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Preliminary communication

Boron hydride insertion into the Zr–C bond of dimeric (η^2-formaldehyde)zirconocene

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Abstract

Insertion of borohydride into the metallaoxirane Zr–C bond takes place upon treatment of the (η^2-formaldehyde)zirconocene dimer **2** with 9-borabicyclo[3.3.1]nonane. The resulting metallacyclic dimer $[Cp_2\overline{ZrOCH_2B(C_8H_{14})H}]_2$ (**4**) has been characterized by X-ray diffraction. Complex **4** is a model for an intermediate stage of the insertion of CO-derived methylene groups into metal–hydrogen bonds, such as is thought to occur in Fischer–Tropsch type processes.

Alkyl chain growth in heterogeneous Fischer–Tropsch chemistry is probably initiated by insertion of surface bound methylene into a metal–hydride bond [1]. In a search for molecular Fischer–Tropsch models, several group 4 metallocene derived metallaoxirane systems have been found to undergo insertion of a CO-derived CH_2 group into a suitable M–H bond [2]. We have now isolated a stable product which represents a molecular model of an early stage of such a methylene insertion process.

The hydrozirconation product of carbon monoxide, $Cp_2\overline{Zr(Cl)(OC}H_2)ZrCp_2Cl$ (**1**) [3], was treated with methyllithium to give dimethylzirconocene and (η^2-formaldehyde)zirconocene; the latter complex was isolated as a dimer, (**2**) [4]. Reaction of **2** with 2 molar equivalents of 9-borabicyclo[3.3.1]nonane [9-BBN] at 25 °C (3 h, toluene) yielded a single product (**4**, m.p. 206 °C, decomp., 71% isolated; ^1H NMR (thf-d_8): δ 6.37 (s, 10H, Cp), 3.77 (d, $^3J(HH)$ 2.4 Hz, 2H, BCH_2O), 2.05–1.50 (m, 12H, 9-BBN-CH_2), 1.18 (br, 2H, 9-BBN-CH), −1.58 (br, 1H, BHZr); ^{13}C NMR (thf-d_8, DEPT): δ 112.9 (Cp), 82.2 (br, BCH_2), 33.3, 33.0 (9-BBN-$BCH\mathit{C}H_2$), 27.3 (br, 9-BBN-$B\mathit{C}HCH_2$), 25.6, 20.7 (9-BBN-$BCHCH_2\mathit{C}H_2$), Anal. Found: C, 63.79; H, 7.47. $C_{38}H_{54}B_2O_2Zr_2 \cdot C_7H_8$ (839.1) calcd.: C, 64.42; H, 7.45%. The X-ray

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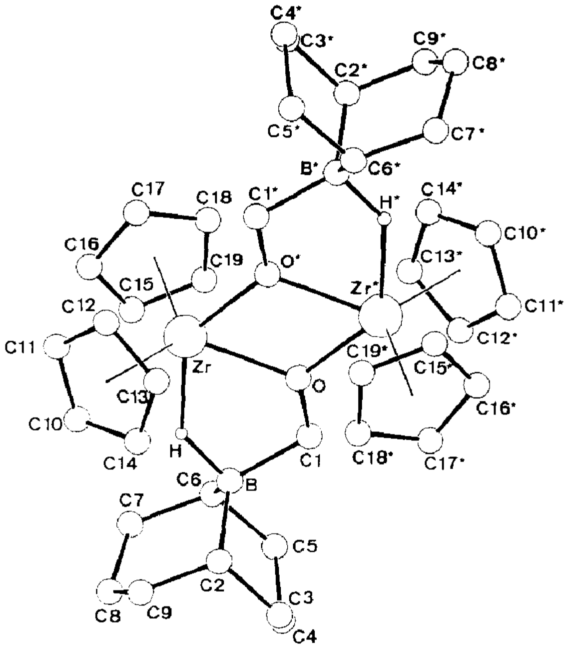
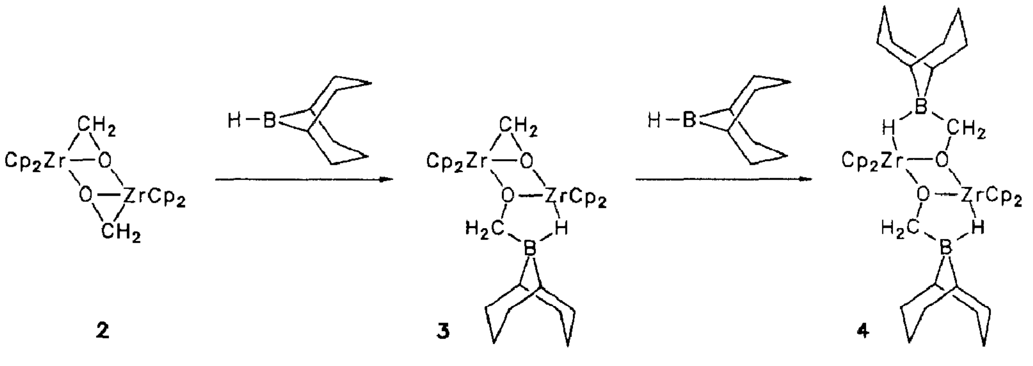


Fig. 1. View of the molecular structure of 4 in the crystal.

crystal structure analysis of 4 [5*] shows that B–H insertion into the zirconium–carbon bond of the CH_2OZr subunit of 2 has taken place, with formation of a five-membered ZrOCBH metallacycle (*d*(Zr–O) 2.148(4) Å, *d*(O–C(1)) 1.448(7) Å, *d*(C(1)–B) 1.64(1) Å, *d*(B–H) 1.33(5) Å, *d*(H–Zr) 1.99(5) Å; angle Zr,O,C(1) 116.8(3)°; O,C(1),B 111.1(5)°; B,H,Zr 138(4)°; H,Zr,O 71(1)°). In the crystal complex 4 is dimeric. Two symmetry related monomeric $Cp_2ZrOCH_2B(C_8H_{14})H$ units are connected through oxygen-bridges using the available lateral coordination site of the bent metallocene unit (connecting bond *d*(Zr–O*) 2.155(4) Å, angles O,Zr,O* 67.3°, Zr,O,Zr* 112.7(2)°).

The borohydride insertion reaction takes place in the undissociated Zr_2O_2-containing cyclodimeric cluster. Reaction of **2** with 1 molar equivalent of 9-BBN



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* Reference numbers with asterisks indicate notes in the list of references.

produced the intermediate **3**, identified by its ^1H NMR spectrum (benzene-d_6: δ 5.88, 5.64 (s, 10H each, Cp), 3.61 (d, $^3J(HH)$ 2.5 Hz, 2H, BCH_2O), 2.65 (s, 2H, $ZrCH_2$), 2.45–1.15 (m, 9-BBN), −0.62 (br, 1H, BHZr)].

It is conceivable that Fischer–Tropsch type reductive coupling of carbon monoxide in solution, e.g. the reported formation of 9-alkyl-9-BBN mixtures from 9-BBN and metal carbonyl complexes [6], is initiated by reaction sequences similar to the **1** → **3**/**4** conversion.

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5 Crystal data: $C_{38}H_{54}B_2O_2Zr_2 \cdot C_7H_8$, $M = 839.1$, monoclinic, space group $C2/c$, a 25.647(4), b 11.064(2), c 14.367(3) Å, β 95.06(2)°, V 4061.1 Å^3, D_{calc} 1.37 g cm^{-3}, $Z = 4$, μ(Mo-K_α) 5.39 cm^{-1}, 9511 reflections measured ($\pm h$, $\pm k$, $+l$), averaged to 4566 independent and 3321 observed reflections [$I > 2\sigma(I)$], no of parameters: 216, $R = 0.053$, $R_w = 0.070$. The atomic coordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

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