

Preparation of a Hafnocene–Ethylene Complex from Bis(η^5 -cyclopentadienyl)hafnacyclopentane and its Characterization

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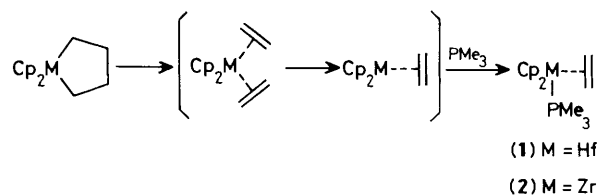
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Addition of PMe_3 to zircona- and hafna-cyclopentane derivatives afforded the corresponding zirconocene- and hafnocene-ethylene complexes, respectively, by C–C bond fission, the latter being the first example of hafnocene-alkene complexes.

Recently we have isolated the first zirconocene-monoalkene complex, $\text{Cp}_2\text{Zr}(\text{PhCH}=\text{CHPh})(\text{PMe}_3)$ (Cp = cyclopentadienyl),^{1,2} and determined its structure.³ Additionally, we have since developed a convenient preparative method for zirconocene-alkene complexes which involves β -elimination reactions of zirconocene dialkyl complexes followed by liberation of 1 equiv. of alkane.⁴ Dialkylhafnocene derivatives are, however, too stable to give hafnocene-alkene complexes. All other attempts to give hafnocene-alkene complexes, *e.g.* by reduction of Cp_2HfCl_2 with Na or Mg in the presence of alkenes, were unsuccessful.

Although conversion of bis(η^5 -cyclopentadienyl)hafnacyclopentane into bis(ethylene)hafnocene and mono(ethylene)hafnocene has been implicated in the formation of

hafnacyclopentene and hafnacyclopentadiene derivatives,^{5,6} there has been no report on the isolation and/or characterization of hafnium complexes such as bis(ethylene)hafnocene and mono(ethylene)hafnocene complexes.



Scheme 1

We describe here the preparation of the first isolated and characterized hafnocene-alkene complex involving carbon-carbon bond cleavage of a hafnacyclopentane complex, which is also adaptable as a novel preparative method for zirconocene-alkene complexes (Scheme 1).

A solution of bis(η^5 -cyclopentadienyl)hafnacyclopentane prepared by the reaction of Cp_2HfCl_2 with $\text{BrMg}(\text{CH}_2)_4\text{MgBr}$ in tetrahydrofuran was refluxed in the presence of an excess of PMe_3 (4 equiv.) for 6 h to give the hafnocene-ethylene complex (**1**) in 66% yield. Its ^1H and ^{13}C n.m.r. spectra showed characteristic peaks that were quite similar to those of the zirconocene-ethylene complex (**2**).^{4,7} Thus, in its ^1H n.m.r. spectrum the signals for the ethylene ligand attached to hafnium appeared as a multiplet at δ -0.10 to -0.02 and an apparent triplet at δ 0.19. The spectrum also revealed two doublets at δ 1.28 (J 6 Hz) and 5.08 (J 2 Hz) assignable to PMe_3 and Cp protons, respectively. The ^{13}C n.m.r. spectrum included the two ethylene carbons as two doublets at δ 10.52 (J 11 Hz) and 14.28 (J 5 Hz) coupled with the phosphorus of PMe_3 , as well as a singlet due to the Cp ligand (δ 98.27) and a doublet due to the methyl carbons of PMe_3 (δ 16.90 J 18 Hz). Its ^{31}P n.m.r. showed one singlet peak at -5.35. To the best of our knowledge complex (**1**) is the first hafnocene-alkene complex that has been isolated and characterized.†

Similarly, the addition of an excess of PMe_3 to bis(η^5 -cyclopentadienyl)zirconacyclopentane, prepared by the reaction of Cp_2ZrCl_2 with $\text{BrMg}(\text{CH}_2)_4\text{MgBr}$, gave the zirco-

nocene-ethylene complex (**2**) in 87% yield. This complex (**2**) was identified by its characteristic ^1H , ^{13}C , and ^{31}P n.m.r. spectra, which were the same as those of an authentic sample obtained from a diethylzirconocene complex.^{4,7}

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† Satisfactory analytical data were obtained.