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C₅H₄BR₂ Bending in Ferrocenylboranes: A Delocalized Through-Space Interaction Between Iron and Boron

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Supporting Information

Calibration for Molecular Structures and Binding Energies

The reliability of a variety of density functional approaches to correctly describe donor-acceptor bonding situations involving boron Lewis acids and nitrogen Lewis bases has been questioned recently.^[1] As the DMAP complexes investigated in this study involve this bonding motif we deemed a careful calibration for the present class of systems particularly important. As a first benchmark, calculated structures at selected levels of theory are compared with X-ray crystallographic results. Due to the lack of experimental calorimetric data for the present class of compounds, we take for four representative boron-nitrogen donor/acceptor complexes accurate binding energies computed at post-HF levels of theory as an exacting testing ground to benchmark the density functional approaches in the description of binding energies. We tested several functionals in combination with two different basis sets with respect to the quality of structure predictions by comparison with X-ray crystal structure analyses. Apart from our general interest to learn about advantages and shortcomings of contemporary implementations of Kohn-Sham methods,^[2] this comparison aims at an identification of a reliable, yet computationally efficient approach to describe structures of borylated ferrocenes.

Several systematic trends become obvious from the data compiled in Tables 1-7. Most notably, for **2** and **3** use of the very small DGA1 fit basis in RI calculations results in optimized structures exhibiting a strong pyramidalization of the BR₂ groups (cf. Tables 2 and 3, torsion angles γ^* , δ , and δ'). Independent of the GGA employed, use of the DGA1 fit basis results in deviations of these angles by about 20° with respect to the experimental structure, which exhibits an essentially planar BBr₂ group. Also the calculated B–Br bond lengths are significantly elongated exceeding the averaged experimental value by 0.099 Å to 0.122 Å. All other computations employing either the pure (non-RI) GGAs or both hybrid functionals, result in only minor deviations from experiment (cf. Table 2). Remarkably, BP86/TZVP(RI) geometry optimizations on **2** and **3** using the TZVP-J Coulomb fit basis of Ahlrichs and coworkers^[3] for all atoms within the Turbomole program yields geometries identical to the non-RI BP86/TZVP results. Thus, the pronounced deviations found in Gaussian RI calculations on **2** and **3** can clearly be identified as a problem in the atomic DGA1 fit basis for Br. In the following we nevertheless report Gaussian RI results obtained with the DGA1 fit basis to document the performance of this approach.

A statistical analysis of the data compiled in Tables 1-7 reveals additional, although less spectacular effects on optimized geometries introduced by the DGA1 fit basis. For example the Fe–X and the Fe–C_{ipso} distances become significantly shorter on average by 0.027 and 0.023 Å, respectively. Hence, it appears as if in addition to interactions with the bromine atoms, also the rather remote interaction between the iron atom and the Cp rings are error-prone due to use of the DGA1 fit basis. The B–C bond as well as the angles α^* , β^* , and γ^* in turn are hardly affected at all by the RI procedure.

When going from the SVP to the TZVP basis, the Fe–X and Fe–C_{ipso} bond lengths are elongated on average by 0.011 or 0.006 Å, respectively, whereas the B–C_{ipso} bond length becomes shorter on average by –0.008 Å. By the same token, α^* becomes smaller on average by merely –1.4°. Other geometry parameters are hardly affected at all. These trends are nearly independent of the method used and also the choice of the DGA1 fit basis in RI computations has no appreciable influence. Hence, general effects of the one-particle basis are somewhat less pronounced.

From a comparison of computed and experimental data for key geometry parameters (Fe–C_{ipso}, B–C_{ipso}, and α^* , cf. Table 8) we can draw the following conclusions: a) Judged from the mean absolute deviations, an excellent description of the Fe–C_{ipso} bond length is found for the BP86 and the HCTH functional in combination with both, the SVP and the TZVP basis sets. Use of the DGA1 fit basis increases the mean deviations significantly and is therefore discouraged. The hybrid functionals B98 and B3LYP tend to overestimate the Fe–C_{ipso} bond length. b) All methods show particularly large deviations for the B–C_{ipso} bond length in **2**. The experimentally determined B–C_{ipso} bond length of **2** (average value 1.479 Å) is significantly shorter than the corresponding length in all other derivatives investigated here (average value 1.544 ± 0.02 Å). In contrast, all theoretically obtained B–C_{ipso} bond lengths for **1-4**, fall within the range of 1.517 Å and 1.563 Å. Therefore we tend to attribute the poor agreement between experiment and theory for **2** to artifacts of the crystal structure analysis. Excluding this species from the comparison results in a significantly improved overall agreement between experiment and theory and we find an excellent performance for all functionals in combination with the TZVP basis set. c) For the present study the accurate description of the dip angle α^* is crucial. From the data compiled in Table 8 we note that this parameter is generally underestimated. Again errors are most pronounced for **2**. As the bending potential for changes of α^* by 5° to 10° about the minimum structure is evidently very shallow (less than 1 kcal mol⁻¹, see below), crystal packing effects might account for the observed deviations in the comparison between experiment and theoretical data.

Finally we note inconsistencies for some method/basis set combinations between the optimized geometries of the **4**•DMAP donor/acceptor complex and the experimentally determined structure. Although the experimental geometry, which shows a perpendicular orientation ($\varepsilon = 87^\circ$, cf. Table 7) of the DMAP ring with respect to the B–C_{ipso} bond, was used as a starting point for all calculations, geometry optimizations at the BP86/TZVP, HCTH/SVP, B3LYP/SVP, and B3LYP/TZVP levels of theory led to a rotation of the DMAP subunit about the B–N bond (by $\varepsilon = 180^\circ$, 136° , 178° , and 180° , respectively). At all other levels both, the perpendicular and the collinear conformer were found. However, the collinear conformer was determined to be more stable than the perpendicular conformer (between 0.1 and 1.3 kcal mol⁻¹). Other geometry parameters, such as the bond angle ζ or the B–N bond length, are almost independent of the orientation of the DMAP ring. We compare in Table 7 the geometries of the perpendicular conformer with experiment where possible. Given the negligible energy difference between the two conformers identified, it appears justified to use the collinear conformer for comparison for those method/basis set combinations not suitable to locate the perpendicular conformer identified experimentally.

Compared to the experimental structure all optimized geometries of **4**•DMAP show too long B–N bonds (+0.031 Å on average). This trend is significantly more pronounced if the DGA1 fit basis is used but quite independent of the one-particle basis set quality. In line with the findings of Gilbert,^[1] we find a superior performance of the pure BP86 and the B98 hybrid compared to the B3LYP functional, irrespective of the basis set quality employed. The HCTH GGA suffers from errors even larger than those observed in the B3LYP structures.

Table 9 shows the computed binding energies (total energy differences) and optimized B–N bond lengths for the donor-acceptor complexes BH₃•NH₃, BH₃•pyridine, BMe₃•NH₃, and BMe₃•pyridine. For BH₃•NH₃ we performed CCSD(T) geometry optimizations employing Dunning's correlation consistent cc-pVDZ, cc-pVTZ, and cc-pVQZ basis sets. At the extrapolated basis set limit (cf. Experimental Section and Computational Details below) we obtain a binding energy of 31.7 kcal mol⁻¹, which serves as the highest level benchmark for this complex. These calculations were feasible only for the BH₃•NH₃ complex due to the extraordinary computational scaling of CCSD(T) calculations with system and basis set size. We also performed geometry optimizations at the RIMP2 level in combination with the same set of Dunning bases, and at the extrapolated basis set limit we obtain a binding energy of 32.3 kcal mol⁻¹, which is in pleasing agreement with the CCSD(T) value. This computationally efficient approach could be used to investigate also the larger complexes BH₃•pyridine, BMe₃•NH₃, and BMe₃•pyridine. As a third post-HF approach we employed the CBS-QB3

extrapolation scheme, which yields a binding energy of 31.8 kcal mol⁻¹ for the BH₃•NH₃ complex in almost perfect agreement with the CCSD(T) extrapolated basis set limit. The binding energies of BH₃•NH₃, BH₃•pyridine, BMe₃•NH₃, and BMe₃•pyridine obtained at the RIMP2 basis set limit and by CBS-QB3 calculations agree within 2 kcal mol⁻¹ (Table 9). Although the CBS-QB3 scheme relies on the use of B3LYP geometries, which are evidently of inferior quality at least for the larger complexes (compared to RIMP2/cc-pVQZ geometries, differences in the B–N bond length amount to up to 0.043 Å for BMe₃•pyridine), we note a fair overall agreement between both methods in the evaluation of binding energies (within 2 kcal mol⁻¹). Apparently, the B–N stretching potential is so weak that too long B–N distances lead to only minor consequences for computed binding energies within the CBS-QB3 scheme. In any case, in the present context we tend to consider the RIMP2 data generally more reliable to describe bonding in this class of donor-acceptor complexes, and in the following we use the RIMP2 extrapolated basis set limit data to assess the performance of the various density functionals employed.

The benchmark computations reveal that pyridine forms stronger bonds to monoboranes than NH₃ (to BH₃ by 4.2 kcal mol⁻¹ and to BMe₃ by 3.1 kcal mol⁻¹). Thus, in agreement with chemical intuition (e.g., pK_B(NH₃) = 9.25; pK_B(Pyridine) = 5.21), we find that pyridine is a stronger Lewis base than NH₃. When going from BH₃ to BMe₃, in turn, the computed binding energies drop significantly (NH₃: -13.2 kcal mol⁻¹ and pyridine: -14.3 kcal mol⁻¹ at the RIMP2 basis set limit), illustrating the weaker Lewis acidity of BMe₃ as compared to BH₃.

For the BH₃•NH₃ adduct, all density functionals investigated yield binding energies in fair agreement with the post-HF benchmarks if used in combination with the TZVP basis set: the largest differences occur for the HCTH and the B3LYP functional, which both underestimate the binding energy by about 2 kcal mol⁻¹. Use of the smaller SVP basis constantly increases the computed binding energies by about 5 kcal/mol, which can probably be attributed to significant basis set superposition errors. Use of the DGA1 Coulomb fit basis has a negligible influence on computed binding energies. The stronger binding of pyridine to BH₃ is reproduced at all density functional levels with the TZVP basis, but compared to the benchmark data, the increase in bond strength is substantially underestimated. With the SVP basis all functionals yield essentially identical binding energies for both complexes. B–N bond strengths in BMe₃ complexes are severely underestimated at all density functional levels and, even worse, the stronger binding of pyridine as compared to NH₃ documented in all benchmark calculations is not reproduced. This is a verification of the findings of Gilbert, who identified severe shortcomings of various flavours of DFT in the description of binding energies in this class of donor-acceptor complexes, with more pronounced

problems the larger the degree of alkyl substitution.^[1] We therefore attribute the discrepancies in the optimized geometries of the **4**•DMAP complexes noted above to a pronounced tendency of all functionals investigated to underestimate B–N bond strengths. It is interesting to note that in particular the highly parameterized HCTH functional suffers most from these problems, but also the otherwise highly successful B3LYP hybrid functional fails dramatically. While the origins of these problems evade an unequivocal interpretation and deserve an in-depth investigation of its own right, we conclude for the present study that we should moderate our expectations with respect to the accuracy of the current functionals to describe B–N bonding situations.

References

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Table 1: Comparison of selected geometry parameters for computed and experimental structures of ferrocene (distances in Å).

	BP86		BP86		HCTH		HCTH		B98		B3LYP		Exp ^a
	SVP/DGA1	SVP	TZVP/DGA1	TZVP	SVP/DGA1	SVP	TZVP/DGA1	TZVP	SVP	TZVP	SVP	TZVP	
Fe-X1 ^b	1.668	1.641	1.679	1.655	1.651	1.620	1.659	1.632	1.674	1.687	1.681	1.694	1.660
Fe-C	2.071	2.048	2.077	2.057	2.051	2.026	2.055	2.033	2.070	2.079	2.074	2.083	2.064
Imag. Freq.	i34	i20	i19	–	i48	i54	i43	i39	–	–	i34	i19	–

^a Experimental data taken from Xu et al.^[115] ^b Distance between the iron atoms and the geometric center of the Cp carbon skeleton

Table 2: Comparison of selected geometry parameters for computed structures of FeBH₂ (1) (distances in Å, angles and torsion angles in °).

	BP86		BP86		HCTH		HCTH		B98		B3LYP	
	SVP/DGA1	SVP	TZVP/DGA1	TZVP	SVP/DGA1	SVP	TZVP/DGA1	TZVP	SVP	TZVP	SVP	TZVP
α^* ^a	25.0	27.3	23.7	26.5	20.1	22.0	18.0	20.1	20.4	18.9	16.8	15.7
β^* ^b	3.4	4.0	3.2	3.7	3.6	4.0	3.4	3.7	2.5	2.4	2.5	2.5
Fe-X1	1.667	1.644	1.678	1.657	1.651	1.627	1.659	1.638	1.679	1.691	1.683	1.697
Fe-X2	1.683	1.656	1.693	1.669	1.666	1.636	1.674	1.647	1.680	1.694	1.687	1.701
Fe-C _{ipso} ^c	2.047	2.030	2.054	2.038	2.040	2.022	2.047	2.032	2.057	2.066	2.064	2.074
Fe-C' _{ipso} ^c	2.095	2.078	2.099	2.085	2.077	2.056	2.081	2.062	2.084	2.093	2.089	2.097
B-C _{ipso}	1.532	1.531	1.524	1.524	1.530	1.528	1.523	1.522	1.526	1.520	1.523	1.517
B-H	1.225	1.220	1.211	1.206	1.222	1.217	1.208	1.203	1.210	1.197	1.209	1.195
γ^* ^d	1.1	2.0	0.7	1.8	-0.3	0.1	0.0	0.1	-0.8	-0.3	-0.4	-0.4
Imag. Freq.	–	–	–	–	–	–	–	–	i6	–	–	–

^a Bending angle defined as $180^\circ - \alpha(X1-C_{ipso}-B)$ ^b Bending angle defined as $180^\circ - \beta(X1-Fe-X2)$ ^c C_{ipso} is the borylated carbon atom in the substituted Cp ring, C'_{ipso} is the corresponding carbon atom of the unsubstituted Cp ring. ^d Non-planarity of the boryl substituent group defined as $180^\circ - \gamma(C_{ipso}-B-H-H')$

Table 3: Comparison of selected geometry parameters for computed structures of FcBBr_2 (**2**) (distances in Å, angles and torsion angles in °).

	BP86		BP86		HCTH		HCTH		B98		B3LYP		Exp ^f		
	SVP/DGA1	SVP	TZVP/DGA1	TZVP	SVP/DGA1	SVP	TZVP/DGA1	TZVP	SVP	TZVP	SVP	TZVP	A	B	Mean
$\alpha^{* a, g}$	12.1	13.5	9.8	11.4	9.5	8.9	7.3	7.5	10.3	8.9	7.9	6.7	17.8	19.0	18.4
$\beta^{* b}$	4.0	2.8	3.5	2.7	4.2	2.9	3.6	2.7	1.96	1.8	2.0	1.9	4.7	4.1	4.4
Fe-X1	1.667	1.645	1.678	1.658	1.651	1.626	1.659	1.637	1.677	1.692	1.684	1.698	1.644	1.642	1.643
Fe-X2	1.682	1.651	1.692	1.665	1.665	1.631	1.672	1.643	1.679	1.692	1.685	1.698	1.655	1.651	1.653
Fe-C _{ipso} ^c	2.073	2.050	2.076	2.060	2.060	2.039	2.059	2.045	2.067	2.077	2.075	2.083	2.025	2.033	2.029
Fe-C' _{ipso} ^c	2.094	2.068	2.097	2.075	2.076	2.046	2.077	2.052	2.080	2.087	2.082	2.090	2.053	2.054	2.054
B-C _{ipso}	1.540	1.531	1.531	1.523	1.544	1.535	1.535	1.526	1.527	1.519	1.526	1.517	1.484	1.473	1.479
B-Br	2.044	1.943	2.053	1.946	2.033	1.930	2.046	1.936	1.934	1.938	1.936	1.940	1.947	1.921	1.934
B-Br'	2.044	1.943	2.053	1.946	2.033	1.930	2.046	1.936	1.934	1.938	1.936	1.940	1.916	1.946	1.931
$\gamma^{* d, g}$	-23.7	1.7	-22.7	2.0	-23.4	1.1	-22.8	1.3	0.7	1.0	0.9	1.3	1.8	3.3	2.6
$\delta^{e, g}$	4.6	-11.1	5.8	-9.7	6.3	-7.5	7.8	-6.6	-8.1	-7.4	-6.7	-5.9	-18.5	-14.5	-16.5
$\delta'^{e, g}$	-4.6	11.1	-5.8	9.7	-6.3	7.5	-7.8	6.6	8.3	7.4	6.7	5.9	9.1	17.3	13.2
Imag.															
Freq.	-	-	-	-	-	-	-	-	i22	i7	-	-	-	-	-

^a Bending angle defined as $180^\circ - \alpha(X1-C_{ipso}-B)$ ^b Bending angle defined as $180^\circ - \beta(X1-Fe-X2)$ ^c C_{ipso} is the borolated carbon atom in the substituted Cp ring, C'_{ipso} is the corresponding carbon atom of the unsubstituted Cp ring ^d Non-planarity of the boryl substituent group defined as $180^\circ - \gamma(C_{ipso}-B-Br)$ ^e Torsion angle δ defined as $\delta(Br-B-C_{ipso}-C2)$ and $\delta'(Br'-B-C_{ipso}-C'2)$ ^f Two independent molecules per unit cell exist in the crystal structure ^g A positive sign indicates that the boron atom / substituents are pyramidalized / bent towards the iron center

Table 4: Comparison of selected geometry parameters for computed structures of FeB(Me)Br (**3**) (distances in Å, angles and torsion angles in °).

	BP86			BP86			HCTH			HCTH			B98			B3LYP			Exp ^f
	SVP/DGA1	SVP	TZVP	TZVP/DGA1	TZVP	SVP/DGA1	SVP	TZVP/DGA1	SVP	TZVP	TZVP/DGA1	SVP	TZVP	SVP	TZVP	SVP	TZVP		
α^* ^a	12.0	14.0	9.5	9.5	12.0	9.1	9.9	6.6	6.6	8.6	10.1	9.3	7.3	8.0	7.3	13.7			
β^* ^b	3.3	2.8	3.0	3.0	2.8	3.4	2.7	3.0	3.0	2.8	2.0	2.1	2.1	2.1	2.1	1.8			
Fe-X1	1.668	1.645	1.679	1.679	1.658	1.652	1.628	1.660	1.660	1.637	1.681	1.691	1.697	1.687	1.697	1.650			
Fe-X2	1.683	1.651	1.693	1.693	1.664	1.667	1.631	1.673	1.673	1.641	1.681	1.692	1.698	1.688	1.698	1.661			
Fe-C _{ipso} ^c	2.075	2.051	2.081	2.081	2.061	2.065	2.038	2.067	2.067	2.050	2.072	2.078	2.084	2.079	2.084	2.035			
Fe-C' _{ipso} ^c	2.095	2.067	2.099	2.099	2.074	2.076	2.044	2.078	2.078	2.045	2.079	2.087	2.090	2.081	2.090	2.052			
B-C _{ipso}	1.543	1.539	1.533	1.533	1.532	1.546	1.542	1.536	1.536	1.534	1.536	1.528	1.526	1.534	1.526	1.530			
B-Br	2.118	1.971	2.133	2.133	1.979	2.103	1.958	2.127	2.127	1.968	1.962	1.970	1.974	1.965	1.974	(1.739)			
B-C(Me)	1.571	1.575	1.564	1.564	1.570	1.569	1.573	1.561	1.561	1.568	1.572	1.567	1.565	1.570	1.565	(1.869)			
γ^* ^d	5.6	2.9	4.2	4.2	2.8	4.4	1.9	3.1	3.1	1.3	1.4	1.5	1.6	1.2	1.6	(11.0)			
δ^e	-21.5	-13.5	-20.5	-20.5	-10.6	-20.1	-9.3	-19.1	-19.1	-6.2	-9.6	-7.8	-6.1	-6.8	-6.1	(-8.2)			
δ'^e	-8.61	10.5	-9.3	-9.3	10.3	11.1	7.9	-12.4	-12.4	8.3	7.2	7.8	6.8	6.6	6.8	(21.4)			
Imag.																			
Freq.	-	-	-	-	-	-	-	-	-	-	i22	i7	-	-	-	-			

^a Bending angle defined as $180^\circ - \alpha(X1-C_{ipso}-B)$ ^b Bending angle defined as $180^\circ - \beta(X1-Fe-X2)$ ^c C_{ipso} is the borylated carbon atom in the substituted Cp ring, C'_{ipso} is the corresponding carbon atom of the unsubstituted Cp ring ^d Non-planarity of the boryl substituent group defined as $180^\circ - \gamma(C_{ipso}-B-Br-C(Me))$ ^e torsion angle δ defined as $\delta(C(Me)-B-C_{ipso}-C2)$ and $\delta'(Br-B-C_{ipso}-C'2)$ ^f Experimental data in parentheses indicate a disordered region in the X-ray structure.

Table 5: Comparison of selected geometry parameters for computed structures of FcBMe₂ (**4**) (distances in Å, angles and torsion angles in °).

	BP86		BP86		HCTH		HCTH		B98		B3LYP		Exp
	SVP/DGA1	SVP	TZVP/DGA1	TZVP	SVP/DGA1	SVP	TZVP/DGA1	TZVP	SVP	TZVP	SVP	TZVP	
α^* ^a	11.8	14.8	9.4	12.1	8.7	10.0	7.3	8.0	10.5	8.4	8.8	6.9	13.0
β^* ^b	2.4	2.4	2.4	2.2	2.5	2.4	2.4	2.2	1.8	1.7	1.8	1.8	1.8
Fe-X1	1.669	1.645	1.680	1.658	1.652	1.626	1.661	1.637	1.677	1.690	1.683	1.697	1.651
Fe-X2	1.680	1.650	1.690	1.663	1.663	1.629	1.670	1.640	1.678	1.692	1.685	1.699	1.656
Fe-C _{ipso} ^c	2.075	2.052	2.085	2.063	2.062	2.040	2.068	2.048	2.073	2.083	2.079	2.089	2.043
Fe-C' _{ipso} ^c	2.087	2.066	2.091	2.073	2.067	2.043	2.070	2.048	2.078	2.086	2.082	2.090	2.063
B-C _{ipso}	1.560	1.555	1.552	1.550	1.563	1.558	1.556	1.553	1.553	1.547	1.551	1.545	1.545
B-C(Me)	1.592	1.590	1.586	1.586	1.590	1.586	1.584	1.582	1.586	1.583	1.584	1.580	1.578
B-C'(Me)	1.590	1.590	1.587	1.586	1.585	1.585	1.583	1.582	1.586	1.583	1.584	1.580	1.571
γ^* ^d	1.9	4.4	1.7	3.7	0.0	2.3	0.5	1.8	1.6	1.6	2.0	1.8	1.9
δ ^e	-11.8	-13.3	-6.2	-10.4	-3.6	-8.0	-4.6	-6.3	-7.0	-5.6	-5.8	-4.4	-9.6
δ' ^e	8.0	13.8	10.0	11.4	10.0	9.5	7.3	7.8	10.5	8.9	9.5	8.0	11.3
Imag.	-	-	-	-	-	-	-	-	-	-	-	-	-
Freq.	-	-	-	-	-	-	-	-	i22	-	-	-	-

^a Bending angle defined as $180^\circ - \alpha(X1-C_{ipso}-B)$ ^b Bending angle defined as $180^\circ - \beta(X1-Fe-X2)$ ^c C_{ipso} is the borolated carbon atom in the substituted Cp ring, C'_{ipso} is the corresponding carbon atom of the unsubstituted Cp ring ^d Non-planarity of the boryl substituent group defined as $180^\circ - \gamma(C_{ipso}-B-C'(Me))$ ^e torsion angle δ defined as $\delta(C(Me)-B-C_{ipso}-C2)$ and $\delta'(C'(Me)-B-C_{ipso}-C'2)$

Table 6: Comparison of selected geometry parameters for computed structures of FcBMe(OH) (5) (distances in Å, angles and torsion angles in °).

	BP86		BP86		HCTH		HCTH		B98		B3LYP		Exp ^f		
	SVP/DGA1	SVP	TZVP/DGA1	TZVP	SVP/DGA1	SVP	TZVP/DGA1	TZVP	SVP	TZVP	SVP	TZVP	A	B	Mean
α^* ^a	6.3	7.3	5.5	5.2	5.5	6.0	4.7	5.2	5.9	5.1	4.7	3.8	10.9	10.3	10.6
β^* ^b	1.4	1.3	1.6	1.4	1.5	1.4	1.6	1.4	0.8	1.1	0.9	1.2	1.9	0.1	1.0
Fe-X1	1.670	1.645	1.680	1.636	1.654	1.624	1.660	1.636	1.678	1.690	1.686	1.697	1.648	1.654	1.651
Fe-X2	1.679	1.648	1.687	1.638	1.663	1.626	1.668	1.638	1.679	1.690	1.686	1.697	1.649	1.654	1.652
Fe-C _{ipso} ^c	2.082	2.061	2.088	2.048	2.065	2.042	2.068	2.048	2.079	2.085	2.085	2.090	2.048	2.047	2.048
Fe-C' _{ipso} ^c	2.082	2.057	2.088	2.043	2.063	2.036	2.066	2.043	2.075	2.084	2.079	2.088	2.043	2.049	2.046
B-C _{ipso}	1.566	1.561	1.556	1.554	1.566	1.562	1.558	1.554	1.559	1.551	1.557	1.548	1.548	1.547	1.548
B-C(Me)	1.378	1.380	1.386	1.382	1.372	1.374	1.381	1.382	1.368	1.375	1.368	1.377	1.370	1.379	1.375
B-O	1.592	1.591	1.587	1.583	1.589	1.588	1.584	1.583	1.588	1.584	1.586	1.581	1.569	1.566	1.568
γ^* ^d	0.7	1.8	1.3	1.9	0.2	1.2	0.6	1.9	1.2	2.1	1.2	2.3	-0.6	0.3	-0.2
δ^e	-4.9	-6.1	-4.5	-4.3	-3.9	-4.3	-3.2	-4.3	-5.2	-4.7	-5.0	-4.3	5.9	-8.8	-1.5
δ'^e	5.8	6.9	5.5	5.7	5.0	6.1	4.8	5.7	5.0	5.1	3.4	3.9	21.3	6.8	13.8
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^a Bending angle defined as $180^\circ - \alpha(X1-C_{ipso}-B)$ ^b Bending angle defined as $180^\circ - \beta(X1-Fe-X2)$ ^c C_{ipso} is the borylated carbon atom in the substituted Cp ring, C'_{ipso} is the corresponding carbon atom of the unsubstituted Cp ring ^d Non-planarity of the boryl substituent group defined as $180^\circ - \gamma(C_{ipso}-B-O-C(Me))$ ^e torsion angle δ defined as $\delta(C(Me)-B-C_{ipso}-C2)$ and $\delta'(O-B-C_{ipso}-C'2)$ ^f Three independent molecules per unit cell exist in the crystal structure; data are given for two conformers, in which the OH group is oriented syn to the methyl group.

Table 7: Comparison of geometry parameters for computed structures of the $\text{FcBMe}_2\bullet\text{DMAP}$ adduct (**4•DMAP**) (distances in Å, angles and torsion angles in °).

	BP86		BP86		HCTH		HCTH		B98		B3LYP		Exp
	SVP/DGA1	SVP	TZVP/DGA1	TZVP	SVP/DGA1	TZVP	SVP/DGA1	TZVP	SVP	TZVP	SVP	TZVP	
α^* ^a	2.0	3.4	2.9	2.0	2.9	2.0	3.9	5.1	2.9	3.4	1.6	-2.3	1.1
β^* ^b	1.2	0.6	0.9	0.2	1.4	1.2	1.9	0.8	1.6	0.5	0.5	0.3	1.1
Fe-X1	1.668	1.644	1.680	1.654	1.651	1.628	1.659	1.635	1.677	1.689	1.682	1.693	1.649
Fe-X2	1.676	1.643	1.687	1.657	1.662	1.626	1.668	1.635	1.677	1.691	1.684	1.698	1.648
Fe-C _{ipso} ^c	2.106	2.082	2.112	2.089	2.089	2.075	2.094	2.073	2.108	2.114	2.110	2.114	2.083
Fe-C' _{ipso} ^c	2.083	2.052	2.087	2.059	2.066	2.034	2.067	2.039	2.077	2.085	2.079	2.086	2.036
B-C _{ipso}	1.637	1.631	1.630	1.621	1.640	1.633	1.633	1.628	1.629	1.623	1.623	1.618	1.625
B-C(Me)	1.636	1.634	1.632	1.635	1.634	1.634	1.631	1.629	1.633	1.629	1.632	1.629	1.619
B-C(Me)	1.636	1.634	1.632	1.635	1.634	1.629	1.631	1.629	1.633	1.629	1.632	1.629	1.622
B-N	1.698	1.684	1.700	1.684	1.729	1.708	1.729	1.712	1.685	1.687	1.697	1.699	1.670
γ^* ^d	49.6	49.5	49.2	49.8	48.4	49.0	48.1	48.4	49.9	49.7	49.7	49.4	51.1
δ ^e	26.9	27.9	27.5	26.4	27.3	40.7	28.0	29.2	28.1	30.8	19.8	26.4	25.5
δ' ^e	-26.9	-28.0	-27.5	-26.5	-27.3	-15.1	-28.0	-29.0	-28.1	-25.6	-3.2	26.4	-27.5
ε ^f	87.4	87.2	87.4	180.0	87.5	135.8	87.7	87.6	88.6	90.9	177.5	180.0	87.3
ζ ^g	102.4	102.1	102.0	105.8	101.5	103.6	101.4	101.8	102.7	102.9	105.8	105.7	102.7
BDE ^h	14.8	14.3	11.2	11.2	9.8	10.2	6.2	5.9	15.3	11.8	(13.7)	(9.8)	
	(15.9)	(15.3)	(12.4)	(12.1)	(10.5)	(10.1)	(7.0)	(6.7)	(16.5)	(13.1)	(13.7)	(9.8)	

^a Bending angle defined as $180^\circ - \alpha(\text{X1-C}_{\text{ipso}}\text{-B})$ ^b Bending angle defined as $180^\circ - \beta(\text{X1-Fe-X2})$ ^c C_{ipso} is the borylated carbon atom in the substituted Cp ring, C'_{ipso} is the corresponding carbon atom of the unsubstituted Cp ring ^d Non-planarity of the boryl substituent group defined as $180^\circ - \gamma(\text{C}_{\text{ipso}}\text{-B-C}(\text{Me}))$ ^e torsion angle δ defined as $\delta(\text{C}(\text{Me})\text{-B-C-C2})$ and $\delta'(\text{C}(\text{Me})\text{-B-C-C'2})$ ^f Torsion angle of the pyridyl group in DMAP defined as $\varepsilon(\text{C}(\text{Py})\text{-N}(\text{Py})\text{-B-C}_{\text{ipso}})$ ^g Bond angle $\zeta(\text{N}(\text{Py})\text{-B-C}_{\text{ipso}})$. ^h Binding energy D_e (total energy differences in kcal mol⁻¹) of DMAP to **4**. Data given in parentheses relate to the collinear conformer (see text).

Table 8: Deviations from experiment (calculated data – experimental data, distances in Å, angles and torsion angles in °)

	BP		BP		HCTH		HCTH		B98		B3LYP	
	SVP/DGA 1	SVP	TZVP/DGA 1	TZVP	SVP/DGA 1	SVP	TZVP/DGA1	TZVP	SVP	TZVP	SVP	TZVP
Fe-C _{ipso}												
Ferrocene	0.007	-0.016	0.013	-0.007	-0.013	-0.038	-0.009	-0.031	0.014	0.027	0.021	0.034
2	0.042	0.018	0.045	0.026	0.027	0.001	0.027	0.007	0.032	0.041	0.037	0.045
3	0.042	0.016	0.047	0.024	0.027	-0.003	0.029	0.004	0.032	0.039	0.037	0.043
4	0.028	0.006	0.035	0.015	0.011	-0.012	0.016	-0.005	0.022	0.031	0.027	0.036
5	0.035	0.012	0.041	-0.001	0.017	-0.008	0.020	-0.001	0.030	0.038	0.035	0.042
4•DMAP	0.035	0.012	0.040	0.015	0.018	-0.005	0.021	-0.004	0.033	0.040	0.035	0.040
Mean	0.032	0.008	0.037	0.012	0.015	-0.011	0.017	-0.005	0.027	0.036	0.032	0.040
B-C _{ipso}												
2	0.062	0.053	0.053	0.045	0.066	0.057	0.057	0.048	0.049	0.041	0.048	0.039
3	0.013	0.009	0.003	0.002	0.016	0.012	0.006	0.004	0.006	-0.002	0.004	-0.004
4	0.015	0.010	0.007	0.005	0.018	0.013	0.011	0.008	0.008	0.002	0.006	0.000
5	0.019	0.014	0.009	0.007	0.019	0.015	0.011	0.007	0.012	0.004	0.010	0.001
4•DMAP	0.012	0.006	0.005	-0.004	0.015	0.008	0.008	0.003	0.004	-0.002	-0.002	-0.007
Mean ^a	0.024	0.018	0.015	0.011	0.027	0.021	0.019	0.014	0.016	0.009	0.013	0.006
	(0.015)	(0.010)	(0.006)	(0.003)	(0.017)	(0.012)	(0.009)	(0.006)	(0.008)	(0.001)	(0.005)	(0.003)
α^*												
2	-6.3	-4.9	-8.6	-7.0	-8.9	-9.5	-11.1	-10.9	-8.1	-9.5	-10.5	-11.7
3	-1.7	0.3	-4.2	-1.7	-4.7	-3.8	-7.1	-5.1	-3.6	-4.5	-5.7	-6.4
4	-1.2	1.9	-3.6	-0.9	-4.3	-2.9	-5.7	-5.0	-2.5	-4.5	-4.2	-6.1
5	-4.2	-3.3	-5.1	-5.3	-5.1	-4.6	-5.9	-5.3	-4.7	-5.5	-5.9	-6.8
Mean	-3.4	-1.5	-5.4	-3.7	-5.8	-5.2	-7.5	-6.6	-4.7	-6.0	-6.6	-7.8

^a Values in parentheses obtained excluding data for 2.

Table 9: Computed binding energies at various levels of density functional theory for the neutral donor-acceptor complexes $\text{BH}_3\bullet\text{NH}_3$, $\text{BH}_3\bullet\text{Pyridine}$, $\text{BMe}_3\bullet\text{NH}_3$, and $\text{BMe}_3\bullet\text{Pyridine}$ (total energy differences given in kcal mol⁻¹).

Method/Basis	$\text{BH}_3\bullet\text{NH}_3$	R(B-N)	$\text{BH}_3\bullet\text{py}$	R(B-N)	$\text{B}(\text{CH}_3)_3\bullet\text{NH}_3$	R(B-N)	$\text{B}(\text{CH}_3)_3\bullet\text{py}$	R(B-N)
BP86/SVP/DGA1	39.2	1.649	39.2	1.610	21.1	1.685	15.2	1.699
BP86/SVP	39.0	1.652	38.9	1.603	19.3	1.691	15.3	1.673
BP86/TZVP/DGA1	34.3	1.659	36.1	1.613	15.7	1.696	12.2	1.690
BP86/TZVP	33.8	1.664	35.8	1.607	14.3	1.702	12.3	1.677
HCTH/SVP/DGA1	35.4	1.650	34.4	1.618	17.4	1.692	9.5	1.724
HCTH/SVP	35.3	1.654	34.2	1.610	15.5	1.692	9.6	1.702
HCTH/TZVP/DGA1	30.4	1.663	31.0	1.623	12.1	1.704	6.5	1.723
HCTH/TZVP	30.0	1.666	30.7	1.615	10.6	1.711	6.5	1.703
B98/SVP	37.6	1.647	36.9	1.612	19.5	1.684	15.2	1.684
B98/TZVP	32.4	1.658	33.7	1.616	14.6	1.695	12.2	1.685
B3LYP/SVP	35.9	1.653	35.1	1.616	17.4	1.696	12.8	1.695
B3LYP/TZVP	30.2	1.665	31.6	1.622	11.9	1.710	9.3	1.700
RIMP2/cc-pVDZ	35.7	1.657	35.9	1.635	23.9	1.680	22.6	1.685
RIMP2/cc-pVTZ	33.9	1.650	37.1	1.620	21.0	1.674	23.3	1.663
RIMP2/cc-pVQZ	32.9	1.646	36.8	1.616	19.9	1.669	22.7	1.659
RIMP2 limit (DTQ) ^b	32.3		36.5		19.1		22.2	
CBS-QB3	31.8	1.664 ^a	35.6	1.621 ^a	18.5	1.704 ^a	20.8	1.702 ^a
CCSD(T)/cc-pVDZ	35.5	1.664						
CCSD(T)/cc-pVTZ	33.7	1.655						
CCSD(T)/cc-pVQZ	32.5	1.650						
CCSD(T) limit (DTQ) ^b	31.7							

^a B3LYP/6-311G** geometry is used in the CBS-QB3 scheme. ^b Extrapolated basis set limit (see text).