DOI: 10.1002/ejic.201101098

Cyclic Phosphonium Bis(fluoroaryl)boranes – Trends in Lewis Acidities and Application in Diels–Alder Catalysis

Anna Schnurr,[a] Michael Bolte,[a] Hans-Wolfram Lerner,[a] and Matthias Wagner*[a]

Keywords: Boron / Homogeneous catalysis / Lewis acids / Perfluoroarenes / Phosphorus

The rigid cyclic Lewis acids $[(C_6F_5)B(CH_2)(C_6F_4)P(t\mathrm{Bu})_2]^+$ ([**1**]$^+$), $[(C_6F_5)B(CH_2)(C_6F_3H)P(t\mathrm{Bu})_2]^+$ ([**2**]$^+$), and $[(C_6H_5)B(CH_2)(C_6F_4)P(t\mathrm{Bu})_2]^+$ ([**3**]$^+$), possess Gutmann acceptor numbers of AN = 87.3, 85.7, and 85.7, respectively, which are among the highest for organoboranes. Starting from (**1**)OTf, adducts [(**1**)Do][OTf] (Do = $OPEt_3$, pyridine, H_2O) have been prepared and fully characterized. In all three cases, X-ray crystallography revealed significantly shorter B–O/N bond lengths than those in the corresponding adducts $(C_6F_5)_3B{\cdot}$Do. Both the free Lewis acid [**1**][Al(O(tBu^F))$_4$] and its triflate adduct (**1**)OTf have successfully been employed as catalysts for the [4+2] cycloaddition reaction between 2,5-dimethyl-1,4-benzoquinone and cyclopentadiene. Moreover, we have shown that chiral phosphonium boranes are accessible by replacement of one tBu group in [**1**]$^+$ by a Me substituent {cf. [**4**]$^+$ = $[(C_6F_5)B(CH_2)(C_6F_4)P(\mathrm{Me})(t\mathrm{Bu})]^+$}.

Introduction

Lewis acidic arylboranes find applications as homogeneous (co)catalysts[1–6] and anion sensors.[7–10] The use of perfluorinated aryl substituents or the incorporation of a positive charge into the molecular framework are tools to optimize the Lewis acid strength for any given task.[11–20] The reinforcing effect of a positive charge on the adduct bond of an anionic Lewis base is merely of an electrostatic nature and therefore distance-dependent. Thus, in order to guarantee a stabilizing effect that is invariable in time, a rigid molecular framework is required so that the distance between the boron atom and the cationic center always remains the same.

Following this concept, we have recently prepared cyclic phosphonium boranes [**A**][WCA] (Figure 1). Because of their high Lewis acidity, the free boranes are only existent in combination with the extremely weakly coordinating anion [WCA]$^-$ = [Al(O(tBu^F))$_4$]$^-$.[21,22] In this paper, we report on the quantitative trend in the Lewis acidities of these compounds as a function of the degree of fluorination at the exocyclic phenyl substituent (i.e., R^1 = C_6F_5, C_6H_5) or the phenylene bridge (i.e., R^2 = F, H). Moreover, we compare the performance of the free acid [**A**][WCA] (R^1 = C_6F_5, R^2 = F, R^3 = tBu) and its corresponding triflate adduct (**A**)OTf[21] as Diels–Alder catalysts, and we explore whether chiral Lewis acids can be generated by variation of the substituent R^3 at the phosphorus atom.

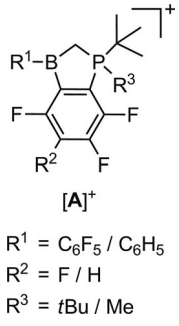
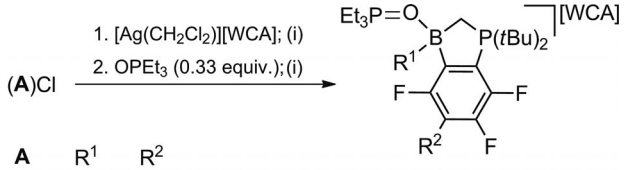


Figure 1. General structural motif of the cationic phosphonium boranes investigated in this work.

Results and Discussion

Assessment of the Lewis Acidities of [A]$^+$-Type Compounds by NMR Spectroscopic Methods

For Lewis acidity determinations by the Gutmann–Beckett method[23–25] we used a protocol similar to that described by Stephan et al.[15a] (Scheme 1): First, the free



A	R^1	R^2
1	C_6F_5	F
2	C_6F_5	H
3	C_6H_5	F

[(**A**)OPEt$_3$][WCA]

[WCA] = [Al(O(tBu^F))$_4$]

Scheme 1. Preparation of cationic phosphonium boranes [**A**][WCA] (**A** = **1**, **2**, **3**) from their corresponding chloro adducts (**A**)Cl and subsequent addition of $OPEt_3$ for Lewis acidity determination by the Gutmann–Beckett method. (i) CD_2Cl_2, room temp., 2 min.

[a] Institut für Anorganische und Analytische Chemie, Goethe-Universität Frankfurt,
Max-von-Laue-Strasse 7, 60438 Frankfurt (Main), Germany
Fax: +49-69-798-29260
E-mail: Matthias.Wagner@chemie.uni-frankfurt.de

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejic.201101098.

Lewis acids $[\mathbf{1}]^+$, $[\mathbf{2}]^+$, and $[\mathbf{3}]^+$ were liberated from their corresponding chloro adducts (**1**)Cl,[21] (**2**)Cl, and (**3**)Cl[21] by addition of $[Ag(CH_2Cl_2)][WCA]$.[26] A substoichiometric amount of $OPEt_3$ was added, and the $^{31}P\{^1H\}$ NMR spectrum was recorded in CD_2Cl_2 to determine the Gutmann acceptor number (AN; Table 1).

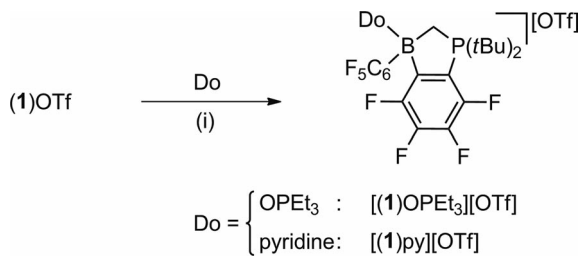
Table 1. $^{31}P\{^1H\}$ NMR chemical shift values of $OPEt_3$ in the Lewis acid–base adducts [(**1**)$OPEt_3$][WCA], [(**2**)$OPEt_3$][WCA], and [(**3**)$OPEt_3$][WCA]. Gutmann acceptor numbers (AN) of the Lewis acids [**1**][WCA], [**2**][WCA], and [**3**][WCA].

Boron-containing Lewis acid	$\delta(^{31}P\{^1H\})$ [ppm][a] $OPEt_3$	AN[b]
None	50.5	21.0[c]
$(C_6F_5)_3B$	77.1[d]	80.0
[**1**][WCA]	80.4	87.3
[**2**][WCA]	79.7	85.7
[**3**][WCA]	79.7	85.7

[a] CD_2Cl_2, 27 °C. [b] $AN = [\delta(^{31}P\{^1H\})_{sample} - 41.0] \times [100/(86.14 - 41.0)]$.[24] [c] $AN(CH_2Cl_2)$ according to our own measurement; literature value: $AN(CH_2Cl_2) = 20.4$.[23] [d] Our own measurement; literature value: $\delta(^{31}P\{^1H\}, CD_2Cl_2) = 78.1$.[15b]

All three phosphonium borane derivatives possess a higher acceptor number (AN = 87.3, 85.7, 85.7, respectively) than the neutral molecule $(C_6F_5)_3B$ (AN = 80.0) and even the phosphonium borane $[(C_6F_5)_2B–(p\text{-}C_6F_4)–P(H)(t\text{Bu})_2]^+$ (AN = 80.2).[15a] The less exhaustively fluorinated species $[\mathbf{2}]^+$ and $[\mathbf{3}]^+$ are slightly weaker Lewis acids than $[\mathbf{1}]^+$ {Δ(AN) = 1.6}. Somewhat surprisingly, replacement of *one* F atom on the phenylene bridge (cf. $[\mathbf{2}]^+$) appears to have a similar effect on the acceptor number than substitution of all *five* F atoms for H atoms on the exocyclic phenyl ring in $[\mathbf{3}]^+$ (this result has been reproduced twice).

The $^{31}P\{^1H\}$ NMR chemical shift value of $OPEt_3$ in its Lewis acid–base adducts is influenced by the position of the association/dissociation equilibrium. In order to obtain data of a sample consisting exclusively of an adduct, we prepared [(**1**)$OPEt_3$][OTf] from the triflate (**1**)OTf[21] (Scheme 2) and measured its $^{31}P\{^1H\}$ NMR spectrum in the solid state (see the Supporting Information for a plot of the spectrum). The chemical shift values of 86.1 ppm (BCH_2P) and 79.9 ppm ($OPEt_3$) deviate by a maximum of 1.1 ppm from those obtained for [(**1**)$OPEt_3$][OTf] {85.2 ppm (BCH_2P), 80.9 ppm ($OPEt_3$)} and [(**1**)$OPEt_3$][WCA] {85.0 ppm (BCH_2P), 80.4 ppm ($OPEt_3$)} in CD_2Cl_2 solution. Since the $OPEt_3$ phosphorus atom of [(**1**)$OPEt_3$][OTf] is *less* shielded in solution than in the solid state, we



Scheme 2. Substitution of the triflate ligand in (**1**)OTf by uncharged donors Do. (i) CH_2Cl_2, room temp., 12 h.

conclude that the solution equilibrium contains essentially no uncoordinated $OPEt_3$.

[(**1**)$OPEt_3$][OTf] crystallizes with two crystallographically independent molecules in the asymmetric unit {[(**1**)$OPEt_3$][OTf], [(**1**)$OPEt_3$][OTf]^A}, of which only [(**1**)$OPEt_3$][OTf] is discussed further (Figure 2).

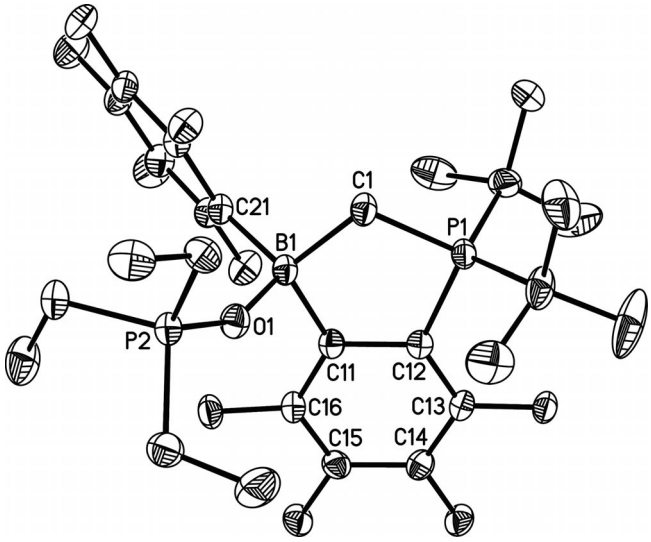


Figure 2. Molecular structure and numbering scheme of the cation of compound [(**1**)$OPEt_3$][OTf]. Displacement ellipsoids are drawn at the 30% probability level; H atoms have been omitted for clarity. Selected bond lengths [Å], bond angles [°], and torsion angles [°]: O(1)–P(2) 1.526(3), B(1)–O(1) 1.523(5), B(1)–C(1) 1.656(6), B(1)–C(11) 1.623(6), B(1)–C(21) 1.643(6), P(1)–C(1) 1.803(4), P(1)–C(12) 1.809(4); B(1)–O(1)–P(2) 152.7(3), B(1)–C(1)–P(1) 107.5(3), C(1)–B(1)–C(11) 106.2(3), C(1)–P(1)–C(12) 98.6(2); C(1)–B(1)–C(11)–C(12) 1.2(5), C(1)–P(1)–C(12)–C(11) 5.3(3).

The X-ray crystal structure analysis confirms that the triflate ion has been replaced by the neutral $OPEt_3$ molecule, thereby maintaining the tetracoordinate state of the boron atom. This substitution reaction does not lead to any significant changes in key structural parameters of the borane fragment. The B(1)–O(1) bond length amounts to 1.523(5) Å, which is shorter by 0.066(5) Å than that of the starting compound (**1**)OTf [1.589(3) Å][21] and still slightly shorter than that of $(C_6F_5)_3B{\cdot}OPEt_3$ [1.533(3) Å].[25] A more significant difference is found in the O–P bond lengths of [(**1**)$OPEt_3$][OTf] [1.526(3) Å] compared to $(C_6F_5)_3B{\cdot}OPEt_3$ [1.497(2) Å][25] (cf. also $OPCy_3$: O–P = 1.490(2) Å; Cy = cyclohexyl).[27] We are aware of the fact that bond lengths in the solid state do not necessarily correlate with bond strengths. However, in the present case, the differences in the Gutmann acceptor numbers of $[\mathbf{1}]^+$ vs. $(C_6F_5)_3B$ are nicely reflected by the trends in the B–O and O–P bond lengths of their corresponding $OPEt_3$ adducts.

As a second independent measure of Lewis acidities, the Childs NMR spectroscopic method,[28] with crotonaldehyde instead of $OPEt_3$, is often employed.[15a] Since crotonaldehyde is not stable over time in the presence of strong Lewis acids, we prepared the pyridine adduct [(**1**)py][OTf] instead and took its $^{13}C\{^1H\}$ NMR chemical shift values as a diagnostic tool.

The compound readily precipitates from a concentrated CH_2Cl_2 solution of (**1**)OTf upon addition of 1 equiv. of pyridine (Scheme 2); crystals of [(**1**)py][OTf] suitable for X-ray diffraction were grown by slow concentration of a dilute CH_2Cl_2 solution.

The $^{11}B\{^1H\}$ NMR spectrum of [(**1**)py][OTf] is characterized by a resonance at 0.7 ppm. In Table 2, the pyridine ^1H and $^{13}C\{^1H\}$ chemical shift values of [(**1**)py][OTf] are compared with those of free pyridine, other selected borane–pyridine adducts, and pyridinium salts. Pyridine protonation results in the shielding of the C-2,6 nuclei and the deshielding of C-4 and C-3,5. Qualitatively similar effects are observed upon borane–pyridine coordination. A closer inspection of the data reveals a continuous upfield shift of the C-2,6 resonances with an overall $\Delta(\delta)$ of –3.6 ppm along the sequence py → Ph_3B·py → $(C_6F_5)_3B$·py → [(**1**)py][OTf], while the C-4 signal and the C-3,5 resonances are shifted to lower field by $\Delta(\delta)$ = 8.0 and 4.0 ppm, respectively. We note analogous trends also for the chemical shift values of 4-H and 3,5-H (the 2,6-H resonances are less meaningful, because they are closer to the borane frameworks and therefore influenced by magnetic anisotropy effects). Even though these measurements do not provide quantitative acceptor numbers, they nevertheless support our previously established order of Lewis acidities, that is, $[\mathbf{1}]^+ > (C_6F_5)_3B > Ph_3B$.

Table 2. Compilation of ^1H and $^{13}C\{^1H\}$ NMR chemical shift values of free and coordinated pyridine.

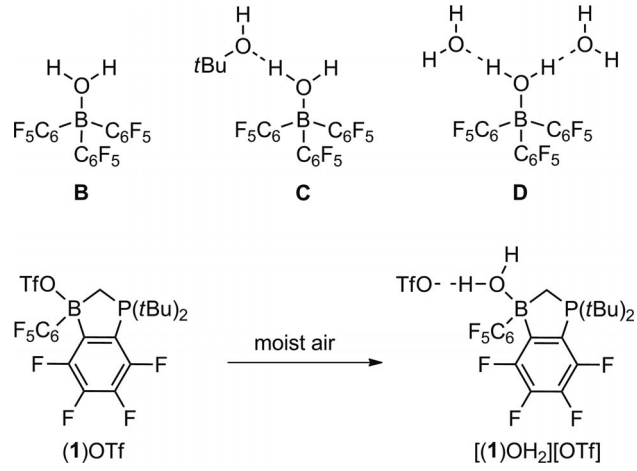
	$\delta(^1H)$[a]			$\delta(^{13}C\{^1H\})$[a]		
	2,6-H	4-H	3,5-H	C-2,6	C-4	C-3,5
Pyridine	8.58	7.67	7.27	150.2	136.1	124.0
Ph_3B·py	8.57	8.06	7.56	148.3	141.0	125.6
$(C_6F_5)_3B$·py	8.61	8.21	7.71	147.2	143.2	126.2
[(**1**)py][OTf]	8.57	8.30	7.92	146.6	144.1	128.0
[H·py][OTs][b]	8.93	8.43	7.94	142.3	146.3	127.6
[H·py][Cl]	8.90	8.51	8.02	141.2	146.1	127.5

[a] CD_2Cl_2, 27 °C. [b] OTs = *p*-toluenesulfonate.

The most revealing structural parameter of [(**1**)py][OTf] (see the Supporting Information for details of its solid-state structure) is the B–N bond length [1.599(4) Å], which is shorter by 0.029(4) Å than the B–N bond in $(C_6F_5)_3B$·py [1.628(2) Å].[29]

In this context, we also became interested in the molecular structure of the water adduct $[(\mathbf{1})OH_2]^+$, which we wanted to compare with the structures of the $(C_6F_5)_3B{\cdot}OH_2$ complexes **B**, **C**, and **D** (Scheme 3). The main emphasis lay on B–O bond length variations as an approximate measure of the degree of O–H bond polarization, which should in turn be influenced by the Lewis acidity of the boron center.

Both the chloroborate (**1**)Cl[21] and the acetoxyborate (**1**)OAc[21] are water-stable, and the solids can be handled and stored in air for extended periods of time. In contrast, (**1**)OTf readily hydrolyzes under similar conditions. Consequently, [(**1**)OH_2][OTf] formed in essentially quantitative yield upon stirring an Et_2O solution of (**1**)OTf in air for 48 h (Scheme 3). The NMR spectroscopic data of the compound are unexceptional {$\delta(^{11}B\{^1H\})$ = 1.9 ppm; $\delta(^{31}P\{^1H\})$ = 86.9 ppm}; in the ^1H NMR spectrum, the OH_2 protons give rise to an extremely broad signal at approximately 5 ppm {cf. the resonance of water in CD_2Cl_2 appears at $\delta(^1H)$ = 1.52 ppm}.[30]



Scheme 3. Top: water adducts of $(C_6F_5)_3B$ known in the literature; bottom: hydrolysis of (**1**)OTf.

Single crystals of [(**1**)OH_2][OTf] were grown from CH_2Cl_2. X-ray crystal structure analysis revealed a water molecule coordinated to the boron atom (Figure 3). Both OH_2 atoms were located in the difference Fourier map and were freely refined. In the solid state, the ion pair [(**1**)-OH_2]$^+$[OTf]$^-$ exists as a centrosymmetric dimer, which is

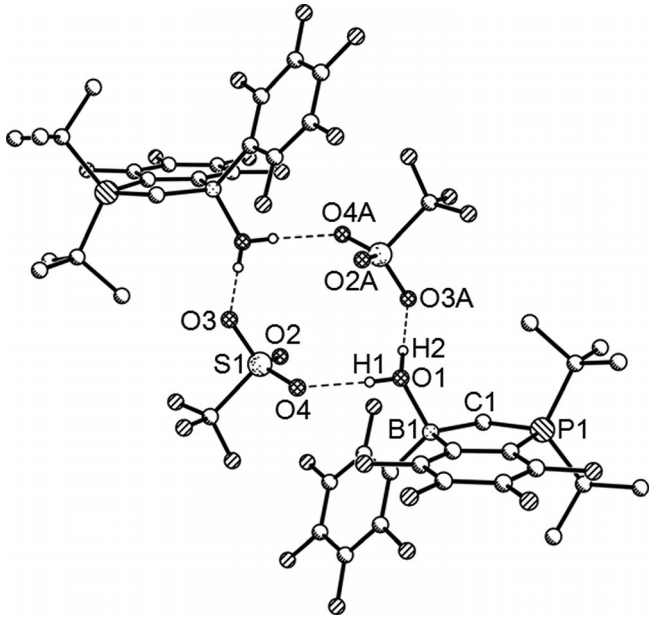


Figure 3. Dimeric structure of [(**1**)OH_2][OTf] in the solid state. Except on the H_2O molecule, H atoms have been omitted for clarity. Selected bond lengths [Å], atom···atom distances [Å], and bond angles [°]: O(1)–H(1) 0.80(2), O(1)–H(2) 0.98(3), B(1)–O(1) 1.553(2), B(1)–C(1) 1.642(2), P(1)–C(1) 1.794(1), H(1)···O(4) 1.84(2), H(2)···O(3A) 1.67(3), O(1)···O(4) 2.647(2), O(1)···O(3A) 2.640(1); O(1)–H(1)···O(4) 177(2), O(1)–H(2)···O(3A) 171(3), B(1)–C(1)–P(1) 108.3(1). Symmetry transformation used to generate equivalent atoms: A = $-x + 1, -y + 1, -z$.

held together by four HO–H···OTf hydrogen bonds. Bonding of the triflate anion to [**1**]$^+$ benefits to a greater degree from Coulomb attraction than water coordination. Nevertheless, the B–O bond of (**1**)OTf [1.589(3) Å] is elongated by 0.036(3) Å relative to that of [(**1**)OH_2][OTf] [1.553(2) Å]. The $(C_6F_5)_3B{\cdot}OH_2$ adducts **B**, **C**, and **D** possess B–O bond lengths of 1.608(3),[31] 1.583(3),[31] and 1.577(1) Å,[32] respectively. Thus, an increasing number of hydrogen bonds about the water molecule, which should in turn increase the average O–H polarity, results in a gradual decrease of the B–O bond lengths. Of all species **B**, **C**, and **D**, compound **D**, which also establishes two hydrogen bonds per water molecule, is most closely related to [(**1**)OH_2][OTf]. We observe a further significant shortening of the B–O bond from 1.577(1) Å in **D** to 1.553(2) Å in [(**1**)OH_2][OTf]. This result conforms to the higher Lewis acidity of [**1**]$^+$ compared to that of $(C_6F_5)_3B$.

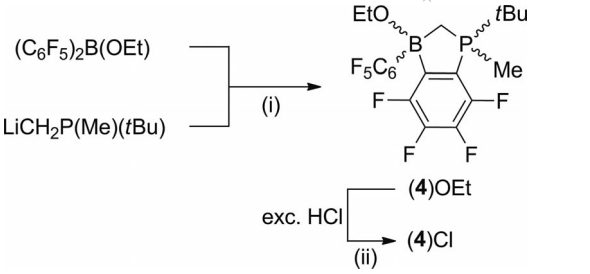
Stereoselectivity of Nucleophilic Substitution Reactions at the Boron Centers of [A]$^+$-Type Compounds

So far, we have gathered spectroscopic and crystallographic evidence for a higher Lewis acidity of [**A**]$^+$-type cations relative to the neutral Lewis acid $(C_6F_5)_3B$. Using a prototypical substitution reaction at boron, we next studied whether the free cationic Lewis acid [**A**]$^+$ is present in the association/dissociation equilibrium with its donor (Do) adduct (**A**)Do to a sufficiently high degree to influence the outcome of the reaction.

The boron atom in (**A**)Do is a chiral center. Introduction of a second chiral center into the molecule will therefore generate (**A**)Do in a specific diastereomeric ratio. If Do is quantitatively substituted by another Lewis base Do′, two different scenarios can be envisioned: (1) The diastereomeric ratio is strictly reversed in (**A**)Do′, which would be indicative of an S_N2 reaction mechanism. (2) The diastereomeric ratio changes as a result of a competing S_N1 pathway (possibly assisted by intermediate OEt_2 coordination). The extent of this change, in turn, correlates with the proportion of the free Lewis acid [**A**]$^+$ {or [**A**(OEt_2)]$^+$} in the reaction mixture.

Replacement of one *t*Bu group in [**1**]$^+$ by a Me substituent offers a convenient way to introduce a second chiral center into the molecule. We therefore treated $(C_6F_5)_2B$-(OEt)[33] with $LiCH_2P(Me)(tBu)$ at –78 °C in toluene and obtained (**4**)OEt in a 1:3 diastereomeric ratio according to NMR spectroscopy [Scheme 4; $LiCH_2P(Me)(tBu)$ (cf. the Supporting Information) was prepared in a fashion similar to $LiCH_2P(tBu)_2$[34]]. The $^{11}B\{^1H\}$ and $^{31}P\{^1H\}$ NMR chemical shift values of both diastereomers of (**4**)OEt are virtually the same, but the *t*Bu proton resonances are well separated and appear as doublets at δ = 0.66 ppm (major diastereomer; C_6D_6) and δ = 0.53 ppm (minor diastereomer; C_6D_6).

(**4**)OEt is a fairly inert compound and therefore has to be activated by transformation into the chloro derivative (**4**)Cl with the help of HCl in Et_2O. This latter reaction is not only crucial for the entire chemistry of [**A**]$^+$-type compounds, but it is also clean and quantitative and therefore qualifies as a test reaction for the stereospecificity of nucleophilic transformations at the boron atom. As expected, upon addition of 4 equiv. of HCl in Et_2O to the diastereomeric mixture of (**4**)OEt in Et_2O (Scheme 4), the exclusive formation of two diastereomers of the chloro adduct (**4**)Cl was observed (for an X-ray crystal structure analysis of the diastereomer in which the Cl atom and the Me substituent are located on the same side of the five-membered heterocycle, see the Supporting Information). The experiment was repeated five times; however, the diastereomeric ratio of (**4**)Cl turned out to be poorly reproducible and changed upon standing and workup. We therefore isolated a pure sample of the major diastereomer of (**4**)OEt by column chromatography and protolyzed it with HCl in Et_2O as described above. Again, ^1H NMR spectroscopy revealed a dynamic behavior with no obvious dependence on solvent polarity or temperature. Since the stereomeric information at boron is lost upon going from (**4**)OEt to (**4**)Cl, we conclude that the phosphonium borane [**4**]$^+$ {presumably in the form of a weak adduct [**4**(OEt_2)]$^+$} is present in a significant amount in the reaction mixture.

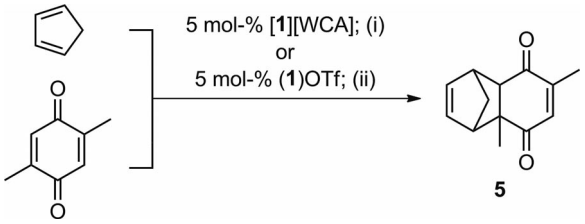


Scheme 4. Synthesis of (**4**)OEt and its transformation into the chloro derivative (**4**)Cl: (i) toluene, –78 °C → room temp., 12 h; (**4**)OEt is obtained as a mixture of two diastereomers in a 1:3 ratio. (ii) Et_2O, room temp., 18 h.

Assessment of the Catalytic Activity of [1]$^+$ in a Diels–Alder Reaction

During the last decade, the potential of (cationic) boranes for the catalysis of, for example, [4+2] and [3+2] cycloaddition reactions has been recognized, and even enantioselective transformations have been developed.[35] We therefore decided to undertake an exploratory investigation of the catalytic activity of [**1**]$^+$ in the well-studied [4+2] cycloaddition reaction between 2,5-dimethyl-1,4-benzoquinone and cyclopentadiene[36] (Scheme 5).

Both the free Lewis acid [**1**][WCA] and the triflate adduct (**1**)OTf were employed. Since [**1**][WCA] is extremely sensitive to any kind of nucleophile, a solution of this compound in CH_2Cl_2 was freshly prepared as described above. Even though the catalyst solution was separated from the AgCl precipitate prior to use, the presence of residual [Ag]$^+$ traces cannot be fully excluded. Thus, we first performed blind tests of the catalytic activity of [Ag(CH_2Cl_2)][WCA] in



Scheme 5. Application of [**1**][WCA] and (**1**)OTf as catalysts for the reaction of cyclopentadiene (CpH) with 2,5-dimethyl-1,4-benzoquinone: (i) 1.2 equiv. CpH, CH_2Cl_2, room temp., 2.5 h. (ii) 1.4 equiv. CpH, CH_2Cl_2, room temp., 24 h.

CH_2Cl_2 solution. Addition of the salt (5 mol-%) to the diene/dienophile mixture at room temp. caused an immediate color change from yellow to dark brown. After 2.5 h, the cycloaddition product **5**[36] was already detectable in the ^{1}H NMR spectrum. In addition to that, broad and ill-defined signals appeared in the alkyl region of the spectrum, and a silver mirror gradually formed on the walls of the reaction vessel. It is known that cyclopentadiene tends to polymerize in the presence of Lewis acids,[37] which, in our case, is most likely a major side reaction.

Table 3 summarizes all catalysis results obtained with [**1**][WCA] and (**1**)OTf (CH_2Cl_2, room temp.). The transformations were monitored by ^{1}H NMR spectroscopy (C_6D_6); conversion rates were determined by signal integration. In the uncatalyzed background reaction, the first product resonances[36] appeared after approximately 5 h (entry 1). About 20 h later, the conversion to **5** had reached 27%, the yellow color of the solution persisted, and no side products were detectable. Similarly moderate yields were obtained in the presence of the precatalyst (**1**)Cl (entry 2). The use of 2 mol-% of [**1**][WCA] gave **5** in 81% spectroscopic yield after only 2.5 h (entry 3). Prolonged stirring did not induce further significant changes. An increase in the catalyst loading to 5 mol-% had only a small effect on the obtained yield of **5** (87% after 2.5 h; entry 4), thereby indicating that the equilibrium concentration has been reached at this stage.

Table 3. Investigation of the Diels–Alder reaction between 2,5-dimethyl-1,4-benzoquinone and cyclopentadiene (CpH) in the presence of different catalysts.[a]

Entry	Catalyst	*c*(Catalyst) [mol-%]	Dienophile/ CpH ratio	Yield[b] [%] after 2.5 h	5 h	10 h	24 h
1	None	0	1 1	0	3	11	27
2	(**1**)Cl	5	1 1	0	4	[c]	19
3	[**1**][WCA]	2	1 1	81	83	[c]	78
4		5	1 1	87	85	[c]	76
5		5	1 1.2[d]	95[e]	87	[c]	76
6	(**1**)OTf	5	1 1	55	58	[c]	81
7		5	1 1.4[f]	49	53	76	91[g]
8		10	1 1.4[f]	55	63	90	96[g]

[a] Reaction conditions: 2,5-dimethyl-1,4-benzoquinone (0.15 mmol), CpH (0.15 mmol), CH_2Cl_2, room temp. [b] Reaction monitored by ^{1}H NMR spectroscopy. [c] Yield not determined. [d] 1 equiv. of CpH was present at the beginning of the reaction; further CpH was added after 1 h (0.2 equiv.). [e] Workup after 2.5 h; isolated yield: 87%. [f] 1 equiv. of CpH was present at the beginning of the reaction; further CpH was added after 4 h (0.2 equiv.) and 6 h (0.2 equiv.). [g] Workup after 24 h; isolated yield: 80%.

Interestingly, we observed a slow decrease in the product concentration (76% after 24 h) with a concomitant increase in the amount of the 2,5-dimethyl-1,4-benzoquinone starting material. Parallel to that, signs of cyclopentadiene polymerization were visible in the NMR spectrum. Thus, extended reaction times result in lower yields of **5**, because cyclopentadiene is continuously removed from the dynamic equilibrium, which favors the back reaction. To validate this interpretation, we repeated the reaction with 5 mol-% catalyst loading, but this time added another 0.2 equiv. of cyclopentadiene 1 h after the beginning of the reaction. In that way, a further improved spectroscopic yield of 95% (2.5 h) was achieved, which, again, decreased over time. In a second run under the same conditions, the reaction was quenched after 2.5 h by admission of air and provided **5** in 87% isolated yield after chromatographic workup.

In a next step, (**1**)OTf was tried as the catalyst, because now any $[Ag]^+$ contaminants can be excluded and this storable compound is easier to handle than [**1**][WCA]. (**1**)OTf also catalyzes the reaction of 2,5-dimethyl-1,4-benzoquinone with cyclopentadiene, albeit at a slower rate: With 5 mol-% of the catalyst, the conversion to **5** was 55% complete after 2.5 h (entry 6). After 24 h, the reaction mixture contained 81% of the target compound; cyclopentadiene polymerization was still negligible. An increase in the amount of added cyclopentadiene improved the spectroscopic yield of **5** to 91% (24 h; entry 7). Finally, the use of 10 mol-% of the catalyst together with 1.4 equiv. of cyclopentadiene resulted in virtually quantitative yield (entry 8).

Conclusions

According to the Gutmann–Beckett NMR spectroscopic method, the rigid cyclic phosphonium boranes $[(C_6F_5)B(CH_2)(C_6F_4)P(t\mathrm{Bu})_2]^+$ ($[\mathbf{1}]^+$), $[(C_6F_5)B(CH_2)(C_6F_3H)P(t\mathrm{Bu})_2]^+$ ($[\mathbf{2}]^+$), and $[(C_6F_5)B(CH_2)(C_6F_4)P(t\mathrm{Bu})_2]^+$ ($[\mathbf{3}]^+$) possess acceptor numbers of AN = 87.3, 85.7, and 85.7, respectively, and are therefore stronger Lewis acids than the popular neutral borane $(C_6F_5)_3B$ (AN = 80.0). This conclusion is supported further by the results of X-ray crystal structure analyses of adducts $[(\mathbf{1})Do]^+$ and $(C_6F_5)_3B{\cdot}Do$ (Do = $OPEt_3$, pyridine, H_2O), which consistently reveal significantly shorter B–O/N bond lengths in the former case.

Starting from diastereomerically pure (**4**)OEt {$[\mathbf{4}]^+$ = $[(C_6F_5)B(CH_2)(C_6F_4)P(Me)(t\mathrm{Bu})]^+$}, the protolytic transformation (**4**)OEt → (**4**)Cl proceeds with the complete loss of stereomeric information at the chiral boron center, thereby indicating that a significant amount of the free Lewis acid $[\mathbf{4}]^+$ is present in the reaction mixture.

In line with that, (**1**)OTf, which possesses an even better leaving group than chloride, can be used to catalyze the [4+2] cycloaddition reaction between 2,5-dimethyl-1,4-benzoquinone and cyclopentadiene. With respect to the unmasked Lewis acid [**1**][$Al(O(t\mathrm{Bu}^F))_4$], (**1**)OTf leads to a slower conversion rate, but, nevertheless, to quantitative yields of the cycloaddition product with no detectable concomitant polymerization of cyclopentadiene.

On the basis on the experience gathered with [**4**]$^+$, we are currently developing enantiomerically pure chiral derivatives, which offer promising perspectives for enantioselective Lewis acid catalysis.

Experimental Section

General Considerations: Unless stated otherwise, all manipulations were carried out under a nitrogen atmosphere by using Schlenk-tube techniques or in an argon-filled glovebox. Solvents were dried by distillation from Na (pentane, hexane), Na/benzophenone (Et_2O, benzene, toluene), or CaH_2 (CH_2Cl_2, pyridine). *i*PrOH was treated with a small amount of Na, distilled, and degassed through several freeze-pump-thaw cycles. NMR spectroscopic data were collected with a Bruker Avance 300 or Avance 400 spectrometer. Chemical shift values (^{1}H/^{13}C{^{1}H}) are reported in parts per million (ppm) relative to Me_4Si and were referenced to (residual) solvent signals (C_6D_6: 7.15/128.0; CD_2Cl_2: 5.32/53.8; $CDCl_3$: 7.26/77.2; [D$_8$]THF: 3.58/67.2). Heteronuclear chemical shift values were referenced to external $F_3B{\cdot}OEt_2$ (^{11}B{^{1}H}), $FCCl_3$ (^{19}F{^{1}H}), and 85% H_3PO_4 (^{31}P{^{1}H}). Abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br. = broad, n.r. = multiplet expected in the ^{1}H NMR spectrum but not resolved, n.o. = signal not observed. The compounds [Ag(CH_2Cl_2)][WCA],[26] $(C_6F_5)_2$B(OEt),[38] $(C_6F_5)_2BH{\cdot}SMe_2$,[39] $LiCH_2P(tBu)_2$,[34] (**1**)Cl,[21] (**1**)OTf,[21] (**2**)OEt,[21] (**3**)Cl,[21] [**1**][WCA],[21] and [**3**][WCA][21] were synthesized according to literature procedures. A convenient optimized synthesis of the known compound $(C_6F_5)_2B(OiPr)$[40] and its transformation into (**1**)O*i*Pr are described in the Supporting Information. $Me_2P(tBu)$ has been mentioned in the literature;[41] however, the isolation of the free phosphane has not been described yet. We therefore provide details of the synthesis, isolation, and NMR spectroscopic characterization of $Me_2P(tBu)$ and $LiCH_2P(Me)(tBu)$ in the Supporting Information. 2,5-Dimethyl-1,4-benzoquinone (Aldrich) was sublimed prior to use. $OPEt_3$ was purchased from Aldrich and used as received.

(2)Cl: HCl in Et_2O (0.91 M; 0.88 mL, 0.80 mmol) was added at room temp. by syringe to a stirred solution of (**2**)OEt (0.10 g, 0.20 mmol) in Et_2O (7 mL), whereupon a colorless precipitate immediately formed. After stirring the resulting suspension for 48 h, all volatiles were removed in vacuo to obtain (**2**)Cl in analytically pure form. Single crystals suitable for X-ray crystallography were obtained by slow concentration of a CH_2Cl_2 solution of (**2**)Cl at room temp. Yield: 0.095 g (0.19 mmol, 95%). ^{1}H NMR (400.1 MHz, C_6D_6): δ = 6.58 (m, 1 H, Ar–H), 1.90 (dd, $^2J_{H,H}$ = 16.3, $^2J_{P,H}$ = 11.6 Hz, 1 H, BCH_2P), 1.33 (dd, $^2J_{H,H}$ = 16.3, $^2J_{P,H}$ = 8.7 Hz, 1 H, BCH_2P), 0.73 [d, $^3J_{P,H}$ = 15.8 Hz, 9 H, $C(CH_3)_3$], 0.45 [d, $^3J_{P,H}$ = 15.5 Hz, 9 H, $C(CH_3)_3$] ppm. ^{11}B{^{1}H} NMR (96.3 MHz, C_6D_6): δ = –2.3 ($h_{1/2}$ = 120 Hz) ppm. ^{13}C{^{1}H} NMR (75.5 MHz, C_6D_6): δ = n.o. (FC, BC_{Ar}, PC_{Ar}), 111.2 (m, Ar-CH), 34.7 [m, $C(CH_3)_3$], 34.3 [m, $C(CH_3)_3$], 27.1 [m, $C(CH_3)_3$], 26.1 [m, $C(CH_3)_3$], 15.2 (m, BCH_2P) ppm. ^{19}F{^{1}H} NMR (282.3 MHz, C_6D_6): δ = –98.2 (m, 1 F), –130.9 (m, 1 F), –131.7 (br., 2 F, C_6F_5), –134.9 (m, 1 F), –159.3 (t, $^3J_{F,F}$ = 21 Hz, 1 F, C_6F_5), –164.7 (m, 2 F, C_6F_5) ppm. ^{31}P{^{1}H} NMR (121.5 MHz, C_6D_6): δ = 86.0 (m) ppm. MS (ESI$^+$): *m*/*z* (%) = 467 (100) [**2**]$^+$. $C_{21}H_{21}BClF_8P$ (502.61): calcd. C 50.18, H 4.21; found C 50.37, H 4.43.

[(1)OPEt$_3$][OTf]: A solution of (**1**)OTf (0.15 g, 0.24 mmol) and $OPEt_3$ (0.032 g, 0.24 mmol) in CH_2Cl_2 (5 mL) was stirred at room temp. for 12 h, then concentrated under reduced pressure to a volume of 0.3 mL and layered with pentane (0.2 mL). Crystallization of [(**1**)$OPEt_3$][OTf] started after 30 min and continued for another 1 d. Single crystals suitable for X-ray diffraction were isolated by decantation. For further characterization, the colorless crystalline material was washed with hexane (4 × 0.5 mL), ground, and dried in vacuo over a period of 6 h. Yield: 0.12 g (0.16 mmol, 67%). ^{1}H NMR (300.0 MHz, CD_2Cl_2): δ = 2.03 (dq, $^2J_{P,H}$ = 11.8, $^3J_{H,H}$ = 7.7 Hz, 6 H, PCH_2CH_3), 1.61 (m, 2 H, BCH_2P), 1.48 [d, $^3J_{P,H}$ = 16.3 Hz, 9 H, $C(CH_3)_3$], 1.24 [d, $^3J_{P,H}$ = 16.2 Hz, 9 H, $C(CH_3)_3$], 1.06 (dt, $^3J_{P,H}$ = 18.7, $^3J_{H,H}$ = 7.7 Hz, 9 H, PCH_2CH_3) ppm. ^{11}B{^{1}H} NMR (96.3 MHz, CD_2Cl_2): δ = 2.3 ($h_{1/2}$ = 250 Hz) ppm. ^{13}C{^{1}H} NMR (75.5 MHz, CD_2Cl_2): δ = n.o. (FC, BC_{Ar}, PC_{Ar}), 36.1 [d, $^1J_{P,C}$ = 32 Hz, $C(CH_3)_3$], 35.9 [d, $^1J_{P,C}$ = 35 Hz, $C(CH_3)_3$], 27.8 [m, $C(CH_3)_3$], 27.1 [m, $C(CH_3)_3$], 18.1 (d, $^1J_{P,C}$ = 65 Hz, PCH_2CH_3), 13.9 (m, BCH_2P), 5.6 (d, $^2J_{P,C}$ = 5 Hz, PCH_2CH_3) ppm. ^{19}F{^{1}H} NMR (282.3 MHz, CD_2Cl_2): δ = –79.0 (s, 3 F, OSO_2CF_3), –120.7 (m, 1 F), –127.4 (m, 1 F), –133.1 (m, 2 F, C_6F_5), –144.9 (m, 1 F), –150.9 (m, 1 F), –155.7 (tt, $^3J_{F,F}$ = 20, $^4J_{F,F}$ = 2 Hz, 1 F, C_6F_5), –162.2 (m, 2 F, C_6F_5) ppm. ^{31}P{^{1}H} NMR (121.5 MHz, CD_2Cl_2): δ = 85.2 (m, 1 P, BCH_2P), 80.9 (s, 1 P, $OPEt_3$) ppm. MS (ESI$^+$): *m*/*z* (%) = 485 (6) [**1**]$^+$, 619 (100) [(**1**)-$OPEt_3$]$^+$. MS (ESI$^-$): *m*/*z* (%) = 149 (100) $[OSO_2CF_3]^-$. $C_{28}H_{35}BF_{12}O_4P_2S$ (768.37): calcd. C 43.77, H 4.59, S 4.17; found C 43.59, H 4.61, S 4.30.

[(1)py][OTf]: A solution of pyridine in CH_2Cl_2 (0.52 M; 0.10 mL, 0.052 mmol) was added at room temp. by syringe to a stirred solution of (**1**)OTf (0.030 g, 0.047 mmol) in CH_2Cl_2 (1 mL). The reaction mixture was stirred for 12 h, whereupon a colorless solid precipitated. The solvent and excess pyridine were removed in vacuo to obtain analytically pure [(**1**)py][OTf]. Yield: 0.033 g (0.046 mmol, 98%). Single crystals suitable for X-ray crystallography were grown by slow concentration of a CH_2Cl_2 solution of [(**1**)py][OTf] at room temp. ^{1}H NMR (300.0 MHz, CD_2Cl_2): δ = 8.57 (d, $^3J_{H,H}$ = 6.1 Hz, 2 H, pyH-2,6), 8.30 (tt, $^3J_{H,H}$ = 7.7, $^4J_{H,H}$ = 1.3 Hz, 1 H, pyH-4), 7.92 (m, 2 H, pyH-3,5), 2.33–2.10 (m, 2 H, BCH_2P), 1.42 [d, $^3J_{P,H}$ = 16.1 Hz, 9 H, $C(CH_3)_3$], 1.37 [d, $^3J_{P,H}$ = 15.9 Hz, 9 H, $C(CH_3)_3$] ppm. ^{11}B{^{1}H} NMR (96.3 MHz, CD_2Cl_2): δ = 0.7 ($h_{1/2}$ = 130 Hz) ppm. ^{13}C{^{1}H} NMR (75.5 MHz, CD_2Cl_2): δ = n.o. (FC, BC_{Ar}, PC_{Ar}), 146.6 (pyC-2,6), 144.1 (pyC-4), 128.0 (pyC-3,5), 36.9 [d, $^1J_{P,C}$ = 31 Hz, $C(CH_3)_3$], 36.4 [d, $^1J_{P,C}$ = 32 Hz, $C(CH_3)_3$], 27.7 [m, $C(CH_3)_3$], 27.5 [m, $C(CH_3)_3$], 13.7 (m, BCH_2P) ppm. ^{19}F{^{1}H} NMR (282.3 MHz, CD_2Cl_2): δ = –78.9 (s, 3 F, OSO_2CF_3), –120.6 (m, 1 F), –126.8 (m, 1 F), –131.7 (m, 2 F, C_6F_5), –143.5 (m, 1 F), –149.8 (m, 1 F), –154.6 (tt, $^3J_{F,F}$ = 20, $^4J_{F,F}$ = 3 Hz, 1 F, C_6F_5), –162.1 (m, 2 F, C_6F_5) ppm. ^{31}P{^{1}H} NMR (121.5 MHz, CD_2Cl_2): δ = 87.5 (m) ppm. MS (ESI$^+$): *m*/*z* (%) = 485 (100) [**1**]$^+$, 564 (9) [(**1**)py]$^+$. MS (ESI$^-$): *m*/*z* (%) = 149 (100) $[OSO_2CF_3]^-$. $C_{27}H_{25}BF_{12}NO_3PS$ (713.32): calcd. C 45.46, H 3.53, N 1.96, S 4.50; found C 44.52, H 3.66, N 1.78, S 4.61. *Note*: The deviation from the calculated value for carbon is due to boron carbide formation during combustion.

[(1)OH$_2$][OTf]: A solution of (**1**)OTf (0.12 g, 0.19 mmol) in Et_2O (10 mL) was stirred in air at room temp. for 48 h. The solvent was removed in vacuo yielding [(**1**)OH_2][OTf] in analytically pure form. Yield: 0.12 g (0.18 mmol, 95%). Slow concentration of a CH_2Cl_2 solution of [(**1**)OH_2][OTf] at room temp. gave X-ray quality crystals. ^{1}H NMR (300.0 MHz, CD_2Cl_2): δ = 4.90 (br., $h_{1/2}$ = 300 Hz, H_2O), 1.89 (dd, $^2J_{H,H}$ = 16.5, $^2J_{P,H}$ = 13.3 Hz, 1 H, BCH_2P), 1.52 (dd, $^2J_{H,H}$ = 16.5, $^2J_{P,H}$ = 8.5 Hz, 1 H, BCH_2P), 1.47 [d, $^3J_{P,H}$ = 16.4 Hz, 9 H, $C(CH_3)_3$], 1.26 [d, $^3J_{P,H}$ = 16.0 Hz, 9 H, $C(CH_3)_3$] ppm. ^{11}B{^{1}H} NMR (96.3 MHz, CD_2Cl_2): δ = 1.9 ($h_{1/2}$ = 380 Hz) ppm. ^{13}C{^{1}H} NMR (75.5 MHz, CD_2Cl_2): δ = n.o. (FC, BC_{Ar}, PC_{Ar}, BCH_2P), 36.2 [d, $^1J_{P,C}$ = 31 Hz, $C(CH_3)_3$], 35.8 [d, $^1J_{P,C}$ = 33 Hz, $C(CH_3)_3$], 27.7 [m, $C(CH_3)_3$], 27.1 [m, $C(CH_3)_3$] ppm. ^{19}F{^{1}H} NMR (282.3 MHz, CD_2Cl_2): δ = –79.3 (s, 3 F, OSO_2CF_3),

–122.5 (m, 1 F), –127.6 (m, 1 F), –133.7 (m, 2 F, C_6F_5), –145.5 (m, 1 F), –152.0 (m, 1 F), –157.3 (t, $^3J_{F,F}$ = 20 Hz, 1 F, C_6F_5), –163.9 (m, 2 F, C_6F_5) ppm. $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2): δ = 86.9 (m) ppm. MS (ESI^+): *m/z* (%) = 485 (100) [**1**]$^+$. MS (ESI^-): *m/z* (%) = 149 (100) $[OSO_2CF_3]^-$. $C_{22}H_{22}BF_{12}O_4PS$ (652.24): calcd. C 40.51, H 3.40, S 4.92; found C 40.56, H 3.61, S 5.44.

Synthesis of (4)OEt: A suspension of $LiCH_2P(Me)(tBu)$ (0.075 g, 0.60 mmol) in toluene (10 mL) was cooled to –78 °C. A solution of $(C_6F_5)_2B(OEt)$ (0.23 g, 0.60 mmol) in toluene (3 mL) was added quickly by syringe. The resulting slurry was gradually warmed to room temp., stirred overnight, and quenched with deionized H_2O (1 mL). The mixture was dried with Na_2SO_4, filtered, and the insoluble material was extracted with toluene (3 × 3 mL). The combined organic phases were concentrated to dryness in vacuo, the oily residue was redissolved in benzene (8 mL) and freeze-dried in vacuo to remove trace amounts of toluene. The colorless solid (**4**)OEt was obtained as a 1:3 mixture of two diastereomers (^1H NMR spectroscopic control). Yield: 0.25 g (0.51 mmol, 85%). The major diastereomer was isolated by column chromatography (silica gel, hexane/EtOAc, 1.5:1). Yield: 0.13 g (0.27 mmol, 45%).

Major Diastereomer: ^1H NMR (300.0 MHz, C_6D_6): δ = 3.94 (m, 1 H, OCH_2CH_3), 3.30 (m, 1 H, OCH_2CH_3), 1.35 (t, $^3J_{H,H}$ = 6.9 Hz, 3 H, OCH_2CH_3), 1.27 (m, 1 H, BCH_2P), 0.70 (d, $^2J_{P,H}$ = 12.8 Hz, 3 H, PCH_3), 0.66 [d, $^3J_{P,H}$ = 16.9 Hz, 9 H, $C(CH_3)_3$], 0.54 (m, 1 H, BCH_2P) ppm. $^{11}B\{^1H\}$ NMR (96.3 MHz, C_6D_6): δ = 2.1 ($h_{1/2}$ = 15 Hz) ppm. $^{13}C\{^1H\}$ NMR (75.5 MHz, C_6D_6): δ = n.o. (FC, BC_{Ar}, PC_{Ar}), 60.0 (OCH_2CH_3), 30.5 [d, $^1J_{P,C}$ = 44 Hz, $C(CH_3)_3$], 24.7 [m, $C(CH_3)_3$], 18.6 (OCH_2CH_3), 15.5 (m, BCH_2P), 6.5 (d, $^1J_{P,C}$ = 46 Hz, PCH_3) ppm. $^{19}F\{^1H\}$ NMR (282.3 MHz, C_6D_6): δ = –126.8 (m, 1 F), –130.2 (m, 1 F), –136.5 (m, 2 F, C_6F_5), –145.8 (m, 1 F), –155.5 (m, 1 F), –160.3 (t, $^3J_{F,F}$ = 21 Hz, 1 F, C_6F_5), –164.6 (m, 2 F, C_6F_5) ppm. $^{31}P\{^1H\}$ NMR (121.5 MHz, C_6D_6): δ = 64.8 (m) ppm.

Minor Diastereomer: ^1H NMR (300.0 MHz, C_6D_6): δ = 3.73 (m, 1 H, OCH_2CH_3), 3.20 (m, 1 H, OCH_2CH_3), 1.28 (t, $^3J_{H,H}$ = 6.9 Hz, 3 H, OCH_2CH_3), 1.07 (d, $^2J_{P,H}$ = 13.4 Hz, 3 H, PCH_3), 1.01 (m, 1 H, BCH_2P), 0.58 (m, 1 H, BCH_2P), 0.53 [d, $^3J_{P,H}$ = 16.8 Hz, 9 H, $C(CH_3)_3$] ppm. $^{11}B\{^1H\}$ NMR (96.3 MHz, C_6D_6): δ = 1.2 ($h_{1/2}$ = 20 Hz) ppm. $^{13}C\{^1H\}$ NMR (75.5 MHz, C_6D_6): δ = n.o. (FC, BC_{Ar}, PC_{Ar}), 59.9 (OCH_2CH_3), 29.8 [d, $^1J_{P,C}$ = 44 Hz, $C(CH_3)_3$], 24.0 [m, $C(CH_3)_3$], 18.7 (OCH_2CH_3), 15.5 (m, BCH_2P), 6.2 (d, $^1J_{P,C}$ = 46 Hz, PCH_3) ppm. $^{19}F\{^1H\}$ NMR (282.3 MHz, C_6D_6): δ = –127.6 (m, 1 F), –127.8 (m, 1 F), –135.7 (m, 2 F, C_6F_5), –146.5 (m, 1 F), –156.1 (m, 1 F), –160.4 (t, $^3J_{F,F}$ = 21 Hz, 1 F, C_6F_5), –164.7 (m, 2 F, C_6F_5) ppm. $^{31}P\{^1H\}$ NMR (121.5 MHz, C_6D_6): δ = 66.3 (m) ppm. MS (ESI^+): *m/z* (%) = 443 (100) [**4**]$^+$. MS (ESI^-): *m/z* (%) = 487 (100) $[M - H]^-$. $C_{20}H_{19}BF_9OP$ (488.13): calcd. C 49.21, H 3.92; found C 49.54, H 3.99.

Synthesis of (4)Cl: A solution of HCl in Et_2O (0.91 M; 2.4 mL, 2.18 mmol) was added quickly by syringe at room temp. to a stirred solution of (**4**)OEt (1:3 mixture of two diastereomers; 0.27 g, 0.55 mmol) in Et_2O (8 mL), whereupon a colorless precipitate immediately formed. The resulting suspension was stirred for 18 h to drive the reaction to completion. All volatiles were driven off under reduced pressure, and (**4**)Cl was obtained as a colorless solid in analytically pure form. Yield: 0.25 g (0.52 mmol, 95%). *Note*: NMR spectroscopic measurements ($CDCl_3$) on samples after workup revealed strong variations in the diastereomeric ratio (range = 1:3 to 1:12; the major diastereomer was always the same). Using the 1:12 mixture, X-ray quality crystals of one diastereomer were grown by slow concentration of a dilute Et_2O/CH_2Cl_2 solution (3:1) at room temp.

Major Diastereomer: ^1H NMR (300.0 MHz, $CDCl_3$): δ = 2.07 (d, $^2J_{P,H}$ = 13.1 Hz, 3 H, PCH_3), 1.94–1.71 (m, 2 H, BCH_2P), 1.26 [d, $^3J_{P,H}$ = 17.1 Hz, 9 H, $C(CH_3)_3$] ppm. $^{11}B\{^1H\}$ NMR (96.3 MHz, $CDCl_3$): δ = –2.1 ($h_{1/2}$ = 120 Hz) ppm. $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$): δ = n.o. (FC, BC_{Ar}, PC_{Ar}), 31.0 [d, $^1J_{P,C}$ = 45 Hz, $C(CH_3)_3$], 24.5 [m, $C(CH_3)_3$], 16.8 (m, BCH_2P), 7.1 (d, $^1J_{P,C}$ = 46 Hz, PCH_3) ppm. $^{19}F\{^1H\}$ NMR (282.3 MHz, $CDCl_3$): δ = –126.0 (m, 1 F), –129.5 (m, 1 F), –132.4 (m, 2 F, C_6F_5), –143.9 (m, 1 F), –154.0 (m, 1 F), –158.3 (tt, $^3J_{F,F}$ = 20, $^4J_{F,F}$ = 2 Hz, 1 F, C_6F_5), –164.0 (m, 2 F, C_6F_5) ppm. $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ = 67.4 (m) ppm.

Minor Diastereomer: ^1H NMR (300.0 MHz, $CDCl_3$): δ = 1.92 (d, $^2J_{P,H}$ = 12.9 Hz, 3 H, PCH_3), 1.94–1.71 (m, 2 H, BCH_2P), 1.42 [d, $^3J_{P,H}$ = 17.3 Hz, 9 H, $C(CH_3)_3$] ppm. $^{11}B\{^1H\}$ NMR (96.3 MHz, $CDCl_3$): δ = –2.1 ($h_{1/2}$ = 120 Hz) ppm. $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$): δ = n.o. (FC, BC_{Ar}, PC_{Ar}), 31.4 [d, $^1J_{P,C}$ = 44 Hz, $C(CH_3)_3$], 25.3 [m, $C(CH_3)_3$], 16.8 (m, BCH_2P), 7.3 (d, $^1J_{P,C}$ = 46 Hz, PCH_3) ppm. $^{19}F\{^1H\}$ NMR (282.3 MHz, $CDCl_3$): δ = –127.2 (m, 1 F), –129.3 (m, 1 F), –133.0 (m, 2 F, C_6F_5), –143.7 (m, 1 F), –154.0 (m, 1 F), –158.7 (tt, $^3J_{F,F}$ = 20, $^4J_{F,F}$ = 2 Hz, 1 F, C_6F_5), –164.2 (m, 2 F, C_6F_5) ppm. $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ = 68.1 (m) ppm. MS (ESI^+): *m/z* (%) = 443 (100) [**4**]$^+$. $C_{18}H_{14}BClF_9P$ (478.52): calcd. C 45.18, H 2.95; found C 45.15, H 3.01.

Gutmann–Beckett Measurements for Lewis Acidity Determination: The Lewis acidities of compounds [**1**][WCA], [**2**][WCA], and [**3**][WCA] were determined by an NMR spectroscopic method as follows: (1) $OPEt_3$ was placed in an NMR tube. (2) In a different flask, CD_2Cl_2 was added to a mixture of $[Ag(CH_2Cl_2)]$[WCA] and the chloro adduct of the respective Lewis acid. (3) The resulting suspension was stirred for 2 min at room temp., filtered, and the clear yellow filtrate was transferred to the NMR tube. (4) The NMR tube was flame-sealed, and the $^{31}P\{^1H\}$ NMR spectrum was recorded at 27 °C. In a similar fashion, a sample of $(C_6F_5)_3B$ as the Lewis acid was investigated to ensure maximum comparability of the data. *Note*: The same NMR spectrometer was used for all measurements.

[(1)OPEt$_3$][WCA]: (**1**)Cl (0.058 g, 0.111 mmol), $[Ag(CH_2Cl_2)]$[WCA] (0.129 g, 0.111 mmol), and $OPEt_3$ (0.005 g, 0.037 mmol) in CD_2Cl_2 (0.7 mL). $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2): δ = 85.0 (m, 1 P, BCH_2P), 80.4 (s, 1 P, $OPEt_3$) ppm.

[(2)OPEt$_3$][WCA]: (**2**)Cl (0.048 g, 0.096 mmol), $[Ag(CH_2Cl_2)]$[WCA] (0.111 g, 0.096 mmol), and $OPEt_3$ (0.004 g, 0.032 mmol) in CD_2Cl_2 (0.6 mL). $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2): δ = 84.1 (m, 1 P, BCH_2P), 79.7 (s, 1 P, $OPEt_3$) ppm.

[(3)OPEt$_3$][WCA]: (**3**)Cl (0.048 g, 0.111 mmol), $[Ag(CH_2Cl_2)]$[WCA] (0.129 g, 0.111 mmol), and $OPEt_3$ (0.005 g, 0.037 mmol) in CD_2Cl_2 (0.7 mL). $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2): δ = 84.3 (m, 1 P, BCH_2P), 79.7 (s, 1 P, $OPEt_3$) ppm.

$(C_6F_5)_3B$·$OPEt_3$: $(C_6F_5)_3B$ (0.057 g, 0.111 mmol) and $OPEt_3$ (0.005 g, 0.037 mmol) in CD_2Cl_2 (0.7 mL). $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2): δ = 77.1 (s) ppm.

Lewis Acid Catalyzed Diels–Alder Reaction of 2,5-Dimethyl-1,4-benzoquinone and Cyclopentadiene (CpH)

Catalysis with [1][WCA] (5 mol-%): (**1**)Cl (0.004 g, 7.5 μmol) and $[Ag(CH_2Cl_2)]$[WCA] (0.009 g, 7.5 μmol) were suspended in CH_2Cl_2 (1 mL) at room temp. The mixture was stirred for 2 min and filtered. 2,5-Dimethyl-1,4-benzoquinone (0.020 g, 0.15 mmol) was dissolved in a stock solution of freshly distilled CpH in CH_2Cl_2 (0.073 M; 2.1 mL, 0.15 mmol), and the catalyst solution was added

quickly by syringe. The color of the resulting mixture immediately changed from bright yellow to red. After 1 h, more of the CpH stock solution (0.073 M in CH_2Cl_2; 0.41 mL, 0.03 mmol) was added, the mixture was stirred for another 1.5 h and then opened to air. The solvent was removed in vacuo, and the crude product was purified by column chromatography (hexane/EtOAc, 19:1). Diels–Alder product **5** was obtained as a pale yellow solid. Yield: 0.026 g (0.13 mmol, 87%). The ^{1}H NMR chemical shift values of **5** were in agreement with the literature values.[36]

Catalysis with (1)OTf (5 mol-%): A stock solution of freshly distilled CpH in CH_2Cl_2 (0.073 M; 2.1 mL, 0.15 mmol) was added at room temp. by syringe to a solid mixture of 2,5-dimethyl-1,4-benzoquinone (0.020 g, 0.15 mmol) and (**1**)OTf (0.005 g, 7.5 μmol). More of the CpH stock solution (0.073 M in CH_2Cl_2; 0.41 mL, 0.03 mmol) was added after 4 h and a further 0.2 equiv. after 6 h, whereupon the color of the mixture gradually changed from bright yellow to dark green. Stirring was continued for 18 h before opening the reaction mixture to air. The workup procedure was the same as described above. Yield: 0.025 g (0.12 mmol, 80%).

X-ray Crystal Structure Analysis of (2)Cl, [(1)OPEt$_3$][OTf], [(1)py][OTf], [(1)OH$_2$][OTf], (1)O*i*Pr × C$_6$H$_6$, and (4)Cl

Data were collected with a STOE IPDS II two-circle diffractometer with graphite-monochromated Mo-K_α radiation. Empirical absorption corrections were performed for all structures by using the MULABS[42] option in PLATON.[43] The structures were solved by direct methods with the program SHELXS[44] and refined against F^2 with full-matrix least-squares techniques with the program SHELXL-97.[45] The crystal of [(**1**)OPEt$_3$][OTf] was twinned (emulating monoclinic symmetry) with a contribution of 9.4(1)% for the minor domain. The twin law was (1 0 0/1 –1 0/0 0 –1). In [(**1**)OH$_2$][OTf], the H atoms bonded to O were freely refined (see also Table 4).

Table 4. Crystal data and structure refinement details for [(**1**)OPEt$_3$][OTf] and [(**1**)OH$_2$][OTf].

	[(**1**)OPEt$_3$][OTf]	[(**1**)OH$_2$][OTf]
Formula	$C_{28}H_{35}BF_{12}O_4P_2S$	$C_{22}H_{22}BF_{12}O_4PS$
FW	768.37	652.24
Color, shape	colorless, block	colorless, plate
Temperature [°C]	–100(2)	–100(2)
Radiation	Mo-K_α, 0.71073 Å	Mo-K_α, 0.71073 Å
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$	$C2/c$
a [Å]	11.4760(4)	20.2478(13)
b [Å]	14.7143(5)	16.5460(9)
c [Å]	21.5525(8)	18.0243(12)
α [°]	86.549(3)	90
β [°]	89.043(3)	119.441(5)
γ [°]	67.235(3)	90
V [Å^3]	3349.7(2)	5258.7(6)
Z	4	8
$D_{calcd.}$ [g cm^{-3}]	1.524	1.648
$F(000)$	1576	2640
μ [mm^{-1}]	0.293	0.299
Crystal size [mm]	0.35 × 0.29 × 0.27	0.33 × 0.18 × 0.09
Reflections collected	41059	35094
Indep. reflections (R_{int})	11828 (0.0709)	6041 (0.0567)
Data/restraints/parameters	11828/0/866	6041/0/378
GOOF on F^2	1.054	1.055
$R1$, $wR2$ [$I > 2\sigma(I)$]	0.0626, 0.1661	0.0352, 0.0947
$R1$, $wR2$ (all data)	0.0707, 0.1786	0.0406, 0.0976
Largest diff. peak and hole [e Å^{-3}]	1.041/–0.553	0.325/–0.454

CCDC-841735 {(**2**)Cl}, -841736 {[(**1**)OPEt$_3$][OTf]}, -841737 {[(**1**)py][OTf]}, -846304 {[(**1**)OH$_2$][OTf]}, -841738 {(**1**)O*i*Pr × C$_6$H$_6$}, and -841739 {(**4**)Cl} contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

^{31}P{^{1}H} MAS NMR Spectroscopic Measurements: ^{31}P{^{1}H} solid-state MAS NMR spectroscopic experiments were carried out with a Bruker Avance WB 600 spectrometer equipped with a 4 mm MAS DVT double resonance probe at Larmor frequencies of 600.1 and 150.9 MHz for ^{1}H and ^{31}P, respectively. Single-pulse excitation spectra were recorded by using 10 kHz sample spinning, a 4 μs excitation pulse, and 100 kHz SPINAL64[46] ^{1}H decoupling during the acquisition time of 50 ms (recycle delay: 5 s). The spectrum was acquired with 128 transients and was referenced to 85% H_3PO_4 indirectly by setting the central line of crystalline triethylphosphane sulfide to 58.4 ppm.

Supporting Information (see footnote on the first page of this article): Synthesis and analytical data of $(C_6F_5)_2B(OiPr)$ and (**1**)O*i*Pr; synthesis and NMR spectroscopic characterization of $Me_2P(tBu)$ and $LiCH_2P(Me)(tBu)$. Selected crystallographic data, plots of the molecular structures, and selected geometric parameters of [(**1**)py][OTf], (**1**)O*i*Pr × C$_6$H$_6$, (**2**)Cl, and (**4**)Cl. ^{31}P{^{1}H} NMR spectrum of [(**1**)OPEt$_3$][OTf] in CD_2Cl_2 solution and ^{31}P{^{1}H} MAS NMR spectrum in the solid state. NMR spectroscopic data of [**2**][WCA].

Acknowledgments

The authors gratefully acknowledge financial support by the Beilstein Institut, Frankfurt/Main, Germany, within the research collaboration NanoBiC. We wish to thank Dr. Johanna Becker-Baldus (BMRZ, AK Glaubitz, Institute of Biophysical Chemistry, Goethe University, Frankfurt) for solid-state ^{31}P{^{1}H} MAS NMR spectroscopic measurements.

[1] K. Ishihara, H. Yamamoto, *Eur. J. Org. Chem.* **1999**, 527–538.
[2] E. Y.-X. Chen, T. J. Marks, *Chem. Rev.* **2000**, *100*, 1391–1434.
[3] E. J. Corey, *Angew. Chem.* **2002**, *114*, 1724–1741; *Angew. Chem. Int. Ed.* **2002**, *41*, 1650–1667.
[4] H. Butenschön, *Angew. Chem.* **2008**, *120*, 3544–3547; *Angew. Chem. Int. Ed.* **2008**, *47*, 3492–3495.
[5] D. W. Stephan, *Dalton Trans.* **2009**, 3129–3136.
[6] D. W. Stephan, G. Erker, *Angew. Chem.* **2010**, *122*, 50–81; *Angew. Chem. Int. Ed.* **2010**, *49*, 46–76.
[7] Y. Kim, T. W. Hudnall, G. Bouhadir, D. Bourissou, F. P. Gabbaï, *Chem. Commun.* **2009**, 3729–3731.
[8] Y. Kim, H. Zhao, F. P. Gabbaï, *Angew. Chem.* **2009**, *121*, 5057–5060; *Angew. Chem. Int. Ed.* **2009**, *48*, 4957–4960.
[9] T. W. Hudnall, C.-W. Chiu, F. P. Gabbaï, *Acc. Chem. Res.* **2009**, *42*, 388–397.
[10] C. R. Wade, A. E. J. Broomsgrove, S. Aldridge, F. P. Gabbaï, *Chem. Rev.* **2010**, *110*, 3958–3984.
[11] V. C. Williams, W. E. Piers, W. Clegg, M. R. J. Elsegood, S. Collins, T. B. Marder, *J. Am. Chem. Soc.* **1999**, *121*, 3244–3245.
[12] V. C. Williams, G. J. Irvine, W. E. Piers, Z. Li, S. Collins, W. Clegg, M. R. J. Elsegood, T. B. Marder, *Organometallics* **2000**, *19*, 1619–1621.
[13] M. H. Lee, T. Agou, J. Kobayashi, T. Kawashima, F. P. Gabbaï, *Chem. Commun.* **2007**, 1133–1135.
[14] T. W. Hudnall, Y.-M. Kim, M. W. P. Bebbington, D. Bourissou, F. P. Gabbaï, *J. Am. Chem. Soc.* **2008**, *130*, 10890–10891.
[15] a) G. C. Welch, L. Cabrera, P. A. Chase, E. Hollink, J. D. Masuda, P. Wei, D. W. Stephan, *Dalton Trans.* **2007**, 3407–3414; b) M. Ullrich, A. J. Lough, D. W. Stephan, *J. Am. Chem. Soc.* **2009**, *131*, 52–53.

[16] E. J. Corey, T. Shibata, T. W. Lee, *J. Am. Chem. Soc.* **2002**, *124*, 3808–3809.
[17] D. H. Ryu, T. W. Lee, E. J. Corey, *J. Am. Chem. Soc.* **2002**, *124*, 9992–9993.
[18] G. Zhou, E. J. Corey, *J. Am. Chem. Soc.* **2005**, *127*, 11958–11959.
[19] G. C. Welch, D. W. Stephan, *J. Am. Chem. Soc.* **2007**, *129*, 1880–1881.
[20] P. Spies, S. Schwendemann, S. Lange, G. Kehr, R. Fröhlich, G. Erker, *Angew. Chem.* **2008**, *120*, 7654–7657; *Angew. Chem. Int. Ed.* **2008**, *47*, 7543–7546.
[21] A. Schnurr, H. Vitze, M. Bolte, H.-W. Lerner, M. Wagner, *Organometallics* **2010**, *29*, 6012–6019.
[22] The free Lewis acids were generated from the chloro adducts (**A**)Cl (R^1 = C_6F_5 or C_6H_5, R^2 = F, R^3 = *t*Bu) and $[Ag(CH_2Cl_2)][Al(O(tBu^F))_4]$ in CH_2Cl_2. Parallel to us, Stephan et al. published the synthesis of a mixture of (**A**)F and (**A**)Cl (R^1 = C_6F_5, R^2 = F, R^3 = *t*Bu), cf. X. Zhao, T. M. Gilbert, D. W. Stephan, *Chem. Eur. J.* **2010**, *16*, 10304–10308.
[23] a) U. Mayer, V. Gutmann, W. Gerger, *Monatsh. Chem.* **1975**, *106*, 1235–1257; b) V. Gutmann, *Coord. Chem. Rev.* **1976**, *18*, 225–255.
[24] M. A. Beckett, G. C. Strickland, J. R. Holland, K. S. Varma, *Polymer* **1996**, *37*, 4629–4631.
[25] M. A. Beckett, D. S. Brassington, S. J. Coles, M. B. Hursthouse, *Inorg. Chem. Commun.* **2000**, *3*, 530–533.
[26] I. Krossing, *Chem. Eur. J.* **2001**, *7*, 490–502.
[27] J. A. Davies, S. Dutremez, A. A. Pinkerton, *Inorg. Chem.* **1991**, *30*, 2380–2387.
[28] R. F. Childs, D. L. Mulholland, A. Nixon, *Can. J. Chem.* **1982**, *60*, 801–808.
[29] F. Focante, P. Mercandelli, A. Sironi, L. Resconi, *Coord. Chem. Rev.* **2006**, *250*, 170–188.
[30] G. R. Fulmer, A. J. M. Miller, N. H. Sherden, H. E. Gottlieb, A. Nudelman, B. M. Stoltz, J. E. Bercaw, K. I. Goldberg, *Organometallics* **2010**, *29*, 2176–2179.
[31] C. Bergquist, B. M. Bridgewater, C. J. Harlan, J. R. Norton, R. A. Friesner, G. Parkin, *J. Am. Chem. Soc.* **2000**, *122*, 10581–10590.
[32] A. A. Danopoulos, J. R. Galsworthy, M. L. H. Green, S. Cafferkey, L. H. Doerrer, M. B. Hursthouse, *Chem. Commun.* **1998**, 2529–2530.
[33] $(C_6F_5)_2B(OEt)$ has been prepared through the reaction of $F_3B{\cdot}OEt_2$ with C_6F_5MgBr in Et_2O (cf. ref.[38]). We note that a more general route to alkoxyboranes $(C_6F_5)_2B(OR)$ is provided by the reaction of anhydrous alcohols HOR with the conveniently accessible adduct $(C_6F_5)_2BH{\cdot}SMe_2$ (cf. A.-M. Fuller, D. L. Hughes, S. J. Lancaster, C. M. White, *Organometallics* **2010**, *29*, 2194–2197 and ref.[39]). Compounds $(C_6F_5)_2B(OR)$ can be used for the synthesis of a broad palette of phosphonium borates (**1**)OR (see the Supporting Information for the synthesis and full characterization of (**1**)O*i*Pr).
[34] F. Eisenträger, A. Göthlich, I. Gruber, H. Heiss, C. A. Kiener, C. Krüger, J. U. Notheis, F. Rominger, G. Scherhag, M. Schultz, B. F. Straub, M. A. O. Volland, P. Hofmann, *New J. Chem.* **2003**, *27*, 540–550.
[35] Selected references: a) ref.[1]; b) ref.[16]; c) ref.[17]; d) ref.[18]
[36] D. H. Ryu, E. J. Corey, *J. Am. Chem. Soc.* **2003**, *125*, 6388–6390.
[37] M. Ouchi, M. Kamigaito, M. Sawamoto, *Macromolecules* **2001**, *34*, 3176–3181.
[38] R. Duchateau, S. J. Lancaster, M. Thornton-Pett, M. Bochmann, *Organometallics* **1997**, *16*, 4995–5005.
[39] A. Schnurr, K. Samigullin, J. M. Breunig, M. Bolte, H.-W. Lerner, M. Wagner, *Organometallics* **2011**, *30*, 2838–2843.
[40] A. Rodriguez-Delgado, E. Y.-X. Chen, *Inorg. Chim. Acta* **2004**, *357*, 3911–3919.
[41] W. D. Jones, V. L. Kuykendall, *Inorg. Chem.* **1991**, *30*, 2615–2622.
[42] R. H. Blessing, *Acta Crystallogr., Sect. A* **1995**, *51*, 33–38.
[43] A. L. Spek, *J. Appl. Crystallogr.* **2003**, *36*, 7–13.
[44] G. M. Sheldrick, *Acta Crystallogr., Sect. A* **1990**, *46*, 467–473.
[45] G. M. Sheldrick, *SHELXL-97. A Program for the Refinement of Crystal Structures*, University of Göttingen, Göttingen, Germany, **1997**.
[46] B. M. Fung, A. K. Khitrin, K. Ermolaev, *J. Magn. Reson.* **2000**, *142*, 97–101.

Received: October 11, 2011
Published Online: November 24, 2011

