The 1,5-Sigmatropic Shift of a BR_2 Unit (R = H, F, OH, NH_2, Cl, or SH) over a Cyclopentadiene System †

Wolfgang W. Schoeller
Fakultät für Chemie der Universität, Postfach 8640, D-4800 Bielefeld 1, Federal Republic of Germany

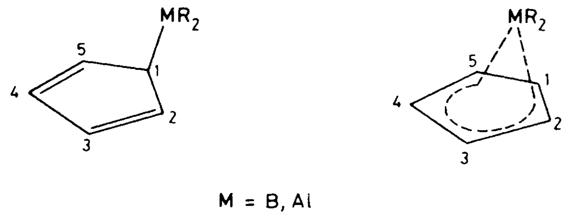
---

A molecular-orbital model supported by energy-optimized MNDO calculations is presented for the substituent effects on the rates of the 1,5-sigmatropic reaction of cyclopentadienylborane compounds. The η^2-structure represents the transition state and the σ-structure the ground state. The degenerate rearrangement is retarded with electron-donating ligands (*e.g.* amino-groups) at the boron atom and/or electron-withdrawing substituents at the C_5H_5 unit. Electron-donating substituents at the C_5H_5 unit facilitate the reaction. In the transition-state geometry, inversion over retention is favoured at the boron atom.

While the dynamics of the 1,5-sigmatropic shift (walk rearrangement) of a MR_3 fragment (R = alkyl, M = C, Si, Ge, *etc.*) over cyclopentadiene have been investigated in detail and are now well understood,‡ corresponding studies of the shift of a MR_2 unit (M = N, P, B, Al, *etc.*) are rare.[2] Recently a systematic investigation of substituent effects on the rate of migration in $PR_2(cp)$ (cp = C_5H_5) compounds was reported.[3,4]

Here, I present a complete theory for the substituent effects on the rate of degenerate rearrangement of cyclopentadienylboranes, $BR_2(cp)$ (R = H, F, OH, NH_2, Cl, or SH). Experimental studies on the fluxional behaviour of $BR_2(C_5Me_5)$ (R = Cl, Br, I, or NMe_2)[5] have been carried out and show that the rate of the (degenerate) rearrangement depends on the Lewis acidity of the boron atom. If R = NMe_2, migration of BR_2 over the cp unit proceeds above 150 °C, while for R = halogen the sigmatropic reaction occurs even below −80 °C. When the boron atom is complexed by Lewis bases (trimethylamine or pyridine) the resulting compounds do not rearrange.[6]

Investigations of the isovalent aluminium analogue, AlR_2(cp), reveal[7,8] that the σ- and η^2-structures are very close in energy. The η^2-structures are also isovalent to the extensively studied[9] bicyclo[3.1.0]hexenyl cation.



Results and Discussion

(*a*) *Qualitative Considerations.*—I begin with an analysis of bonding in the η^2-structure of $BR_2(cp)$. Following a previous study,[4] the structure can be considered as being formed by orbital interaction of a BR_2 fragment with a cp system. This is illustrated by extended Hückel § calculations (ref. 10 and subsequent publications) shown in the Figure. The cp unit (A) possesses (within local D_{5h} symmetry) the two familiar, degenerate sets of π-orbitals. The frontier orbitals of fragment (B) are similar to those of a carbene.[11] Presumably various structural alternatives are possible for the mutual interaction between the frontier orbitals of both fragments (shown below). Overlap can occur between the orbitals p [in (*a*)], $p + \sigma$ [in (*b*)], and σ [in (*c*)] with the π-orbitals at the cp unit. Formally, the various geometrical alternatives refer to a transition state in the 1,5-sigmatropic shift with retention [in (*a*)] or inversion [in (*b*)] of configuration at the migrating atom.

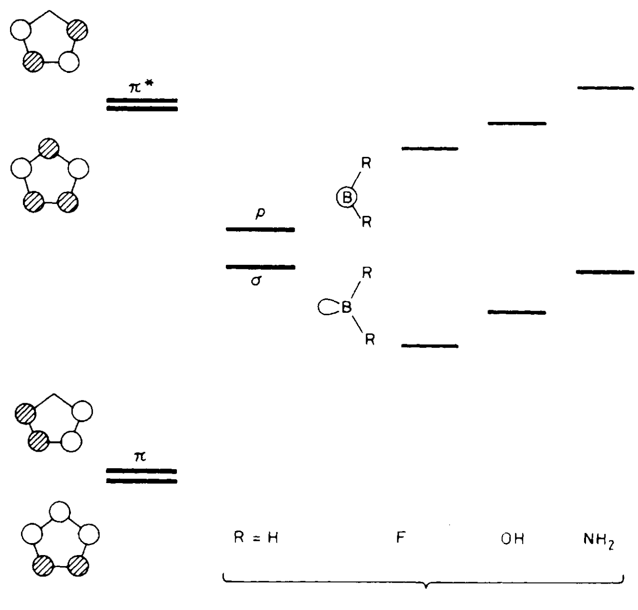
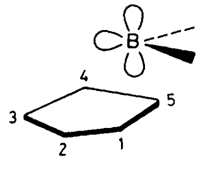
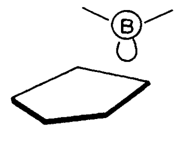


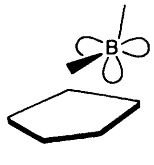
Figure. π-Orbitals of a cyclopentadiene unit (A) and frontier orbitals of BR_2 (B), extruded from extended Hückel calculations



(*a*)



(*b*)



(*c*)

Which is the most favourable of the various η^2-structures? In the degenerate rearrangement of $PR_2(cp)$, the η^2-structures

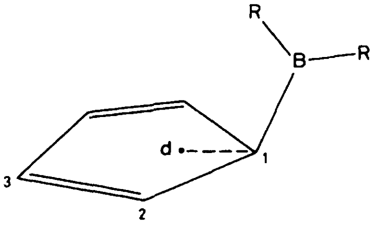
---

† *Non-S.I. unit employed:* cal = 4.184 J.

‡ For a review see ref. 1*a*,*b*; for theoretical treatments of sigmatropic shifts of alkyl (silyl) groups in cp see ref. 1*c*—*g*.

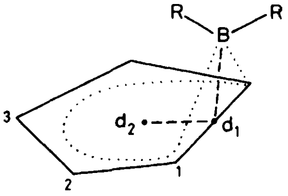
§ Valence ionization potentials are chosen according to J. Hinze and H. H. Jaffé (*J. Chem. Phys.*, 1963, **38**, 1834) and Slater exponents according to J. C. Slater (*Phys. Rev.*, 1930, **36**, 57).

Table 1. Bonding parameters (bond lengths in Å, bond angles in degrees) for the σ-structures. All parameters are optimized with respect to C_s symmetry. The upper values (first entries) correspond to inversion and the lower values (second entries) to retention of configuration at boron with respect to the walk reaction



R	B–C(1)	C(1)–C(2)	C(2)–C(3)	B–R	B–C(1)–d	R–B–R	ΔH_f/kcal mol^{-1}
H	1.555	1.528	1.363	1.160	127.6	117.7	40.13
	1.549	1.526	1.362	1.160	135.4	117.7	39.43
F	1.597	1.528	1.362	1.321	129.9	113.0	−142.45
	1.595	1.527	1.361	1.321	133.6	112.8	−142.35
OH	1.602	1.528	1.363	1.364	131.0	111.1	−123.78
	1.602	1.528	1.362	1.364	134.5	110.2	−122.33
NH_2	1.593	1.528	1.528	1.412	131.6	118.4	−12.75
	1.594	1.530	1.362	1.414	134.9	117.2	−10.77
Cl	1.568	1.529	1.362	1.775	129.6	115.4	−26.78
	1.565	1.528	1.361	1.777	134.6	114.6	−26.31
SH	1.575	1.526	1.362	1.713	131.6	111.2	4.90
	1.576	1.530	1.361	1.717	136.1	108.6	7.31

Table 2. Bonding parameters (bond lengths in Å, bond angles in degrees) for the η^2-structures (C_s symmetry imposed). First entries correspond to inversion and second entries to retention of configuration



R	B–C(1)	C(1)–C(2)	C(2)–C(3)	B–R	B–d_1–d_2	R–B–R	ΔH_f/kcal mol^{-1}
H	1.666	1.448	1.415	1.164	111.0	117.4	57.39
	1.805	1.434	1.413	1.169	110.9	113.0	90.81
F	1.751	1.442	1.414	1.334	113.2	112.5	−108.77
	1.943	1.427	1.416	1.323	109.6	110.4	−84.35
OH	1.800	1.436	1.414	1.372	113.7	110.6	−86.00
	1.943	1.430	1.414	1.363	109.7	108.4	−66.44
NH_2	1.793	1.436	1.413	1.423	114.3	117.4	26.90
	1.914	1.433	1.414	1.417	110.0	115.1	45.46
Cl	1.672	1.451	1.414	1.809	114.5	112.5	−3.49
	1.843	1.432	1.415	1.799	110.5	108.8	27.18
SH	1.706	1.444	1.414	1.746	115.5	106.9	35.63
	1.849	1.434	1.414	1.734	110.9	103.0	61.74

of type (*a*) and (*b*) are close in energy. In the case discussed here, (*b*) (inversion of configuration at the migrating boron atom) is expected to predominate over the alternatives (*a*) and (*c*), because orbital symmetry controls[12,*] the reaction. Structure (*c*) is disfavoured compared to (*b*), since in the latter the *p* orbital [at (B)] overlaps together with the π-orbitals [at (A)]. As will be shown in the following section, this orbital interaction determines the rate of the degenerate 1,5-sigmatropic reaction.

(*b*) *Numerical Evaluation of Ground- and Transition-state Geometries.*—The results obtained from the energy-optimized MNDO[13] calculations are now presented. Initially BR_2(cp) (parent) (R = H, F, OH, NH_2, Cl, or SH) is discussed. The ligands R model the whole variety of possible substituents at boron. The most important bonding parameters obtained from the SCF calculations are collected in Table 1 for the σ-structures and in Table 2 for the η^2 counterparts. For all cases, during the optimization C_s symmetry was assumed. The two stereochemical alternatives, inversion or retention of configuration at boron were also considered. For a given substituent these refer to the first and second entries in the Tables.

The calculated σ-structures show that the rotational barriers around the B–C bond are negligible and independent of the substituent R. Their magnitudes are equal to the differences in heats of formation between the two entries of

---

[*] Structure (*b*) refers to the transition state with inversion of configuration at the migrating atom.

Table 3. Activation enthalpies (kcal mol^{-1}) for BR$_2$(cp) and other various substituted-cyclopentadienyl systems, determined from energy-optimized MNDO calculations. For the computations C_s symmetry was imposed on the ground- and transition-state geometries, and inversion of configuration at boron. The bond lengths B–C(5) (Å) for the transition-state geometries are given in parentheses

System	C_5H_5	C_5Me_5	C_5F_5	C_5Cl_5
R = H	18.0	16.5	19.7	25.8
	(1.67)	(1.68)	(1.68)	(1.68)
F	33.6	31.8	37.5	38.8
	(1.75)	(1.78)	(1.81)	(1.79)
OH	36.3	30.5	39.8	39.4
	(1.80)	(1.84)	(1.91)	(1.86)
NH_2	37.8	30.6	40.7	39.8
	(1.79)	(1.83)	(1.88)	(1.83)
Cl	22.9	18.9		
	(1.67)	(1.68)		
SH	28.3	18.7	32.1	31.5
	(1.71)	(1.73)	(1.76)	(1.74)

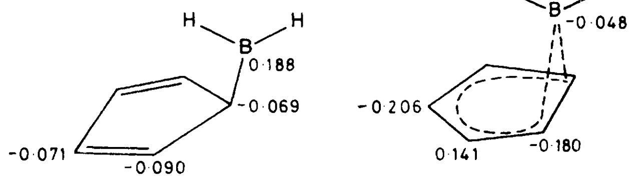
Table 1. For all R, the σ-structures are more stable than their η^2 counterparts. The boron adopts a planar (sp^2) conformation.

On the contrary for the η^2-structures the rotational barriers around the B–C bond are rather sizeable. Structures with inversion of configuration at boron are always favoured (see Table 2, first *versus* second entries). The structures (*b*) are always more strongly bonded compared to (*c*). The alternative structure (*a*) has also been examined: independent of the chosen substituent R it is not a stable entity on the electronic hypersurface, but rearranges to (*c*).

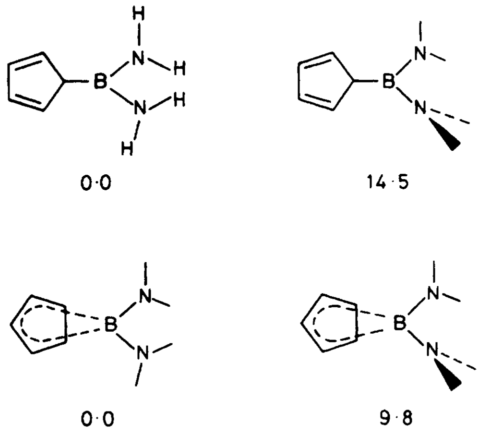
So far considerations have been restricted to an analysis of substituents at boron. In addition therefore, the electron demand of the cp system was varied, *i.e.* by introducing various substituents (CH$_3$, F, or Cl) into the ring. The energy barriers thus obtained are collected in Table 3.

In contrast to the corresponding PR$_2$(cp) compounds,[4] in the transition state geometries (η^2-structures) the B–C(1) [B–C(5) rsp.] bond lengths do not vary with the substituent attached to boron. The overall barriers for the 1,5-sigmatropic reaction increase with increasing ability of the ligand R to donate electrons towards the electron-deficient boron atom.[*] Electron-withdrawing substituents (*e.g.* F or Cl) in the cp unit raise, and electron-donating substituents (*e.g.* CH$_3$) lower, the overall reaction enthalpies.

The transition state (η^2-structure, R = H) is polarized as shown below. According to MNDO calculation, valence charge density accumulates at the boron atom and depletes in the 2- and 4-positions of the cp ring. On this basis, a structural candidate for a 'frozen in' η^2-structure, *i.e.*, the transition state being more stable than the ground state (σ-structure) requires a cp unit substituted by π-donors (*e.g.* methoxy) and alkyl groups for the ligands R. In other words, in this electronic arrangement the electron deficit at boron is compensated for predominantly by the electron-rich cp unit.



Finally the rotational barriers (E_{rel}/kcal mol^{-1}) around the bond axis, B–ligand(R), with R = NH$_2$ as a representative example, are shown below. The barrier for rotation of only one amino-group is large in the σ-structure and comparable with those measured in aminoboranes.[14] In the η^2-structure rotation is easier, and this tendency is also seen in the lengthening of the B–N bonds.



Conclusions

The results can be summarized as follows. (*i*) The 1,5-sigmatropic rearrangement of cyclopentadienylboranes can be analyzed as a BR$_2$ fragment interacting with a cp fragment. (*ii*) The σ-structure is lower in energy than the η^2-structure, with the latter as a transition state in the degenerate rearrangement. Its stability depends on the ability of the cp unit as well as the ligands R to donate electrons to the empty *p*-orbital at the (electron-deficient) boron atom, In this respect, it resembles classical electron-deficient compounds, such as B$_2$H$_6$.[15] Theoretical findings are in complete accord with the recent experimental investigations on a variety of pentamethylcyclopentadienylboranes.[5] (*iii*) In all cases studied here, inversion over retention is favoured at the boron atom, in accordance with the qualitative expectations of the Woodward–Hoffmann rules.[12] These findings are in contrast to the transition states in the degenerate rearrangement of the corresponding cyclopentadienylphosphanes.[4]

Finally it should be noted that the conclusions have been reached by semi-empirical SCF calculations which are open to criticism regarding their numerical accuracy.[16] Hence the predications of the numerical calculations must be considered as semi-quantitative. The predictions of the qualitative trends are correct and in complete accord with the experimental investigations.

Acknowledgements

This work was supported by the Fonds der Chemischen Industrie and the Deutsche Forschungsgemeinschaft. The computer time was generously provided by the Rechenzentrum der Universität Bielefeld. I also thank Professor Jutzi for helpful discussions.

---

[*] In fact the energy barriers for a given system (*e.g.* parent cp) parallel the Hammett σ_m values (S. Ehrenson, R. T. C. Brownlee, and R. W. Taft, *Prog. Phys. Org. Chem.*, 1973, **10**, 1) for the ligands R. A quantitative assessment of ligand π-donation towards boron is given in the important work of H. Nöth and B. Wrackmeyer, *Chem. Ber.*, 1974, **107**, 3070, 3089.

References

1 (*a*) N. M. Sergeyev, *Prog. Nucl. Magn. Reson. Spectrosc.*, 1973, **9**, 71; (*b*) V. A. Mironov, E. V. Sobolev, and A. N. Elizarova, *Tetrahedron*, 1963, **19**, 1939; (*c*) J. R. de Dobbelaere, J. M. F. van Dijk, J. W. de Haan, and H. M. Buck, *J. Am. Chem. Soc.*, 1977, **99**, 392; (*d*) M. J. S. Dewar, *Chem. Br.*, 1975, **11**, 97; (*e*) N. T. Anh, M. Elian, and R. Hoffmann, *J. Am. Chem. Soc.*, 1978, **100**, 110; (*f*) G. A. Shchembelov and Yu. A. Ustynyuk, *ibid.*, 1974, **96**, 4189; (*g*) S. Cradock, R. H. Findlay, and M. H. Palmer, *J. Chem. Soc., Dalton Trans.*, 1974, 1650.

2 P. Jutzi, *Nachr. Chem. Tech. Lab.*, 1978, **26**, 422.

3 P. Jutzi and H. Saleske, *Chem. Ber.*, 1984, **117**, 222.

4 W. W. Schoeller, *Z. Naturforsch., Teil B*, 1983, **38**, 1635.

5 P. Jutzi and A. Seufert, *Chem. Ber.*, 1979, **112**, 2481; P. Jutzi and A. Seufert, *Angew. Chem.*, 1977, **89**, 339; *Angew. Chem., Int. Ed. Engl.*, 1977, **16**, 330; H. Grundke and P.1. Paetzold, *Chem. Ber.*, 1971, **104**, 1136.

6 H. D. Johnson, T. W. Hartford, and C. W. Spangler, *J. Chem. Soc., Chem. Commun.*, 1978, 242.

7 A. Haaland and J. Weidlein, *J. Organomet. Chem.*, 1972, **40**, 29; D. A. Drew and A. Haaland, *Acta Chem. Scand.*, 1973, **27**, 3735; O. Gropen and A. Haaland, *J. Organomet. Chem.*, 1975, **92**, 157; P. R. Schonberg, R. T. Paine, and C. F. Campana, *J. Am. Chem. Soc.*, 1979, **101**, 7726.

8 See also, N. Giannini and S. Cesca, *Gazz. Chim. Ital.*, 1961, **91**, 597; W. R. Kroll and W. Naegele, *Chem. Commun.*, 1969, 246; W. R. Kroll, J. R. McDivitt, and W. Naegele, *Inorg. Nucl. Chem. Lett.*, 1969, **5**, 973; J. Stadelhofer, J. Weidlein, and A. Haaland, *J. Organomet. Chem.*, 1975, **84**, C1; J. Stadelhofer, J. Weidlein, P. Fischer, and A. Haaland, *ibid.*, 1976, **116**, 55.

9 R. F. Childs and S. Winstein, *J. Am. Chem. Soc.*, 1968, **90**, 7146; P. Vogel, M. Saunders, N. M. Hasty, jun., and J. A. Berson, *ibid.*, 1971, **93**, 1551; W. J. Hehre, *ibid.*, 1974, **96**, 5207.

10 R. Hoffmann, *J. Chem. Phys.*, 1963, **39**, 1397.

11 W. W. Schoeller, *Tetrahedron Lett.*, 1980, 1505; W. W. Schoeller, *Angew. Chem.*, 1981, **93**, 685; *Angew. Chem. Int. Ed. Engl.*, 1981, **20**, 698.

12 R. B. Woodward and R. Hoffmann, *Angew. Chem.*, 1969, **81**, 797; 'The Conservation of Orbital Symmetry,' Verlag Chemie, Weinheim, 1970.

13 M. J. S. Dewar, M. L. McKee, and H. S. Rzepa, *J. Am. Chem. Soc.*, 1978, **100**, 3607 and refs. therein.

14 K. N. Scott and W. S. Brey, jun., *Inorg. Chem.*, 1969, **8**, 1703; R. H. Neilson and R. L. Wells, *ibid.*, 1977, **16**, 7.

15 H. C. Longuet-Higgins, *J. Chem. Soc.*, 1943, 250; E. Switkes, R. M. Stevens, W. N. Lipscomb, and M. D. Newton, *J. Chem. Phys.*, 1969, **51**, 2085; R. J. Buenker, S. D. Peyerimhoff, L. C. Allen, and J. L. Whitten, *J. Chem. Phys.*, 1966, **45**, 2835; W. Kutzelnigg, 'Einführung in die Theoretische Chemie,' Verlag Chemie, Weinheim, 1978, vol. 2.

16 M. V. Basilevsky, *Adv. Chem. Phys.*, 1975, **33**, 345; J. A. Pople, *J. Am. Chem. Soc.*, 1975, **97**, 5306; M. J. S. Dewar, *ibid.*, p. 6591.

Received 3rd October 1983; *Paper* 3/1748