SHORT PAPER

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The *s-cis* and *s-trans* π complexes of *B*-bromocatecholborane and (*E*)-2-butenal

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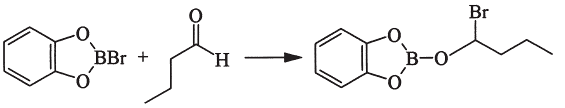
(*E*)-2-Butenal reacts with *B*-bromocatecholborane in CD_2Cl_2 at –78°C to form two species in a 1:1 ratio which does not vary between –20°C and –100°C; IR and NMR experiments (^1H–^1H COSY and ^1H–^{13}C HETCOR and ^1H–^1H ROESY [CAMELSPIN]) demonstrate that the two species are π complexes in which the aldehyde exists in *s-cis* and *s-trans* conformations which interconvent slowly (^1H–^1H EXSY NMR).

Keywords: *E*-2-butenal, *B*-bromocatecholborane, π complexes, 1-D and 2-D NMR

The interaction of π systems, cations, and anions with π systems is a topic of current interest.[1-4] Lewis acid-base complexes have also been extensively studied in recent years[5-11] because their structures are important in understanding the origin of stereoselectivities in Lewis acid-catalysed reactions. In conjunction with our studies focused on the measurement of the strength of Lewis acids both in the solid[12] and the solution[13] phase by NMR spectroscopy,[14,15] we discovered an interesting new mode of bonding between a Lewis acid and base, one involving the formation of π-complexes.

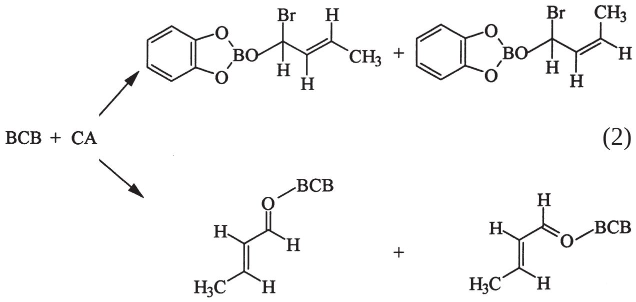
Control experiments involving the treatment of butanal (butyraldehyde; BA) with the π-electron rich *B*-bromocatecholborane (BCB) at –20° in CD_2C1_2 by ^1H NMR spectroscopy revealed that the aldehyde hydrogen had shifted upfield by more than 3 ppm, while the other resonances only shifted slightly. FTIR of a similar solution (in CH_2Cl_2 at –17°) showed that the carbonyl stretch at 1722 cm^{-1} had disappeared. These results are consistent with the B–Br bond of BCB adding across the carbonyl group of BA to give the borate shown below.



(1)

(*E*)-Butenal (crotonaldehyde; CA) behaved differently. When BCB in CD_2Cl_2 was titrated with CA at –20°, the original ^{11}B resonance for BCB at δ 28.2 was incrementally replaced by a broader resonance at δ 23.8, suggesting the formation of a single product. The ^1H NMR spectrum of a 1:1 mixture of CA and BCB in CD_2Cl_2 at –20° was obtained (Table 1) and demonstrated that more than one product formed. Unlike all other known complexes of CA with Lewis acids,[13,14] there were no downfield shifts of the four CA resonances. Instead the four resonances moved upfield dramatically and became eight multiplets. Integration of the BCB and new CA resonances suggested that two CA + BCB adducts in an approximately 1:1 ratio had been formed in the reaction. There was virtually no change in the ratio of the peak areas between –20°C and –100°C. In spite of this fact, 2D ^1H–^1H EXSY NMR proved that the CA portion of each adduct exchanged chemically with the other. When the solution was quenched with H_2O, the expected products, CA, 3-bromobutanal (the product arising from the addition of HBr to CA) and catechol were formed. Reaction of CA with *B*-chlorocatecholborane in CD_2Cl_2 yielded a similar ^1H NMR spectrum.

Analysis of the splitting patterns, relative intensities of the peaks, coupling constants and the ^1H–^1H COSY spectrum (not shown) confirmed the existence of two CA-BCB adducts. Relevant ^1H and ^{13}C NMR data of the two species, as well as those for CA and protonated CA (CAH^+), are also recorded in Table 1. There are two plausible interpretations of these data: (1) The two species are adducts similar to the one shown in Eqns. (1), and (2) the two adducts are *s-cis* and *s-trans* π complexes. Based on three lines of evidence discussed below (vibrational spectroscopy, ROESY, and Diels–Alder reaction), the two species are assigned to *s-trans* and *s-cis* π complexes of CA and BCB.



(2)

(1) One might have expected CA to react with BCB in a manner analogous to the reaction between CA and BA, but this was not the case. FTIR of the adducts in CH_2CI_2 at -18° showed, for example, that the carbonyl group had been retained (1687.7 cm^{-1} for CA; 1672.3 cm^{-1} the complexes). Raman spectroscopy revealed the absence of species with C–Br bonds. The NMR data provided still further structural information.

(2) In the *s-trans* complex, J_{12} is larger than the corresponding coupling constant in CA, as is also the case for CAH^+; this is consistent with an increase in the C_1–C_2 double bond character of the complex. However, J_{23} decreases significantly for this species, due to weakening of its C_2–C_3 double bond character. A ^1H–^1H ROESY spectrum revealed a strong H_1–H_3 through-space interaction for this complex. Neither the *s-cis* complex nor one formed from (*Z*)-2-butenal is capable of yielding such an interaction.

In the *s-cis* complex J_{12} is smaller than J_{12} in CA, which is consistent with a *cis*-like, three-bond coupling; J_{23} is also much smaller than the value observed for CA. The ^1H–^1H ROESY spectrum of this species revealed a H_2–CH_3 through-space interaction, but no H_1–H_3 interaction. This is the behaviour expected for an *s-cis* complex, but not for one containing (*Z*)-2-butenal.

The ROESY spectrum also revealed through-space interactions between the methyl group and H_3 and the BCB aromatic hydrogens for both the *s-trans* and *s-cis* complexes.

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† This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*

Table 1 NMR data for CA and its drivatives

	^1H chemical shift (J/Hz)				^{13}C chemical shift			
	CA[a,b]	CAH+[c]	*s-trans* complex[a]	*s-cis* complex[a]	CA[a]	CAH+[d]	*s-trans* complex[a,e]	*s-cis* complex[a,e]
1	9.42(8.0)	9.59(10)	7.02(11.8)	6.68(5.7)	194.0	206.1	139.7	137.2
2	6.05(8.0,15.9,1.5)	7.07(10,16)	5.82(11.8,10.0)	5.25(5.7,10.6)	134.5	130.4	119.3	117.5
3	6.88(6.9,15.9)	8.61(8,16)	4.86(6.7,10.0)	5.39(6.7,10.6)	154.9	193.2	46.7	41.4
CH_3	1.97(6 9)	2.67(8)	1.86(6.7)	1.81(6 7)	18.6	23.6	26.9	26.7

[a]This work. [b](Z)-2-butenal afforded: H_1-10.06(8.3); H_2-5.88(8.3, 11.1); H_3-6.73 (7.6, 11.1); CH_3-2.11(7.6, 1.8). [c]R.F. Childs, E.F. Lund, A.G. Marshall, W.J. Morrisey, C.V. Rogerson, *J. Am. Chem. Soc.*, 1976, **98**, 5924. [d]R.F. Childs, M. Manendran, C. Blackburn, and G. Antoniadis, *Can. J. Chem.*, 1988, **66**, 1355. [e]Assignments confirmed by a ^1H–^{13}C HETCOR.

This confirms the assumption that the upfield shifts of the ^1H and ^{13}C resonances are due to π complexation, with CH_3 and H_3 for both species sitting over the benzene ring of BCB. It was also possible to build a model of the complexes because distances can be calculated using the ROESY spectrum.[16] By assuming that the H_1–H_3 distance in the *s-trans* complex is the same as in CA, one can deduce the average distance between CH_3 and H_3 and the aromatic hydrogens for both complexes. Based on this analysis, the *s-trans* complex has the structure shown in Fig. 1. In the *s-cis* complex the methyl-benzene distance is about 3.5Å and the H_3-benzene and H_2 benzene distances are 2.3Å and 2.1Å, respectively.

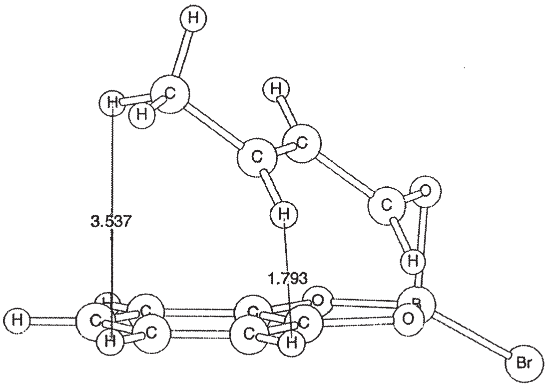

Fig. 1 *s-trans* complex

(3) Treatment of the mixture of the two complexes with 1.5 equivalents of cyclopentadiene (CP) cleanly yielded the *endo* (N) and *exo* (X) Diels-Alder adducts of CP and CA. No adducts of CP and (*Z*)-2-butenal were formed in the reaction, thus demonstrating that neither BCB complex contained (*Z*)-2-butenal. Each complex underwent the Diel–Alder reaction. If a single complex had reacted, a plot of 1n (N:X) versus 1/Temp(K) should have been linear. As one can surmise from the data below, where the N:X ratio is almost temperature independent between –78° and 24°, this is not the case. Unfortunately, it is not possible with the current data to deduce the selectivity due to each complex.

Reaction temp. (°C)	N:X
+24	79:21
–22	86:14
–78	83:17

These data nicely complement the results of Yamamoto and coworkers[17] who found that: (1) enones π complex inside the cavity of the π-electron rich, propeller-shaped Lewis acid aluminum tris(2,6-diphenylphenoxide) and (2) the complexes are *exo*-selective in reactions with CP. Other electron rich Lewis acid/enone π complexes may yield additional interesting Diels–Alder reactions.

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