and stirred for 24 h at 0–5 °C (^{31}P NMR yield 51%). ^{31}P NMR (81 MHz, THF, 85% H_3PO_4) δ 49.1 ppm.

4.7.1. Preparation of diethyl 2-(4-chlorophenyl)ethylphosphonate (8c).[25] The resulting mixture of diethyl 2-(4-chlorophenyl)-1,2-zircono-ethylphosphonate was treated with 3 N HCl and stirred for 1 h. Then it was carried out in a similar way to that described above to get 140 mg of the title compound as a colorless liquid (isolated yield 48%). ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si) δ 1.25–1.34 (m, 6H), 1.97–2.08 (m, 2H), 2.86–2.92 (m, 2H), 4.07–4.12 (m, 4H), 7.12–7.32 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si) δ 6.5 (d, $^3J_{PC}$=6.2 Hz), 27.5 (d, $^1J_{PC}$=139.1 Hz), 28.0 (d, $^2J_{PC}$=4.4 Hz), 61.7 (d, $^3J_{PC}$=6.8 Hz), 128.7, 129.5, 132.2, 140.5 (d, $^3J_{PC}$=18.3 Hz); ^{31}P NMR (81 MHz, $CDCl_3$, 85% H_3PO_4) δ 32.4. Positive ion ESI-MS: *m*/*z*=277.1, 279.0 (M+H$^+$). HRMS calcd for $C_{12}H_{18}ClO_3P$, 276.0682; found, 276.0685.

4.7.2. Preparation of diethyl (*E*)-2-(4-chlorophenyl) ethenylphosphonate (10c).[26] The resulting mixture of diethyl 2-(4-chlorophenyl)-1,2-zircono-ethylphosphonate was treated with NCS (1 mmol, 133.5 mg) or I_2 (1 mmol, 254 mg) and stirred for 30 min at room temperature. Then it was carried out in a similar way to that described above to get 82 mg of the title compound as a colorless liquid (yield 30%). ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si) δ 1.36 (t, $^3J_{HH}$=6.8 Hz, 6H), 4.08–4.18 (m, 4H), 6.23 (t, $^2J_{PH}$=17.3 Hz, $^3J_{HH}$=17.3 Hz), 7.13–7.52 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si) δ 16.4 (d, $^3J_{PC}$=6.5 Hz), 61.9 (d, $^2J_{PC}$=6.0 Hz), 114.8 (d, $^2J_{PC}$=190.0 Hz), 128.9, 129.1, 133.4 (d, $^3J_{PC}$=23.7 Hz), 136.1, 147.2 (d, $^2J_{PC}$=6.5 Hz); ^{31}P NMR (81 MHz, $CDCl_3$, 85% H_3PO_4) δ 19.5. Positive ion ESI-MS: *m*/*z*=274.9, 276.9 (M+H$^+$), 296.9, 298.9 (M+Na$^+$). HRMS calcd for $C_{12}H_{16}ClO_3P$, 274.0526; found, 274.0522.

Acknowledgements

This work was supported by the National Natural Science Foundation of China 20372041 (20572058) and Beijing Department of Education (XK100030514).

References and notes

1. (a) Kaboudin, B.; Nazari, R. *Tetrahedron Lett.* **2001**, *42*, 8211–8213; (b) Kim, D. Y.; Rhie, D. Y. *Tetrahedron* **1997**, *53*, 13603–13608; (c) Schultz, P.; Lerner, R. A. *Acc. Chem. Res.* **1993**, *26*, 391–395; (d) Stewart, J. D.; Liotta, L. J.; Benkovic, S. J. *Acc. Chem. Res.* **1993**, *26*, 396–404; (e) Cox, R. J.; Mayo-Martín, M. B.; Hadfield, A. T. *Chem. Commun.* **2001**, 1710–1711.
2. (a) Han, L.-B.; Tanaka, M. *Chem. Lett.* **1999**, 863–864; (b) Han, L.-B.; Choi, N.; Tanaka, M. *J. Am. Chem. Soc.* **1996**, *118*, 7000–7001; (c) Lai, C.; Xi, C.; Chen, C.; Ma, M.; Hong, X. *Chem. Commun.* **2003**, 2736–2737.
3. (a) Deprele, S.; Montchamp, J.-L. *J. Am. Chem. Soc.* **2002**, *124*, 9386–9387; (b) Stockland, R. A., Jr.; Taylor, R. I.; Thompson, L. E.; Patel, P. B. *Org. Lett.* **2005**, *7*, 851–853; (c) Montchamp, J.-L. *J. Organomet. Chem.* **2005**, *690*, 2388–2406.
4. (a) Shulyupin, M. O.; Francio, G.; Beletskaya, I. P.; Leitnerb, W. *Adv. Synth. Catal.* **2005**, *347*, 667–672; (b) Tayama, O.; Nakano, A.; Iwahama, T.; Sakaguchi, S.; Ishii, Y. *J. Org. Chem.* **2004**, *69*, 5469–5494; (c) Reichwein, J. F.; Patel, M. C.; Pagenkopf, B. L. *Org. Lett.* **2001**, *3*, 4303–4306; (d) Mirzaei, F.; Han, L.-B.; Tanaka, M. *Tetrahedron Lett.* **2001**, *42*, 297–299; (e) Han, L.-B.; Mirzaei, F.; Zhao, C.-Q.; Tanaka, M. *J. Am. Chem. Soc.* **2000**, *122*, 5407–5408.
5. Zhao, C.-Q.; Han, L.-B.; Tanaka, M. *Organometallics* **2000**, *19*, 4196–4198.
6. (a) Negishi, E.; Cederbaum, F. E.; Takahashi, T. *Tetrahedron Lett.* **1989**, *27*, 2829–2832; (b) Takahashi, T.; Swanson, D. R.; Negishi, E. *Chem. Lett.* **1987**, 623–626.
7. (a) Takahashi, T.; Murakami, M.; Saburi, M.; Uchida, Y.; Kozwa, K.; Uchida, T.; Sanson, D. R.; Negishi, E. *Chem. Lett.* **1989**, 761–764; (b) Buchw, S. L.; Buchwald, S. L.; Waston, B. T. *J. Am. Chem. Soc.* **1987**, *109*, 2544–2546; (c) Negishi, E.; Nguyen, T.; Maye, J. P.; Choueiri, D.; Suzuki, N.; Takahashi, T. *Chem. Lett.* **1992**, 2367–2370.
8. Alt, H. G.; Denner, C. E.; Thewalt, U.; Rausch, M. D. *J. Organomet. Chem.* **1988**, *356*, C83–C85.
9. Swanson, D. R.; Negishi, E. *Organometallics* **1991**, *10*, 825–826.
10. Swanson, D. R.; Rousset, C. J.; Negishi, E.; Takahashi, T.; Seki, T.; Saburi, M.; Uchida, Y. *J. Org. Chem.* **1989**, *54*, 3521–3523.

11. Suzuki, N.; Rousset, C. J.; Aoyagi, K.; Kotora, M.; Takahashi, T. *J. Organomet. Chem.* **1994**, *473*, 117–128.
12. Xi, C.; Ma, M.; Li, X. *Chem. Commun.* **2001**, 2554–2555.
13. Takahashi, T.; Seki, T.; Nitto, Y.; Saburi, M.; Rousset, C. J.; Negishi, E. *J. Am. Chem. Soc.* **1991**, *113*, 6266–6268.
14. (a) Lai, C.; Xi, C.; Feng, Y. *Phosphorus Sulfur Silicon Relat. Elem* **2004**, *179*, 449–456; (b) Baldwin, I. C.; Beckett, R. P.; Williams, J. M. *Synthesis* **1996**, 34–36.
15. Balczewski, P.; Pietrzykowski, W. M. *Tetrahedron* **1996**, *52*, 13681–13694.
16. Binns, M. R.; Haynes, R. K.; Katsifis, A. G.; Schober, P. A.; Vonwiller, S. C. *J. Am. Chem. Soc.* **1988**, *110*, 5411–5423.
17. Lopin, C.; Gouhier, G.; Gautier, A.; Piettre, S. R. *J. Org. Chem.* **2003**, *26*, 9916–9923.
18. Balczewski, P.; Mikolajczyk, M. *Synthesis* **1995**, *4*, 392–396.
19. Wnuk, S. F.; Bergolla, L. A.; Garcia, P. I. *J. Org. Chem.* **2002**, *67*, 3065–3071.
20. Balczewski, P.; Pietrzykowski, W. M. *Tetrahedron* **1997**, *53*, 7291–7304.
21. Xu, Y. B.; Flavin, M. T.; Xu, Z. Q. *J. Org. Chem.* **1996**, *61*, 7697–7701.
22. Kobayashi, Y.; William, A. D. *Adv. Synth. Catal.* **2004**, *346*, 1749–1757.
23. Tashtoush, H. I.; Sustmann, R. *Chem. Ber.* **1993**, *126*, 1759–1762.
24. (a) Cristau, H. J.; Pirat, J. L.; Drag, M.; Kafarski, P. *Tetrahedron Lett.* **2000**, *41*, 9781–9786; (b) Zhong, P.; Xiong, Z. X.; Huang, X. *Synth. Commun.* **2000**, *30*, 273–278.
25. Brindaban, C.; Guchhait, S. K.; Ghosh, K. *J. Org. Chem.* **1998**, *63*, 5250–5251.
26. (a) Sheng, S. R.; Zhou, W.; Liu, X. L.; Song, C. S. *Synth. Commun.* **2004**, *34*, 1011–1016; (b) Yokomatsu, T.; Yamagishi, T.; Suemune, K.; Yoshida, Y.; Shibuya, S. *Tetrahedron* **1998**, *54*, 767–768.