

# **Borabenzene Derivatives of Main Group Elements**

Von der Fakultät für Mathematik, Informatik und Naturwissenschaften  
– Fachbereich 1 –  
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zur Erlangung des akademischen Grades eines Doktors  
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- (3) X. Zheng, U. Englert, G. E. Herberich, J. Rosenplänter, *Inorg. Chem.* **2000**, *39*, 5579–5585.
- (4) X. Zheng, G. E. Herberich, *Organometallics* **2001**, *20*, im Druck.
- (5) X. Zheng, G. E. Herberich, *Eur. J. Inorg. Chem.* **2001**, eingereicht.

Meiner Familie

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## Abbreviation

|                    |                                                          |                 |                                                |
|--------------------|----------------------------------------------------------|-----------------|------------------------------------------------|
| bipy               | 2,2'-bipyridine                                          | Me              | methyl                                         |
| br                 | broad (NMR)                                              | mp              | melting point                                  |
| Bu <sup>n</sup>    | normal butyl                                             | $M_w$           | molecular weight                               |
| Bu <sup>t</sup>    | tert-butyl                                               | MS              | mass spectroscopy                              |
| Cp                 | cyclopentadienyl                                         | $m/z$           | mass-to-charge ratio (MS)                      |
| Cp*                | 1,2,3,4,5-pentamethyl-<br>cyclopentadienyl               | $\mu$           | absorption coefficient (X-ray)                 |
| $\delta$           | chemical shift (NMR)                                     | NMR             | nuclear magnetic resonance                     |
| D                  | Debye                                                    | $\nu$           | resonance frequency (NMR)                      |
| d                  | doublet (NMR)                                            | Nu              | nucleophile                                    |
| $d_{\text{calcd}}$ | calculated density (X-ray)                               | Ph              | phenyl                                         |
| DFT                | density functional theory                                | Pr <sup>i</sup> | isopropyl                                      |
| DMSO               | dimethylsulfoxide                                        | py              | pyridine                                       |
| Et                 | ethyl                                                    | R               | discrepancy indices (X-ray)                    |
| GOF                | goodness of fit (X-ray)                                  | $R^2$           | correlation coefficient                        |
| $h$                | Planck's constant                                        | $R/S$           | absolute configuration of a<br>chiral molecule |
| HOMO               | highest occupied molecular<br>orbital                    | $r_i$           | ionic radius                                   |
| Hz                 | Hertz                                                    | rt              | room temperature                               |
| $I_{\text{rel}}$   | relative intensity (MS)                                  | $\sigma$        | shielding (NMR)                                |
| K                  | Kelvin                                                   | s               | singlet (NMR)                                  |
| $k$                | first-order rate constant (NMR)                          | $T$             | temperature                                    |
| $\kappa$           | transmission coefficient in<br>the Eyring equation (NMR) | t               | triplet (NMR)                                  |
| $K_B$              | Boltzmann's constant                                     | THF             | tetrahydrofuran                                |
| $J$                | scalar nuclear spin-spin cou-<br>pling constant (NMR)    | THP             | tetrahydropyran                                |
| $\lambda$          | wave length                                              | $T_c$           | coalescence temperature                        |
| LDA                | lithium diisopropylamide                                 | TMEDA           | $N,N,N',N'$ -tetramethyl-<br>ethylenediamine   |
| LUMO               | lowest unoccupied molecular<br>orbital                   | $V$             | volume of unit cell (X-ray)                    |
| m                  | multiplet (NMR)                                          | $\omega$        | interplanar angle                              |
|                    |                                                          | Z               | formula units per unit cell<br>(X-ray)         |
|                    |                                                          | 6 <sub>1</sub>  | six-fold screw axis                            |