## Metallo-phosphorylation of olefins: reaction of diethyl chlorophosphate with zirconocene–ethylene complex<sup>†</sup>

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## Zirconocene–ethylene complex $Cp_2Zr$ ( $CH_2 = CH_2$ ) reacted with chlorophosphate to form zircono-ethylphosphonate, which could be converted into various functionalized ethylphosphonates.

Introduction of a heteroatom to multiple carbon-carbon bonds is attractive from the synthetic viewpoint.<sup>1</sup> In this regard, a particularly attractive and interesting subject is the simultaneous introduction of a metal and another heteroatom to multiple carbon-carbon bonds, since it is a more versatile and elegant synthetic elaboration. While the related carbometallation of multiple carbon-carbon bonds has been extensively studied,<sup>2</sup> only a few reactions for the preparation of such a complex, which contains a metal and a heteroatom to a carbon-carbon bond, have been studied. In this paper, we would like to report novel reaction of zirconocene-ethylene complex  $Cp_2Zr(CH_2 = CH_2)$  with chlorophosphate to form zirconoethylphosphonate (1) (Scheme 1), which can be converted into various functionalized ethylphosphonates.

A typical experiment was carried out as follows. To a solution of zirconocene–ethylene complex  $Cp_2Zr(CH_2 = CH_2)$ ,<sup>3</sup> generated by the reaction of  $Cp_2ZrCl_2$  with 2 equiv. of EtMgBr in THF, was added one equiv. of diethyl chlorophosphate. The reaction mixture was kept at room temperature for 24 hours, and then it was quenched with 2M HCl. Purification of crude product was carried out by column chromatography on silica gel (ethyl acetate–petroleum ether = 2:1). Ethylphosphonate (**2a**) was obtained in 87% yield.

The product ethylphosphonate did not come from the reaction of EtMgBr with chlorophosphate: hydrolysis was replaced by iodination of the reaction mixture and 2-iodoethylphosphonate (**2b**) was obtained in 85% yield, which suggested that the intermediate of the reaction of zirconocene–ethylene complex with chlorophosphate contains a Zr–C bond before hydrolysis.

Zircono-ethylphosphonate could be converted into functionalized ethylphosphonate by coupling with various electrophiles such as I<sub>2</sub>, NBS, acyl chloride and allyl bromide. The various reactions are summarized in Table 1. The reaction of zirconoethylphosphonate with I<sub>2</sub> or NBS gave 2-iodoethylphosphonate or 2-bromoethylphosphonate (**2c**) in 85% and 73% yields, respectively. Moreover, treatment of zircono-ethylphosphonate with allyl bromide obtained (**2d**) in 77% yield, in which the new carbon–carbon bond was formed. It is noteworthy that without CuCl the reaction of zircono-ethylphosphonate with acyl



† Electronic supplementary data available: experimental procedure and NMR data. See http://www.rsc.org/suppdata/cc/b1/b107755d/



chloride did not proceed. The zircono-ethylphosphonate requires initial reaction with CuCl to give the alkylcopper reagent,<sup>4</sup> which then undergoes smooth reaction with acyl chloride to give (2e). This is due to the different reactivity of the carbon attached to zirconium in the zircono-ethylphosphonate.

The reaction of zirconocene-ethylene complex Cp<sub>2</sub>Zr  $(CH_2 = CH_2)$  with various unsaturated compounds such as alkynes,<sup>5</sup> alkenes,<sup>3</sup> ketone, and nitriles,<sup>6</sup> in which the reactions afforded five-membered zirconacycles was investigated. To elucidate the intermediate of this reaction, the reaction of  $Cp_2Zr(CH_2 = CH_2)$  with chlorophosphate was followed by <sup>31</sup>P NMR spectroscopy. Immediately following the addition of chlorophosphate at -78 °C, the reaction mixture was analysed by <sup>31</sup>P NMR. The <sup>31</sup>P NMR spectrum showed only one peak at 3.2 ppm, which was confirmed to be due to the phosphorus of the chlorophosphate. Then, the reaction mixture was stirred for 10 minutes from -78 °C to room temperature. Three peaks appeared in the <sup>31</sup>P NMR spectrum. One appeared at 3.2 ppm and another at -3.8 ppm. The latter signal is consistent with phosphorus of coordination number five.7 The third signal was at 33.7 ppm and was assigned to the phosphorus of zirconoethylphosphonate (1). Following continuous stirring of the reaction mixture for 30 minutes at room temperature, the peak at 3.2 ppm completely disappeared and the peak at 33.7 ppm increased. Finally, the peak at -3.8 ppm disappeared after the reaction mixture was stirred for 24 hours at room temperature.

Based on the above results, a proposed reaction mechanism is shown in Scheme 2. The reaction of  $Cp_2ZrCl_2$  with 2 equiv. of EtMgBr gives  $Cp_2ZrEt_2$ , which smoothly decomposes at 0 °C to give resonance hybrids  $Cp_2Zr$ -ethylene and zirconacyclopropane (3).<sup>3</sup> The Zr–C bond of zirconacyclopropane (3) reacts with chlorophosphate to form five-membered zirconacycle (4). Then, elimination of chloride from zirconacycle (4) takes place to form zircono-ethylphosphonate.

Table 1 Reaction of a mixture of  $\text{Cp}_2\text{Zr}\text{Et}_2\,\text{and}$  chlorophosphate with electrophiles

Entry	Electrophile	T/°C	Time/h	Product	Yield (%) <sup>a</sup>
1	HCl	rt	1	OEt	87 (63)
				ري OEt <b>2a</b>	
2	$I_2$	rt	3	OEt	85 (60)
				ິ່0⊑t <b>2b</b>	
3	NBS	rt	3	Br P OEt	73 (49)
				ο΄ ΟΕΙ <b>2C</b>	
4	Br	rt	6	// OEt	77 (56)
				O OEt 2d	
$5^b$	MeCOCl	50	6	O DEt	64 (45)
				CH <sub>3</sub> O OEt <b>2e</b>	

 $^a$  GC yields. Isolated yields are given in parentheses;  $^b$  CuCl (1 equiv.) was added.

To further explore this reaction, other olefins were used. During the course of our study, we found that styrene also reacted with chlorophosphate in the presence of zirconocene species. When  $Cp_2ZrBu_2$  (Negishi reagent) was treated with 2 equiv. of styrene and chlorophosphate successively, 2-phenyl-ethylphosphonate was observed in 43% yield. In this case, the reaction proceeded *via* the  $\beta$ ,  $\beta'$  carbon–carbon bond cleavage of the zirconacyclopentane.<sup>8</sup>

Further investigations are still in progress in this area.

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