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Ausema, Johannes B.; Hessen, Bart; Teuben, Jan H.

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STEREOSELECTIVE ADDITION OF BENZOPHENONE TO (C₅Me₅)Hf(s-cis-C₆H₁₀)Cl

Johannes B. Ausema, Bart Hessen and Jan H. Teuben
Department of Inorganic Chemistry, University of Groningen, Nijenborgh 16, 9747 AG Groningen, The Netherlands

Abstract. The reaction of (C₅Me₅)Hf(s-cis-C₆H₁₀)Cl with benzophenone results in sequential insertion of two ketone molecules in the Hf-diene bond through adduct intermediates. The final 1,3-dioxa-2-hafnacyclonon-6-ene has a cis-configuration around the double bond, in contrast with related products from (C₅H₅)₂Zr(diene).

In recent years, 1,3-butadiene complexes of the early transition metals (Group 4 and 5) have been the subject of much interest. Especially the Cp₂M(diene) (M = Zr, Hf) 18-electron system has been investigated [1], and it became clear that the s-cis diene complexes behaved like σ,π-metal-lacyclopentene species, with pronounced nucleophilic character of the diene methylene carbon atoms. Thus insertion of polar unsaturated molecules like ketones and nitriles into the metal-diene bond is observed, with large regio- and stereoselectivity [1]. Here we wish to report the reactivity of the 14-electron s-cis 2,3-dimethyl-1,3-butadiene (C₆H₁₀) complex Cp*Hf(C₆H₁₀)Cl (1, Cp* = η⁵-C₅Me₅) [2] with benzophenone, where the steric and electronic unsaturation of the mono(pentamethylcyclopentadienyl) system leads to a different stereoselectivity.

Yellow 1 reacts with one mole of Ph₂CO, initially to give a green 16 electron adduct, 1.OCPh₂ [3], which in solution (hexane, -15°C) rapidly forms the pale yellow singly inserted product Cp*Hf(O-CPh₂-CH₂-C(Me)=C(Me)-CH₂-CPh₂-O)Cl (2) [4]. This compound is analogous to the products found in the metalloocene Zr system [5]. 2 can react with a second equivalent of Ph₂CO, again initially forming an adduct, 2.OCPh₂. This adduct is less stable than 1.OCPh₂, and can only be detected by its transient, intense green colour. It rapidly reacts to form the colourless doubly inserted product Cp*Hf(O-CPh₂-CH₂-C(Me)=C(Me)-CH₂-CPh₂-O)Cl (3) [6].

Apart from the possibility to detect and even isolate intermediate adducts, the product formation in this system shows several differences with that in the Cp₂Zr-system. Firstly, in the zirconocene system doubly inserted products could only be obtained with dienes without substituents on the 2- and/or 3-position. Secondly, whereas the doubly inserted products in the zirconocene system have a trans-configuration around the double bond in the 1,3-dioxa-2-zirconacyclonon-6-ene, the configuration around the double bond in 3 is cis. This can be seen from the NMR-spectra of 3, as the two methyl groups of the former 2,3-dimethyl-1,3-butadiene ligand are identical, indicating a mirror plane in the molecule, and thus a cis-configuration around the double bond. These differences in product formation are probably due to a different reaction mechanism for the second insertion step. The Cp₂Zr-2-oxacyclohept-5-ene is not accessible for the ketone, and reaction only takes place after rearrangement, through a bicyclic transition state leading to a trans-configuration in the final product (Scheme 1). This transition state is too severely hindered for products from 2- or 2,3-substituted dienes [1a]. The mono(pentamethylcyclopentadienyl) Hf-system is sterically hindered on one side of the molecule only, and an adduct can be formed. Through a 4-center transition state the second insertion can then take place without rearrangement or significant influence from the substitents on the 2,3-
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Scheme 1

Scheme 2

Scheme 3

References and Notes


[3] The adduct 1,OCPh₂ precipitates from pentane at -30°C and can be handled as a solid at 0°C. IR (KBr/silicon grease): 1553 cm⁻¹ (C=O), 110 cm⁻¹ lower than in free Ph₂CO.

[4] 1, 1H-NMR (90 MHz, d₆-benzene): δ 1.86 (s, 15H, Cp*); δ 1.72 (s, 3H, Me); δ 1.41 (s, 3H, Me); δ 3.01 (d, 2J 12.8 Hz, 1H, CH₂CO); δ 2.85 (d, 2J 12.8 Hz, 1H, CH₂CO); δ 1.00 (d, 2J 11.4 Hz, 1H, CH₂Hf, the other signal around 1.8 ppm partially obscured); δ 7.5-6.9 ppm (m, 10H, Ph). C₅H₃HfClO (613.53): calcd. C, 56.77; H, 5.75; Cl, 5.78; found C, 56.85; H, 5.62; Cl, 5.84.


[6] 3, 1H-NMR (90 MHz, d₆-benzene): δ 1.88 (s, 15H, Cp*); δ 1.27 (s, 6H, Me); δ 4.20 (d, 2J 13.8 Hz, 2H, CH₂); δ 2.84 (d, 2J 13.8 Hz, 2H, CH₂); δ 7.6-7.1 (m, 20H, Ph). 13C-NMR (22.6 MHz, d₆-benzene): δ 11.7 (q, 2J 127 Hz, Cp*-Me); δ 20.10 (q, 2J 126 Hz, =C(C₃H₃)); δ 48.64 (t, 2J 126 Hz, CH₂); δ 121.10 (s, Cp*-ring); δ 127.14 (d, J 158 Hz, Ph CH); δ 127.71 (d, J 157 Hz, Ph CH); δ 133.01 (s, C(Me)); δ 147.19 (s, Ph C); δ 150.65 (s, Ph C).

C₅(H₃)HfClO (795.74); calcd. C, 63.40; H, 5.70; Cl, 4.45; Hf, 22.43; found C, 63.68; H, 5.70; Cl, 4.50; Hf, 22.21.