Organocatalysis

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Anion-Binding Catalysis by Electron-Deficient Pyridinium Cations**

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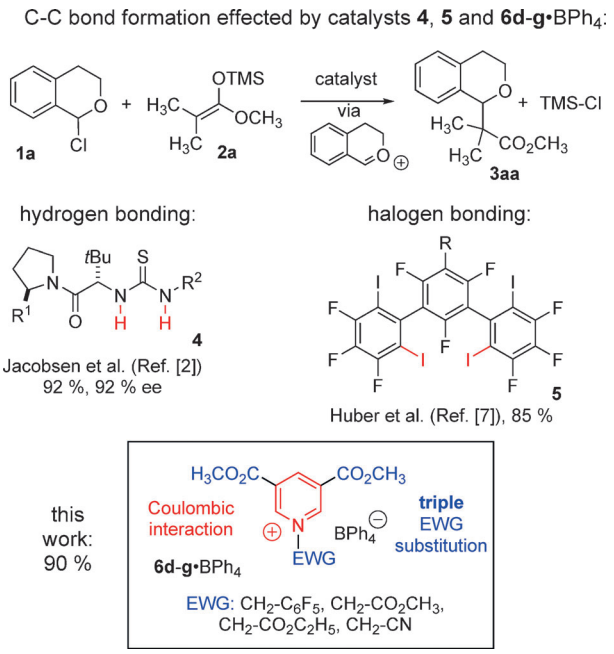
Abstract: *A new activation principle in organocatalysis is presented: halide binding through Coulombic interactions. This mode of catalysis was realized by using 3,5-di(carbomethoxy)pyridinium ions that carry an additional electron-withdrawing substituent on the nitrogen atom, for example, pentafluorobenzyl or cyanomethyl. For the N-pentafluorobenzyl derivative, Coulombic interaction with the pyridinium moiety is complemented in the solid state by anion–π interactions with the perfluorophenyl ring. Bromide and chloride are bound by these cations in a 1:1 stoichiometry. Catalysis of the C–C coupling between 1-chloroisochroman (and related electrophiles) with silyl ketene acetals occurs at −78 °C and at low catalyst loading (2 mol %).*

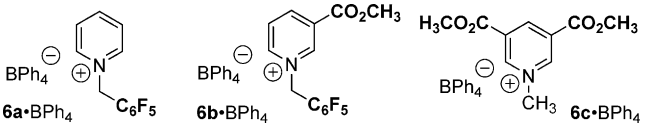
Anion-binding catalysis,[1] in which the catalyst facilitates the release of an anion from one of the starting materials by binding it in a reversible fashion, is a relatively new concept in noncovalent organocatalysis. A prominent example was reported by Jacobsen et al. in 2008,[2] with hydrogen bonding as the anion-binding motif.[3] The chiral thiourea **4** shown in Scheme 1 abstracts chloride from the substrate **1a** to furnish an oxonium cation, which is then alkylated by the silyl ketene acetal **2a**. Since the prochiral oxonium cation intermediate in the C–C bond forming step carries a chiral counterion (**4**·Cl^-), the alkylation product **3aa** is formed not only in high yield but also with superb enantioselectivity.

There are alternatives to hydrogen bonding in anion binding, in particular halogen bonding (Scheme 1).[4] The latter has been studied intensively as a structure-determining factor in crystal engineering, and recent results point to it as an important force in the interaction between proteins/enzymes and halogenated ligands (e.g. enzyme inhibitors).[5] It was not until recently that the promotion of chemical reactions through halogen bonding was proven experimentally.[6] In 2013, Huber et al. disclosed that the neutral double halogen-bond donor **5** catalyzes the reaction between 1-chloroisochroman (**1a**) and the silyl ketene acetal **2a** (Scheme 1).[7] It is assumed that the promotion of oxonium ion formation from the substrate **1a** by chloride excision underlies the catalytic activity of the neutral halogen-bond-donor catalyst **5**, just as it does for the hydrogen-bond donor **4**. Yet another mode of anion binding hinges on the interaction of anions with electron-poor π surfaces[8,9]—a process for which Matile et al. have recently reported first catalytic applications.[10,11]



Scheme 1. Organocatalytic α-haloether alkylation and anion-binding motifs: hydrogen bonding, halogen bonding, and Coulombic interaction with electron-deficient pyridinium cations (this work).

Our goal was to exploit electron-deficient pyridinium cations for anion-binding catalysis.[12] Our attention was drawn to pyridinium ions because their halide-binding ability is well documented, with regard to both structure[13] and complex stabilities.[14] Our attempts to effect the 1-chloroisochroman alkylation shown in Scheme 1 with pyridinium ions carrying one (**6a**·BPh_4) or two electron-withdrawing substituents (**6b**·BPh_4; **6c**·BPh_4) met with frustration. Therefore, further reduction of electron density in the pyridinium core



was sought by attaching a third electron-withdrawing substituent. This approach led to the triply substituted pyridinium salts **6d**·BPh_4, **6e**·BPh_4, **6f**·BPh_4, and **6g**·BPh_4 (Scheme 2), and afforded the first organocatalysts that

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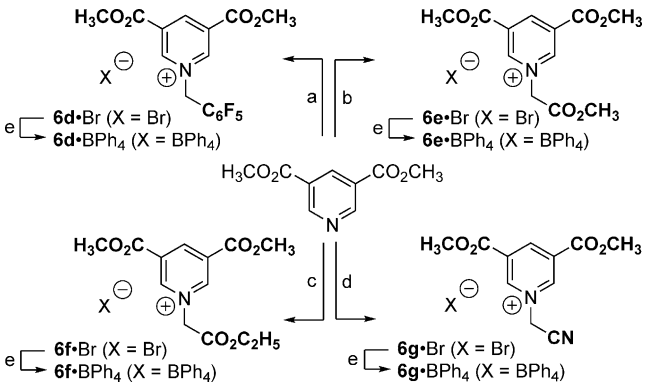


Scheme 2. Preparation of the pyridinium salts **6d–g**: a) $C_6F_5CH_2Br$, 49%; b) $BrCH_2CO_2CH_3$, 83%; c) $BrCH_2CO_2C_2H_5$, 94%; d) $BrCH_2CN$, 87%; e) tetraphenylborates by anion exchange in aqueous $NaBPh_4$, 82–96%.

promote 1-chloroisochroman alkylation through Coulombic anion binding.

As summarized in Scheme 2, the *N*-benzylation/alkylation of 3,5-dicarbomethoxypyridine smoothly afforded the pyridinium bromides **6d–g**·Br. The X-ray crystal structure of the 3,5-dicarbomethoxypyridinium bromide **6d**·Br is shown in Figure 1a. As with the other pyridinium halides (see Figure 1b for the structure of **6g**·Br and the Supporting Information for the X-ray crystal structures of **6e**·Br and the pyridinium iodide **6c**·I), a pertinent feature is the charge-dominated interaction between the bromide ion and the pyridinium moiety.[13,14] However, there is an additional intramolecular contact between the centroid of the pentafluorophenyl ring and the bromide ion. The distance between the two ($d_{Hal-C_6F_5} = 3.409$ Å) is shorter than the sum of the van der Waals radii ($d = 3.52$ Å), thus indicating anion–π bonding. We were also able to generate and crystallize the isostructural chloride equivalent of the pyridinium bromide **6d**·Br, that is, **6d**·Cl (see below), for the generation of **6d**·Cl, see Supporting Information for X-ray data). In the last step of catalyst preparation, the bromides **6d–g**·Br were converted into the tetraphenylborates **6d–g**·BPh_4, with anion metathesis being enforced by precipitation of the products **6d–g**·BPh_4 from aqueous $NaBPh_4$. The X-ray crystal structure of **6d**·BPh_4 is shown in Figure 1c (see the Supporting Information for the X-ray crystal structures of **6a–c,e–g**·BPh_4). There is tight stacking of one of the tetraphenylborate phenyl rings with the pyridinium unit, and another of the tetraphenylborate phenyl rings stacks with the C_6F_5 moiety (see the Supporting Information for packing diagrams).

As may be expected from their crystal structures, the bromide **6d**·Br and the tetraphenylborate **6d**·BPh_4 show significantly different chemical shifts for the resonances of the 2,6-protons on the pyridinium ring, and even more so for the protons of the benzylic methylene group. An approximately 2 ppm upfield shift of the benzyl ^1H resonance results from exchange of bromide for tetraphenylborate (see the Supporting Information for the spectral data). To investigate chloride binding, ^1H NMR spectroscopy was applied in titration experiments (Figure 2) that 1) showed a thermodynamic preference for chloride over tetraphenylborate binding, with a formal association constant for **6d**·Cl (from **6d**·BPh_4 and

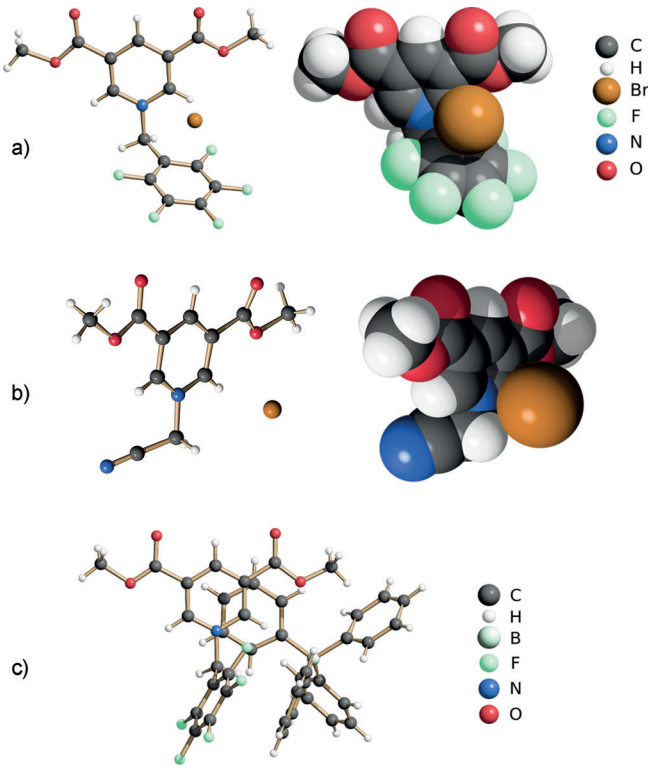


Figure 1. X-Ray crystal structures of **6d**·Br (a), **6g**·Br (b), and **6d**·BPh_4 (c).

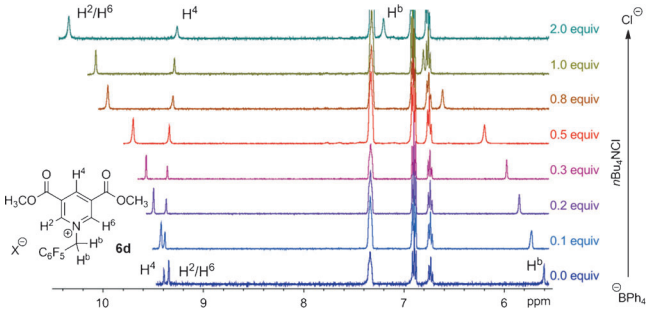
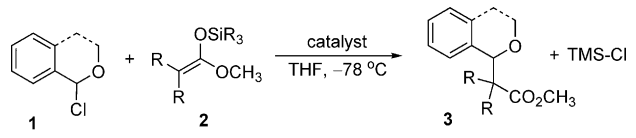


Figure 2. Changes in the ^1H NMR spectra resulting from the titration of **6d**·BPh_4 against nBu_4NCl; [D_8]THF/CD_3CN 9:1 (v/v), RT.

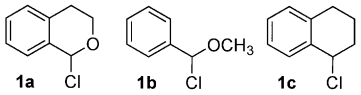
TBACl) in the range of 200 M^{-1} (see the Supporting Information for titration curves), and 2) confirmed the 1:1 stoichiometry of chloride binding in solution (see the Supporting Information for Job plots).

Catalytic activity, as summarized in Table 1, was assessed by adding the nucleophiles **2a–e** to a precooled solution of the catalysts **6d–g**·BPh_4 and the electrophiles **1a**, **1b**, or **1c** in THF, and quenching with sodium methoxide (excess in methanol) after 12 h at −78 °C. Note that there is no measurable background reaction between the most reactive substrate **1a** and any of the silyl ethers **2a–e** at −78 °C, over 12 h (Table 1, entry 1). After evaporation of the solvent, the

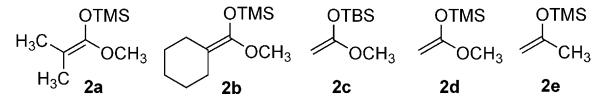
Table 1: Catalytic activity of the pyridinium salts **6d**–**g**·BPh_4 and **6d**·Br (Scheme 2) in the reaction of the electrophiles **1a**–**c** with the silyl ether nucleophiles **2a**–**e**.



electrophiles:



nucleophiles:



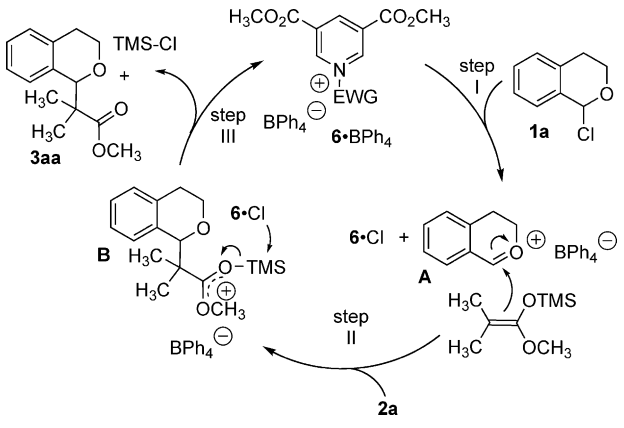
Entry[a]	Electrophile **1**	Nucleophile **2**	Pyridinium salt **6**	Catalyst Loading [mol%]	Conversion of **1** [%]	Yield of **3** [%]
1	**1a**	**2a**–**e**	none	–	0	–
2	**1a**	**2a**	**6d**·BPh_4	5	quant.	90[b]
3	**1a**	**2a**	**6d**·BPh_4	2	quant.	89[b]
4	**1a**	**2b**	**6d**·BPh_4	5	quant.	92[b]
5	**1a**	**2c**	**6d**·BPh_4	5	77	70[b]
6	**1a**	**2d**	**6d**·BPh_4	5	82	n.d.
7	**1a**	**2e**	**6d**·BPh_4	5	0	–
8	**1b**	**2a**	**6d**·BPh_4	10	quant.	83[b]
9	**1b**	**2b**	**6d**·BPh_4	10	quant.	86[b]
10	**1b**	**2c**	**6d**·BPh_4	10	ca. 80[c]	48[b,d]
11	**1b**	**2d**	**6d**·BPh_4	10	ca. 80[c]	56[b,d]
12	**1c**	**2a**	**6d**·BPh_4	10	0	–
13	**1a**	**2a**	**6e**·BPh_4	5	quant.	85
14	**1a**	**2a**	**6f**·BPh_4	5	quant.	87
15	**1a**	**2a**	**6g**·BPh_4	5	quant.	88
16	**1a**	**2a**	**6d**·Br[e]	5	0	–
17	**1a**	**2a**	**6d**·BPh_4[f]	5	<10	–
18	**1a**	**2a**	none[g]	–	0	–

[a] All reactions were carried out at −78 °C in THF for 12 h, as described in the Experimental Section. [b] Yield of isolated product **3** after column chromatography. [c] Methanolate induced partial elimination to methyl cinnamate, thus complicating quantitative analysis. [d] A different workup was required for product isolation (see the Supporting Information). [e] Acetonitrile (10 vol%) was added. [f] 10 mol% tetra-*n*-butylammonium chloride was added. [g] 10 mol% of TMS-Cl or BPh_3 was added.

ratio of alkylation product **3** to nonreacted electrophile could easily be determined by ^{1}H NMR integration of, for example, the proton at the C1 position of the isochroman **3aa** ($\delta =$ 5.17 ppm) versus the C1−H of the methyl acetal ($\delta =$ 5.45 ppm) that result from the quenching of unreacted **1a** with methanolate. As shown in Table 1, the conversions determined by this method coincide well with the gravimetrically determined product yields following chromatographic isolation. The alkylation of 1-chloroisochroman (**1a**) by the silyl ketene acetal **2a** with the catalyst **6d**·BPh_4 was additionally monitored by low-temperature ^{1}H NMR spectroscopy. The concentration/time profiles thus obtained confirmed smooth and parallel conversion of the starting materials, and concomitant formation of the reaction products. There was no evidence for the build-up of reaction intermediates (see the Supporting Information).

The results summarized in Table 1 allow the following conclusions: 1) Most importantly, the triply substituted pyridinium tetrafluoroborates **6d**–**g**·BPh_4 indeed act as efficient catalysts for the alkylation of 1-chloroisochroman (**1a**) and also of the acyclic chlorobenzyl ether **1b**, with all four of the silyl ketene acetals (**2a**–**d**) tested (Table 1, entries 2–6,8–11,13–15). For the more reactive electrophile **1a** in combination with the silyl ketene acetal **2a**, catalyst loading as low as 2 mol% is sufficient to achieve full conversion within a few hours at −78 °C (entry 3). 2) Substrate scope: both chlorobenzyl ethers **1a** and **1b** are transformed smoothly. However, 1-chlorotetralin (**1c**) is not reactive (i.e. readily ionizable) enough to be alkylated by the silyl ketene acetal **2a** (Table 1, entry 12). The same holds for the silyl enol ether **2e** as the nucleophile, even with the most reactive electrophile **1a** (entry 7).[15] 3) Despite lower steric hindrance at their nucleophilic α-carbon atoms, the α-unsubstituted silyl ketene acetals **2c** and **2d** give lower conversions and product yields relative to their dimethyl (**2a**) and cyclohexylidene (**2b**) analogues (entries 5,6 versus 2,4 and 10,11 versus 8,9). We attribute this effect to competing and irreversible catalyst deactivation owing to C4 alkylation of the pyridinium moiety,[16] an effect that occurs at the low reaction temperature only for the unsubstituted silyl ketene acetals **2c** and **2d** and not for **2a** and **2b**. 4) Catalyst inhibition by halides: as shown in Table 1, entry 17, the catalytic activity of the tetraphenylborate **6d**·BPh_4 is strongly inhibited by addition of tetra-*n*-butylammonium chloride. Unsurprisingly, the pyridinium bromide **6d**·Br is catalytically inactive (Table 1, entry 16). 5) An additional control experiment confirmed that neither TMS-Cl nor BPh_3 catalyze the reaction between **1a** and **2a** (Table 1, entry 18).

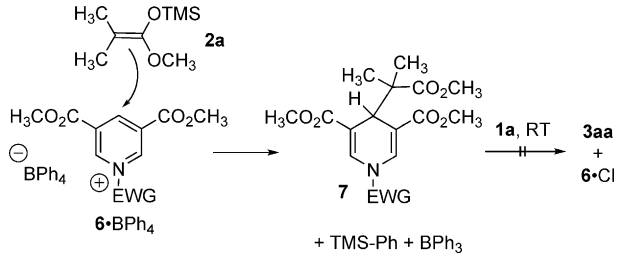
Scheme 3 summarizes our mechanistic interpretation of the catalysis effected by the tetraphenylborates **6d**–**g**·BPh_4, as exemplified by the substrates **1a** and **2a**. Step I consists of the ionization of the substrate **1a** to the oxonium cation **A**. Halide excision from **1a** is effected by Coulombic interaction with the pyridinium catalyst **6**·BPh_4, with concomitant formation



Scheme 3. Mechanistic proposal for the alkylation of the α-haloether **1a** by the silyl ketene acetal **2a**, catalyzed by the halide-binding pyridinium cations **6d**–**g**·BPh_4.

of **6**·Cl. In fact, when the catalyst **6d**·BPh_4 is exposed to 1-chloroisochroman (**1a**) alone, in THF at RT, crystalline **6d**·Cl starts to precipitate after approximately one day (material used for the X-ray crystal structure shown in the Supporting Information). In step II of the catalytic cycle, C–C bond formation occurs as the oxonium cation **A** is attacked by the silyl ketene acetal **2a**, thereby resulting in the cationic species **B**. The cation **B** acts as a highly reactive silylating agent and transforms the chloride **6**·Cl back into the active catalyst **6**·BPh_4, with concomitant formation of the product **3aa** and TMS-Cl (step III). Chloride excision from substrate **1a** by cation **B**, that is, a "shortcut" chain reaction not involving step III, can be excluded based on control experiments (see the Supporting Information): AgO_2CCF_3 or $NaBPh_4$ as chloride traps in the absence of a catalyst **6**·BPh_4 induce just stoichiometric conversion of the substrate **1a**.[17]

Yet another alternative pathway may be envisaged in which a covalent intermediate (**7**) is generated from the pyridinium catalyst **6**·BPh_4 by attack of the nucleophile **2a** at C4 (Scheme 4). Compounds of type **7** have recently been



Scheme 4. C4 Alkylation of catalysts **6**·BPh_4 by the silyl ketene acetal **2a**.

reported to transfer their C4 substituent to reactive electrophiles, albeit slowly and at temperatures above 100 °C.[18] However, the typical ^{1}H NMR resonances of compound **7** were not detectable under in situ monitoring conditions (200 K) and nor does isolated **7** undergo any transformation when exposed to the electrophile **1a**, even at room temperature for >20 h. We therefore conclude that no covalent intermediate is involved in the catalytic cycle.

In summary, we describe a new motif for organocatalysis: anion binding by electron-deficient pyridinium cations. To our knowledge, this is the first case of anion-binding catalysis effected solely by Coulombic interactions. The first representatives of this novel type of organocatalyst appear to show effectiveness similar to hydrogen-bonding thioureas and exceed halogen-bonding catalysts with regard to reaction rate. Further work to explore the scope of this novel anion-binding motif is underway.

Experimental Section

Alkylation of 1-chloroisochroman (**1a**) by silyl ketene acetal **2a**, catalyzed by 3,5-dicarbomethoxy *N*-[(pentafluorophenyl)methyl]pyridinium tetraphenylborate (**6d**·BPh_4): Catalyst **6d**·BPh_4 (3.50 mg, 2.00 μmol, 0.05 equiv) was dissolved in 1.00 mL anhydrous THF in a Schlenk flask in a glove box. To this mixture, 100 μL of a 1.0 M solution of 1-chloroisochroman (**1a**, 0.10 mmol, 1.00 equiv) in anhydrous THF was added, followed by another 1.00 mL of anhydrous THF. The reaction vessel was sealed with a rubber septum and taken from the glovebox. The solution was cooled to −78 °C with stirring. After 10 min, the silyl ketene acetal **2a** (30 μL, 0.15 mmol, 1.50 equiv) was added. After stirring for another 12 h at −78 °C, the reaction was quenched by adding a solution of sodium methoxide in methanol (30 wt %, 200 μL, 10.0 equiv) at −78 °C. The solution was diluted with 2 mL of an *n*-pentane/diethyl ether (1:1) mixture, filtered through silica, and thoroughly eluted with *n*-pentane/diethyl ether (1:1). The solvent was evaporated under reduced pressure, and the remaining crude product was subjected to column chromatography (silica gel, *n*-pentane/diethyl ether 9:1). The product **3aa** was obtained as a clear liquid (42.0 mg, 0.18 mmol, 90 %). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta =$ 7.19 (m, 3H), 6.97 (m, 1H), 5.17 (s, 1H), 4.16 (ddd, $J = 10.7$, 5.3, 1.6 Hz, 1H), 3.75 (s, 3H), 3.60 (m, 1H), 3.04 (ddd, $J = 15.6$, 12.0, 5.3 Hz, 1H), 2.54 (d, $J = 15.8$ Hz, 1H), 1.12 (s, 3H), 1.10 ppm (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 177.5$, 136.4, 134.7, 128.7, 126.4, 125.8, 125.7, 80.1, 63.9, 51.9, 49.0, 30.2, 21.1, 20.9 ppm; ESI-MS: 257.1 $[M+Na]^+$; IR (ATR): $\tilde{\nu} =$2953, 2870, 1743, 1693, 1384, 1153, 985, 746 cm^{-1}.

CCDC 983184 (**6d**·Br), 983185 (**6d**·BPh_4), 983186 (**6c**·I), 983187 (**6c**·BPh_4), 983188 (**6d**·Cl), 983189 (**6b**·BPh_4), 983190 (**6a**·BPh_4), 1002110 (**6f**·BPh_4), 1002111 (**6g**·Br), 1002112 (**6e**·Br), und 1002113 (**6e**·BPh_4) 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.

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