

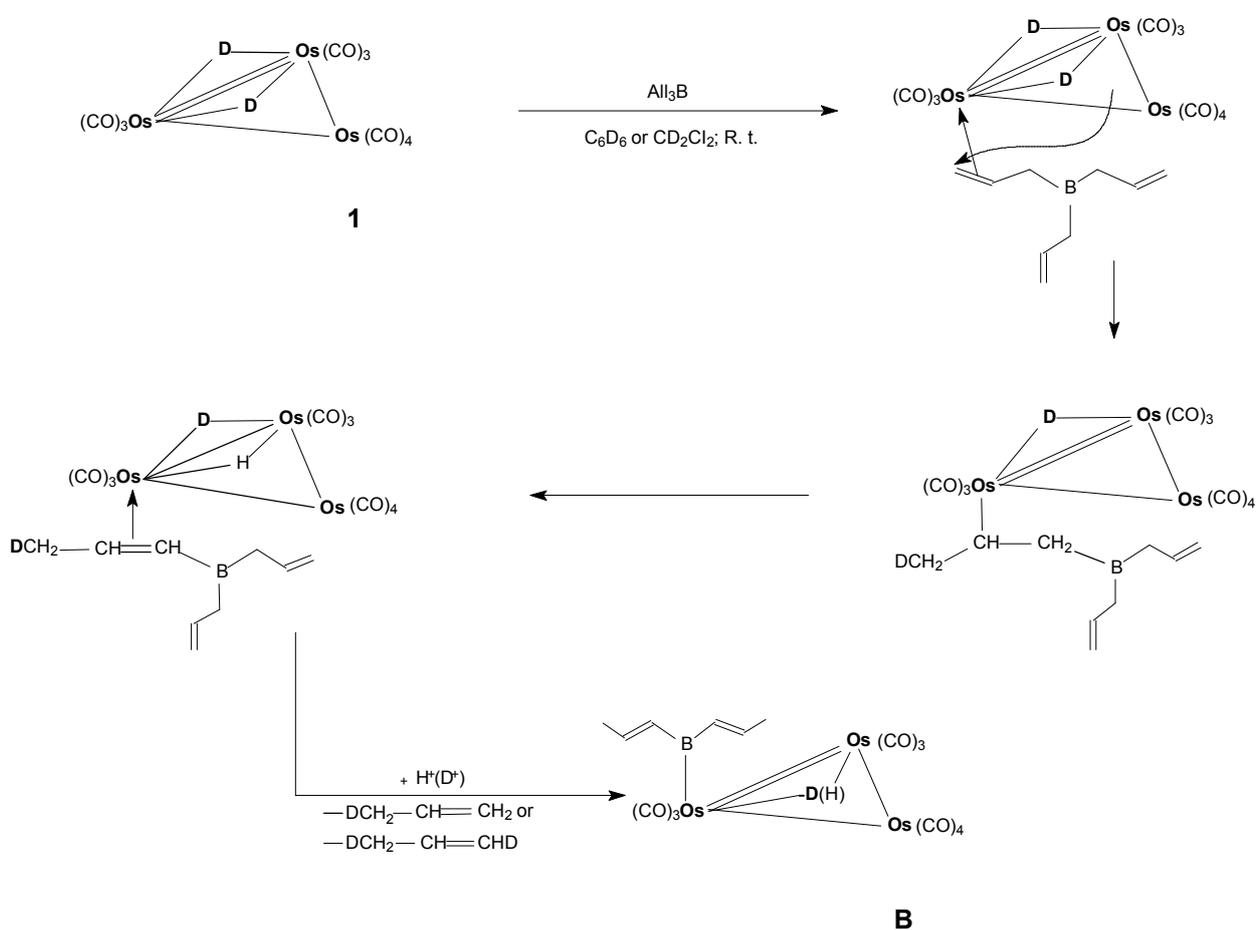
## Supporting Information

Crystallographic data in CIF format for complexes 2-4.

### Part I.

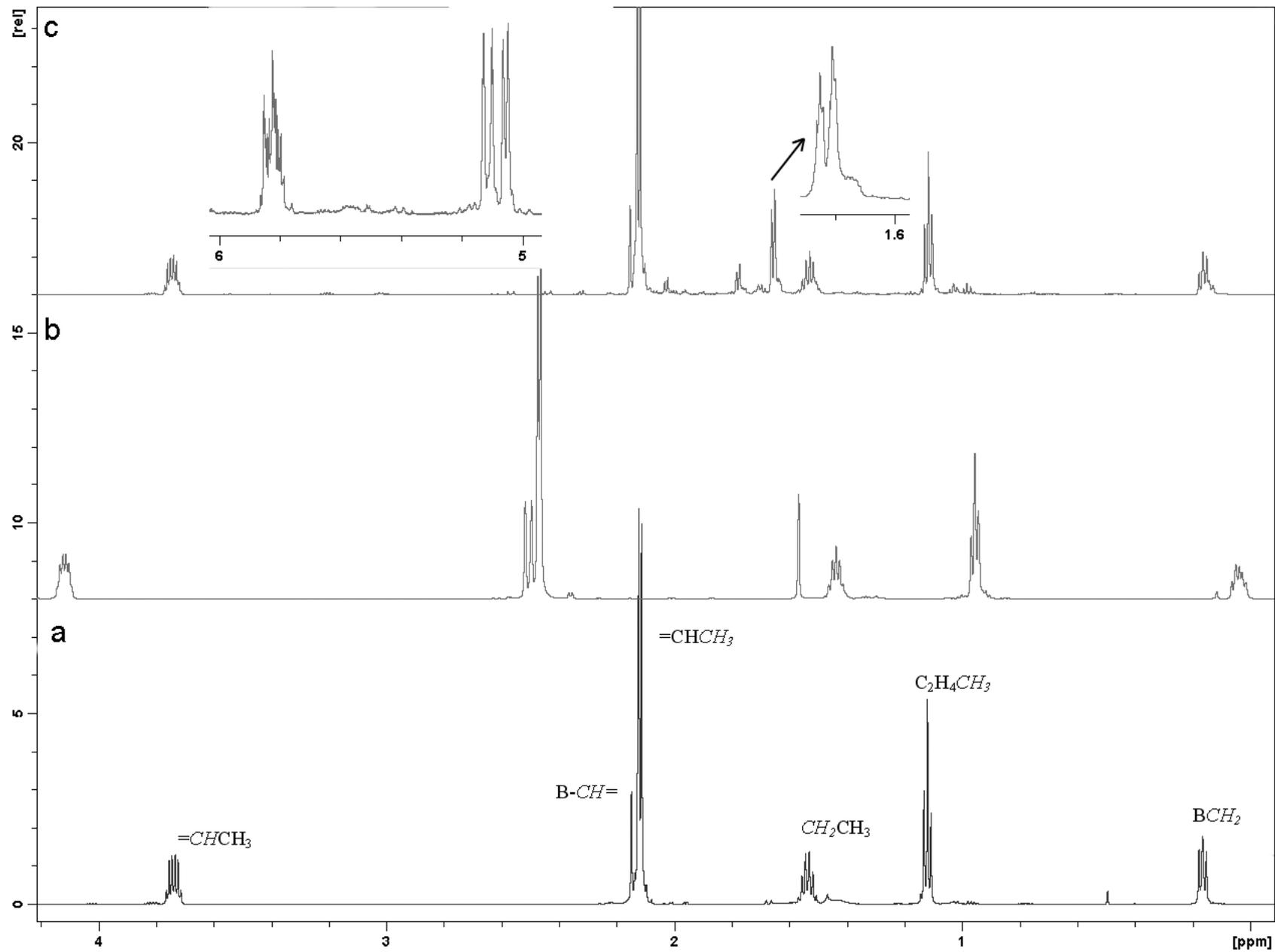
The methylene propylene proton is observed as a complex multiplet; the terminal methylene protons are observed as two doubles of multiplets with coupling constants 17.2 and 9.9 Hz; methyl protons are observed as a double triplet with coupling constants 6.5 and 1.6 Hz. In the  $^1\text{H}$   $\{^{11}\text{B}\}$  NMR spectrum there are the same signals.

### Part II



The reaction pathway in Scheme 1 is in agreement with the propylene loss but there are some points incompatible with it. Not only one but two other boron-bonded allyl groups can undergo such transformations decreasing the yield of the final product (cluster **2**). Be it the case, the methyl groups of the propenyl and propyl groups would have been deuterated, but this deuteration was not observed. In addition, no deuterium was observed at the methylene carbon of propylene,

whereas it should be the case for the protolysis of the boron propenyl bond.<sup>[1]</sup> Thus the classical scheme for the interaction of olefins with transition metal complexes<sup>[2-4]</sup> is not realized for the reaction of **1** with triallylborane. This is presumably caused by ability of the B-C bond to undergo protolysis, since the hydride ligands in **1** are substantially acidic.<sup>[5]</sup> The formation of propylene in this reaction was proven by <sup>1</sup>H NMR data (Figure 4s, c).



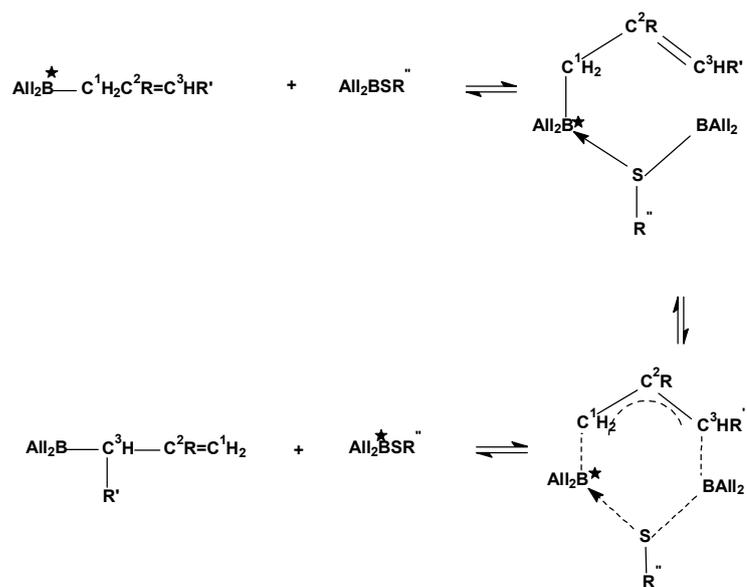
**Figure 4 s**  $^1\text{H}$  NMR spectra for (a) **2** in  $\text{C}_6\text{D}_6$ , (b) **2<sup>d</sup>** in  $\text{CD}_2\text{Cl}_2$ , (c) reaction mixture of **1<sup>d</sup>** with triallylborane in  $\text{C}_6\text{D}_6$

### Part III.

The  $^1\text{H}$  NMR spectrum of the reaction mixture taken immediately after addition of triallylborane to **1<sup>d</sup>** shows three sets of propenyl resonances the intensity ratio of which is changing during the reaction. We tentatively assign these resonances to three different intermediate complexes bearing non-coordinated propenyl ligands at the boron atom.

We describe here the signals for one of the intermediates: the doublet of quartets at 6.8 ppm with the coupling constants 17.1 and 6.35 Hz is assigned to the  $\beta$ -methyne proton, the double quartet at 6.5 ppm with the coupling constants 17.1 and 1.2 Hz is assigned to the  $\alpha$ -methyne proton, and the double doublet at 1.78 ppm with the coupling constants 6.35 and 1.2 Hz is assigned to the methyl group of the propenyl fragment. Two other propenyl intermediates have close chemical shifts of the characteristic protons described above; the coupling constant values coincide. The accurate assignment of the signals to each of three propenyl fragments was based on two-dimensional COSY experiments. The reaction was also monitored by IR spectroscopy. At the initial period of the reaction the two bands at  $1617\text{ cm}^{-1}$  and  $1634\text{ cm}^{-1}$  appear successively in the region characteristic for the carbon-carbon double bond stretch,<sup>[1a]</sup> then in the course of the reaction the first one disappears and the intensity of the second one increases. The band at  $1634\text{ cm}^{-1}$  can be tentatively assigned to  $\nu(\text{C}=\text{C})$  of the intermediate **B**, in which dipropenylborane coordinates to the cluster via the boron atom rather than through the double C=C bond since the low-frequency shift of  $\nu(\text{C}=\text{C})$  band was not observed in the spectrum.

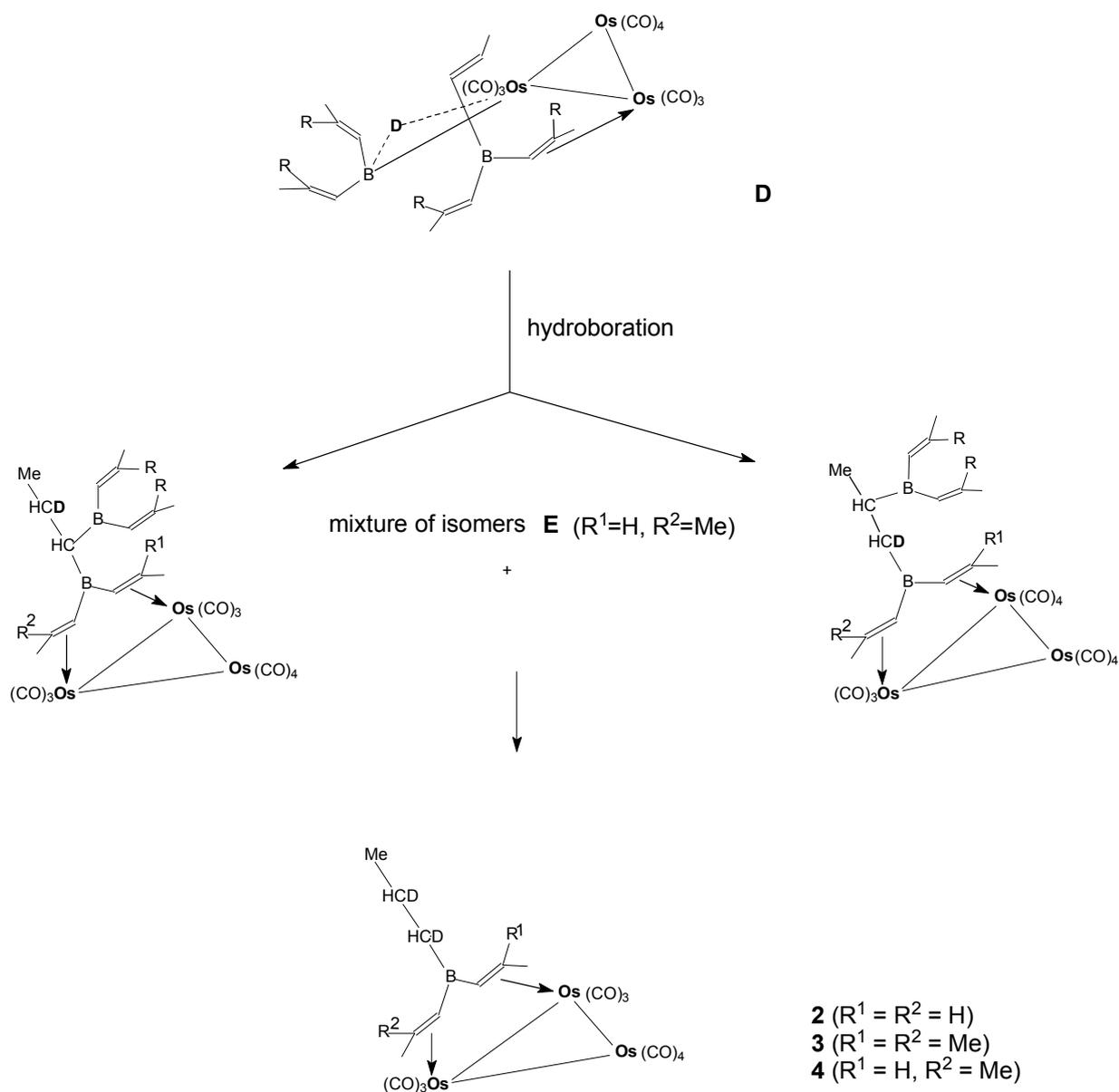
Part IV.



All - Allyl, Methallyl, Krotyl;  
 R = H, CH<sub>3</sub>; R' = H, CH<sub>3</sub>; R'' = CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>.

Scheme 2 s.

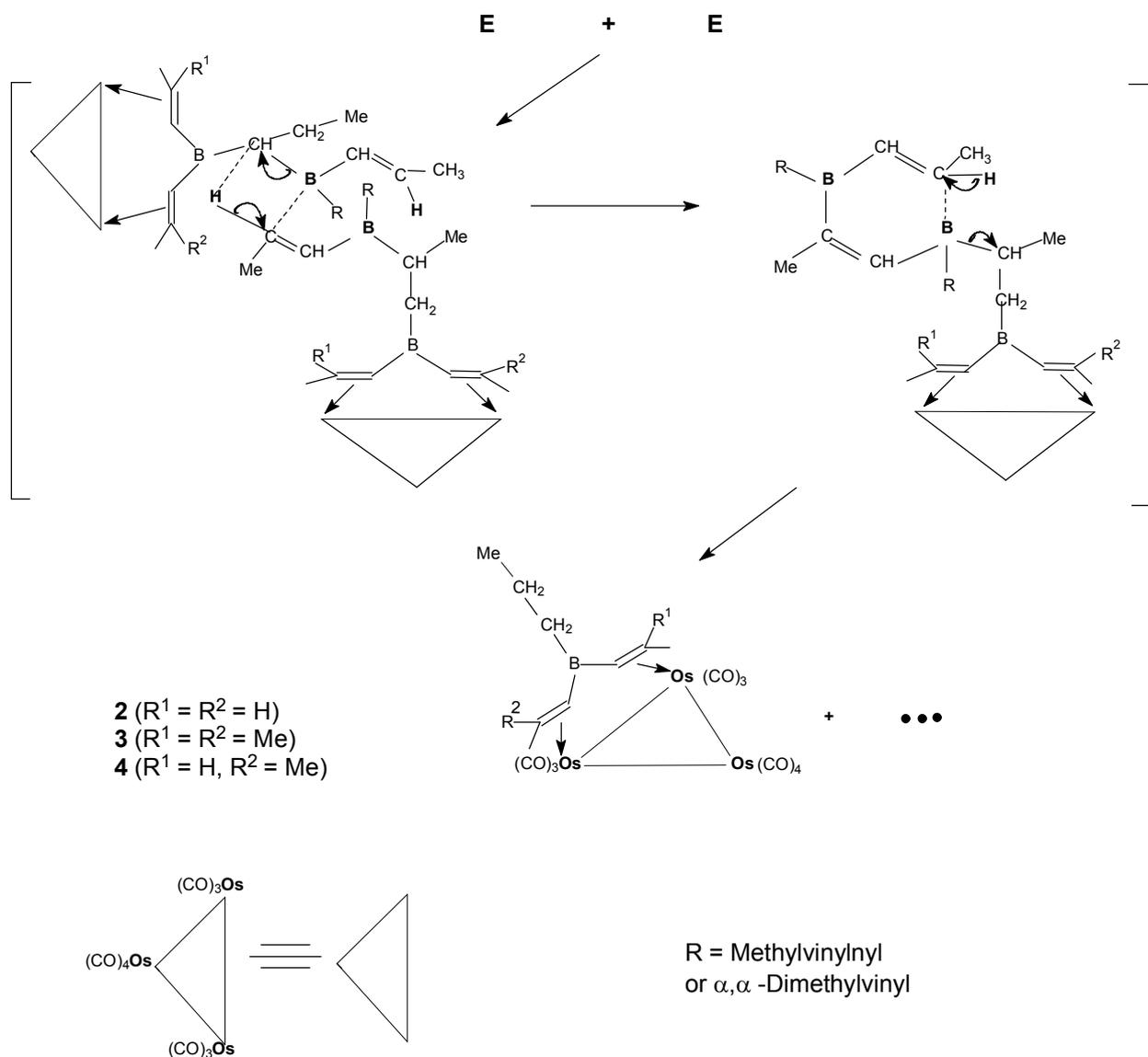
Part V.



Scheme 3 s

An intramolecular hydroboration of the non-coordinated methylvinyl fragment in **D** can occur to form  $\eta^2, \eta^2$ -intermediate **E**, the similar  $\mu$ -H structures at the M-B bond were reported.<sup>[6]</sup> We failed to obtain spectroscopic or synthetic evidences for the formation of **E** and for its further transformation into **2** (**3**, **4**) as well. Also remains unclear the source of hydrogen needed for the conversion of **E** into the reaction products **2-4**. Despite water as hydrogen source was excluded in the sealed tube reactions of **1** (**1<sup>d</sup>**) with triallylborane the formation of the propyl fragment in the

final clusters **2** (**3**, **4**) was still observed. We therefore suppose that the transformation of **E** into the final products involves an intermolecular condensation of two intermediates **E** as it shown in Scheme 4 s with the protons required taken from the boron-bonded methylvinyl groups. According to our assumption, the yield of **2** in the reaction of **1** with triallylborane only as well as the ratio of **2**, **3** and **4** in the reaction of **1** with the mixture of allylboranes ( $\text{All}_3\text{B}$  /  $\text{Methallyl}_3\text{B}$  or  $\text{All}_3\text{B}$  /  $\text{AllBPin}$ ) depend on the quantity of (free) uncoordinated boron-methylvinyl fragments in **E**. We believe that this assumption allows to explain both items.



Scheme 4 s

## Part VI.

In the  $^{11}\text{B}$  NMR spectrum the successive appearance of the signals in a region characteristic for boryl complexes<sup>[7,8]</sup> (at 71.5, 62, 48.5, and 10.5 ppm) was observed, the intensities of which gradually increase and decrease up to the complete disappearance of the signals leaving only the signals of the final products (see experimental part). At the same time in  $^1\text{H}$  NMR spectrum the high field signals at -15.46, -20.65, and -21.2 ppm appeared successively with the similar changes of their intensities. These hydride signals are weak, broadened at room temperature and narrowed by 5% upon  $^{11}\text{B}$  decoupling. Such upfield shifted signals for the bridged hydride atoms were observed in clusters having no organic ligands<sup>[9a]</sup>, having one  $\sigma,\pi$ -ligand<sup>[3]</sup>, allyl<sup>[9b,c]</sup> or more complicated ligands.<sup>[9d,e]</sup> On this basis we assign tentatively the signals  $^1\text{H}$  -15.46 ppm and  $^{11}\text{B}$  71.5 ppm to the intermediate **B**;  $^1\text{H}$  -20.65 ppm and  $^{11}\text{B}$  62 ppm to the intermediate **C**;  $^1\text{H}$  -21.2 ppm and  $^{11}\text{B}$  48.5 and 10.5 ppm to the intermediate **D**.

## References

- 1 B.M. Mikhailov,; Yu.N. Bubnov, *Organoboron Compounds in Organic Synthesis*, Harwood. Acad. Sci. Publ.: Chur, London, New York, 1984. (a) p 514, (b) idem, ibet, p 511.
- 2 J.B. Keister, J.R. Shapley, *J. Am. Chem. Soc.*, 1976, **98**, 1056-1057.
- 3 J. Lewis, B.F.J. Johnson, *Gazzetta Chimica Italiana*. 1979, **109**, 271-289.
- 4 D.V. McGrath, R.H. Grubbs, *Organometallics*, 1994, **13**, 224-235.
- 5 R.H. Crabtree, in *The Organometallic Chemistry of the Transition Metals III*, Wiley & SONS, INC.: New York, Chichester, Weinheim, Brisbane, Singapore, Toronto 2001, pp. 70, 372, 385.
- 6 (a) S. Schlecht, J.F. Hartwig, *J. Am. Chem. Soc.*, 2000, 122, 9435-9443. (b) R.T. Baker, D.W. Ovenall, J.C.J. Calabrese, *J. Am. Chem. Soc.*, 1990, 112, 9399-9400.
- 7 G.J. Irvine, M.J.G. Lesley, T.B. Marder, N.C. Norman, C.R. Rice, E.G. Robins, W.R. Roper, G.R. Whittell, L.J. Wright, *Chem. Rev.*, 1998, **98**, 2685-2721.
- 8 C.E.F. Rickard, W.R. Roper, A. Williamson, L.J. Wright, J. Wright, *Organometallics*, 2000, **19**, 4349; 2002, **21**, 4862-4872.
- 9 (a) D.H. Hamilton, J.R. Shapley, *Organometallics*, 2000, **19**, 761-769. (b) A.J. Deeming, S. Hasso, M.J. Underhill, *Organometal. Chem.*, 1974, C 53-C55; (c) B.E. Hanson, B.F.G. Jonson, J. Lewis, P.R. Raithby, *J. Chem. Soc. Dalton Trans.*, 1980, 1852-1857. (d) A.J. Deeming, M.S.B. Felix, D. Nuel, *Inorg. Chem. Acta.*, 1993, **213**, 3-10; (e) W-Y. Yeh, Y-C. Liw, S-M. Peng, G-H. Lee, *Organometallics*, 2003, **22**, 2361-2363.