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Preliminary Communication

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STERESELECTIVE ADDITION OF BENZOPHENONE TO $(C_5Me_5)Hf(s-cis-C_6H_{10})Cl$ (2,3-DIMETHYL-1,3-BUTADIENE) Cl

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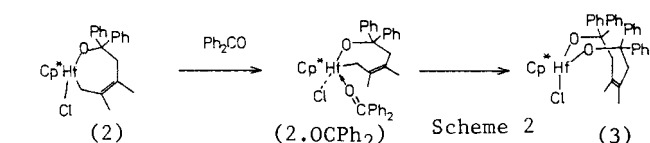
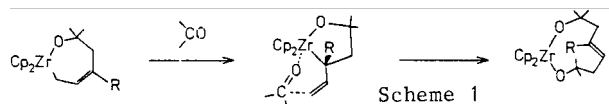
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Abstract. The reaction of $(C_5Me_5)Hf(s-cis-C_6H_{10})Cl$ with benzophenone results in sequential insertion of two ketone molecules in the Hf-diene bond through adduct intermediates. The final 1,3-dioxa-2-hafnacyclonon-6-ene has a *cis*-configuration around the double bond, in contrast with related products from $(C_5H_5)_2Zr(diene)$.

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 $Cp_2M(diene)$ ($M = Zr, Hf$) 18-electron system has been investigated [1], and it became clear that the *s-cis* diene complexes behaved like σ^2, π -metallacyclopentene 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 (C_6H_{10}) complex $Cp^*Hf(C_6H_{10})Cl$ (**1**, $Cp^* = \eta^5-C_5Me_5$) [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 Ph_2CO , initially to give a green 16 electron adduct, **1**. $OCPh_2$ [3], which in solution (hexane, $-15^\circ C$) rapidly forms the pale yellow singly inserted product $Cp^*Hf(O-CPh_2-CH_2-C(Me)=C(Me)CH_2)Cl$ (**2**) [4]. This compound is analogous to the products found in the metallocene Zr system [5]. **2** can react with a second equivalent of Ph_2CO , again initially forming an adduct, **2**. $OCPh_2$. This adduct is less stable than **1**. $OCPh_2$, and can only be detected by its transient, intense green colour. It rapidly reacts to form the colourless doubly inserted product $Cp^*Hf(O-CPh_2-CH_2-C(Me)=C(Me)-CH_2-CPh_2-O)Cl$ (**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 Cp_2Zr -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 Cp_2Zr -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 substituents on the 2,3-



-positions of the original diene (Scheme 2). This yields a product with a *cis*-arrangement around the double bond.

Preliminary results for the reaction of 1 with 2,6-xylylnitrile include formation of an adduct of much greater stability than the benzophenone adduct, and, upon heating this adduct in toluene at 60°C, disproportionation to yield equimolar amounts of 1 and a doubly inserted product. Our further attention will be directed to a more complete understanding of the selectivity in this kind of reactions, and also towards the reactivity of the Ti-analogue of 1 [2a], as the reactivity of Ti-butadiene complexes is virtually unexplored.

References and Notes

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- [2] a. J. Blenkins, H.J. de Liefde Meijer, and J.H. Teuben, *Organometallics*, **2**, 1483 (1983).
b. J. Blenkins, B. Hessen, F. van Bolhuis, A.J. Wagner, and J.H. Teuben, *Organometallics* **6**, 459 (1987).
- [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] 2, 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). C₂₉H₃₅HfClO (613.53): calcd. C, 56.77; H, 5.75; Cl, 5.78; found C, 56.85; H, 5.62; Cl, 5.84.
- [5] a. Y. Kai, N. Kanehisa, K. Miki, M. Akita, H. Yasuda, and A. Nakamura, *Bull. Chem. Soc. Jpn.* **56**, 3735 (1983).
b. G. Erker, K. Engel, J.L. Atwood, and W.E. Hunter, *Ang. Chem.* **95**, 506 (1983).
- [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, J 127 Hz, Cp*-Me); δ 20.10 (q, J 126 Hz, =C(CH₃)); δ 48.64 (t, J 126 Hz, CH₂); δ 90.00 (s, CO); 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). C₄₂H₄₅HfClO₂ (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.