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Preliminary Communication

Bis(tert-butylcyclopentadienyl)-(divinyl)hafnium from bis(tert-butylcyclopentadienyl)hafnium dichloride and vinyllithium

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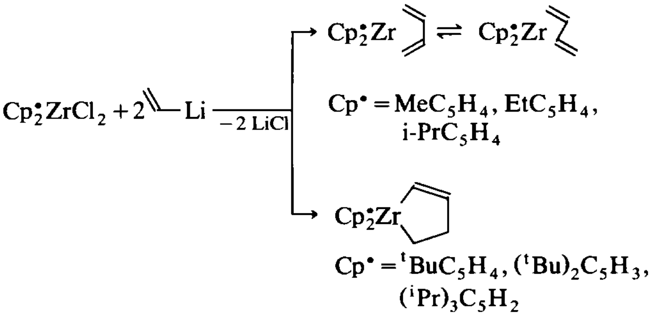
Abstract

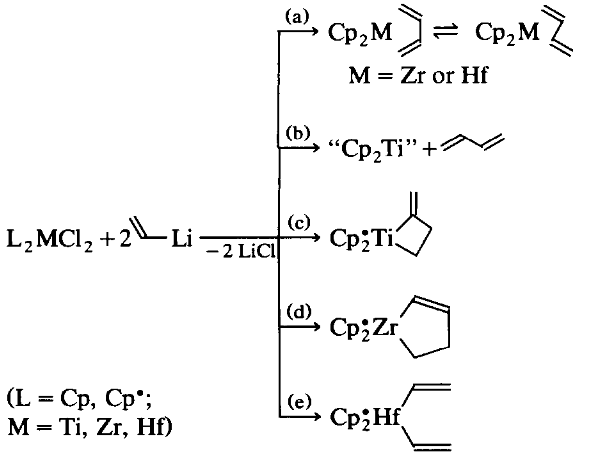
The chloride $(^tBuC_5H_4)_2HfCl_2$ and vinyllithium react in the mole ratio 1:2 to give the divinyl complex $(^tBuC_5H_4)_2Hf(CH{=}CH_2)_2$.

Key words: Hafnium; Zirconium; Cyclopentadienyl; Vinyl

Vinyl–transition-metal compounds are intermediates in catalytic reactions such as the hydrogenation and oligomerization of acetylenes and also in the C–H-activation of ethylene. Extensive investigations on the structure and reactivity of vinyl compounds of early transition metals have been carried out [1]. In the case of zirconium, these may be illustrated as follows



It has been found that there is a relationship between the nature of metallocene complexes and their reactivities towards vinyllithium. In the case of cyclopentadienyl complexes of Ti, Zr and Hf it has been found that diene complexes are formed, reactions (a) and (b), whereas with pentamethylcyclopentadienyl (Cp*) complexes of these metals titanacyclobutane, reaction (c), and zirconacyclopentene, reaction (d), are produced; in the case of pentamethylcyclopentadienylhafnium, however, it has been found that the divinyl compound, reaction (e), is formed instead.



By choosing the metal and cyclopentadienyl ligand it is, thus, possible to control the metal-induced coupling of vinyl groups so as to yield different types of product. The various products from reactions (a), (c) and (d) could be useful for the synthesis of organic heterocycles.

In order to study the influence of substituents attached to the cyclopentadienyl rings of metallocene compounds we have now synthesized bis(tert-butylcyclopentadienyl)hafnium dichloride and investigated its reaction with vinyllithium. For this reaction the bis(tert-butylcyclopentadienyl)hafnium dichloride was dissolved in tetrahydrofuran and the solution cooled to −78 °C. Freshly prepared vinyllithium was added and, since no reaction occurred at −78 °C, the solution was allowed to warm to room temperature with stirring. It was stirred overnight at room temperature and gradually became yellow. The solvent was evaporated under vacuum, pentane was added, and the mixture was filtered. Evaporation of the solvent gave a yellow oil. The ^{13}C-NMR data for the product (Table 1) indicate that the major product of the reaction is bis(tert-butylcyclopentadienyl)hafnium divinyl

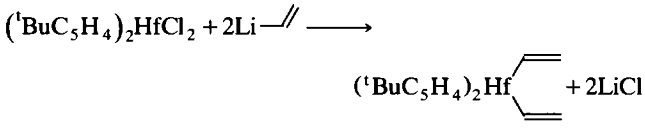


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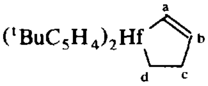
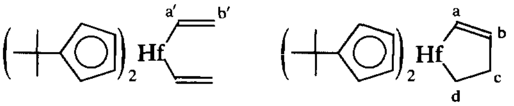
TABLE 1. ^{13}C-NMR data for the product from bis(tert-butylcyclopentadienyl)hafnium dichloride and vinyllithium (solvent $CDCl_3$, 20°C)

$({}^{t}BuC_5H_4)_2Hf(CH{=}CH_2)_2$	187.6	-CH=
	126.6	C_5H_4 [a]
	117.5	$=CH_2$
	98.5	C_5H_4
	97.3	C_5H_4
	21.3	$(H_3C)_3C$
	20.4	$(H_3C)_3C$
 (minor product)	182.1	a
	129.2	b
	102.4	C_5H_4
	100.9	C_5H_4
	42.2	c
	35.0	d
	20.8	$(H_3C)_3C$
	20.2	$(H_3C)_3C$

[a] Signal for the carbon atom to which the tert-butyl group is attached.

It is therefore concluded that the tert-butylcyclopentadienyl ligand has a similar influence to the pentamethylcyclopentadienyl ligand on this type of reaction.

The spectrum shows that there is a minor component present. This compound has peaks in positions characteristic of a metallacyclopent-1-ene [1,2]. It was not possible to assign all peaks for the minor product unambigously. This type of rearrangement (divinyl complex to metallacyclopent-1-ene) was known previously for zirconocene compounds [3],



but to our knowledge this is the first report of such a rearrangement for a hafnium compound.

Acknowledgment

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