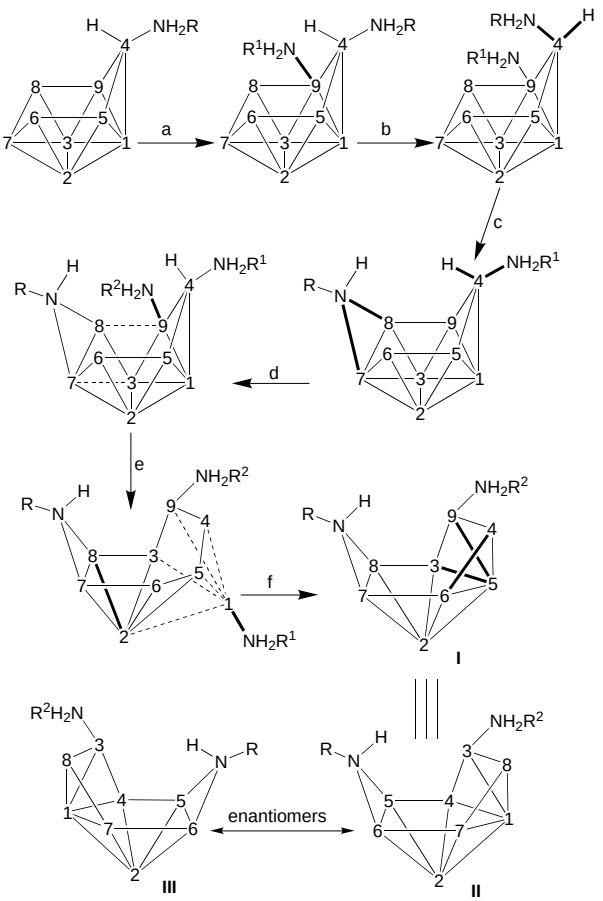

Scheme 2. Mechanistic pathway of the conversion of the nonaborane cluster into the azanonaborane cluster (**I** IUPAC numbering of the B_9 cluster, **II** and **III** IUPAC numbering of the B_8N cluster).[10] Bold lines: new bonds; dashed lines: bonds to be broken.

experiments with the Et- and Br-substituted clusters) and B^3 (concluded from the experiments with a tetradeuterated cluster). Computed ^{11}B NMR chemical shifts, supported by 2D–^{11}B COSY and ^1H CW ^{11}B NMR spectra showed the Et group to be connected to B^6, opposite to the *exo*-amino ligand at B^3 in the B_8N cluster **9**; the data further indicated that the Br atom at B^6 in the B_9 cluster **5** is located at B^7 and not at B^4 in the B_8N cluster **11**. The fate of the boron atoms B^5, B^8, and B^9 has not been clarified, but the proposed mechanism would require only a minimal rearrangement of the bonds (one DSD rearrangement and the closing of the cluster after the loss of B^1). The loss of B^1, which is *not* part of the open face, is surprising. Quantum-mechanical computations might give indications about the feasibility of the proposed pathway, the relative stability of the proposed intermediates, the origin of the H atoms which leave together with B^1, and the rearrangement of the other H atoms.

Experimental Section

1, **8**–**12**: Isopropylamine (0.1 g, 1.74 mmol) was added to a solution of $(Me_2S)B_9H_{13}$ in dry benzene (10 mL, 0.1 g) at room temperature. The mixture was heated to reflux for 3 h. All volatile components were removed under vacuum and the resulting substance was recrystallized from ethanol:water (1:1). Compounds **8** and **9** were purified by TLC by using CH_2Cl_2 as eluent ($R_f = 0.31$). For further purification the substance was dissolved in $CHCl_3$:hexane (1:3) at −20 °C. The solution was filtered and the resulting filtrate was evaporated to dryness to yield the purified product. **1** (DCI): *m*/*z* (%) 214 (95) [M^+]; **8**, **9** MS (EI, 750 eV, 200 °C): *m*/*z* (%) 242 (24) [M^+]; **10**, **11**, (EI, 750 eV, 200 °C): *m*/*z* (%) 293 (18) [M^+]; **12** (FAB$^+$): *m*/*z* (%) 217 (100) [M^+].

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Fluorous Biphasic Catalysis without Perfluorinated Solvents: Application to Pd-Mediated Suzuki and Sonogashira Couplings**

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In catalytic reactions easy handling of the catalyst together with its straightforward recovery and possible reuse remain an important topic. A widespread solution to reach these goals is the application of immobilized catalysts. Immobilization can be achieved by covalent attachment to organic polymers or inorganic support materials.[1] Alternatively, catalysts can be adsorbed on silica gel[2–4] or on reversed-phase silica gel.[5] In some cases the immobilization has a beneficial effect on the catalyst's stability.[6,7] One profound advantage of such supported catalysts is the easy separation from the reaction

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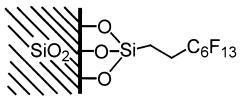
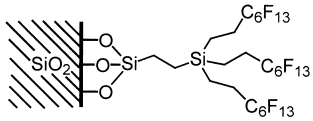
product by filtration or decantation. Ideally, without further purification, there should be little or no contamination of the product with transition metals, which is important when the substances are to be tested in biological assays. A further aspect is the straightforward recovery and reuse of the catalyst. Generally, simplification of workup protocols and handling of small amounts of catalysts is especially important in multiparallel and automated synthesis in combinatorial chemistry.[8,9]

Biphasic systems comprising perfluoro-tagged catalysts, which can be extracted out of organic products with fluorous solvents, have emerged as alternative tools for the separation, recovery, and reuse of catalysts as well as for simplified product isolation.[10–15] This method, known as fluorous biphasic catalysis (FBC), has been applied to numerous catalytic reactions.[8,10,16–31] Although perfluorinated solvents have certain advantages, they are expensive and environmentally persistent.[32] Thus, it would be beneficial to perform separation and recovery of perfluoro-tagged catalysts without recourse to a perfluorinated solvent as a second liquid phase. Recently, the thermomorphic solution behavior of a fluorous phosphane was utilized in this context.[33] While fluorous reversed-phase silica gel (FRPSG) has found application as the stationary phase for chromatographic separation of perfluoro-tagged compounds,[34,35] it has not been used to support catalysts.

Our rational was to substitute fluorous solvents by FRPSG, thus gaining easy separation and at the same time retaining the advantages of soluble perfluoro-tagged catalysts. As a first example for this strategy, we report on the immobilization of perfluoro-tagged bis(triphenylphosphane)palladium complexes on FRPSG and their successful application to the Suzuki and Sonogashira C–C coupling reactions without need for a fluorous solvent.



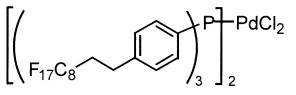
1



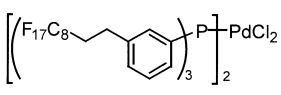
2

The fluorous solid supports **1** and **2** were prepared by adapted standard procedures.[36,37] Palladium complexes **3a–c**were synthesized by our established procedures.[30]

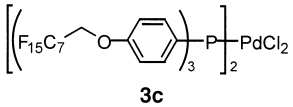
To immobilize the complexes, FRPSG was added to a solution of the respective complex in diethyl ether and hexafluorobenzene and the solvent was evaporated. The immobilized precatalyst is an air-stable, free-flowing powder. For ease of handling, especially in separations, FRPSG with a coarse grain (100–300 μm particle size) was used. Silica gels **1** containing 0.1, 1.0, 10, and 100 mg complex per g FRPSG, respectively, were evaluated in the Suzuki cross-coupling of phenylboronic acid and *para*-nitrobromobenzene and in the Sonogashira coupling of phenylacetylene and *para*-nitrobromobenzene (Table 1).



3a



3b



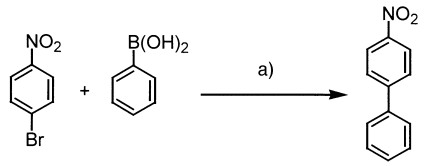
3c

Table 1. Suzuki and Sonogashira reactions with different amounts of complex **3a**.

Entry	Catalyst loading of FRPSG [mg g^{-1}]	Catalyst loading [mol%]	Yield [%][a]
Suzuki			
1	100	1.5	> 98 (> 98, 92)
2	10	0.1	> 98 (> 98)
3	1	0.01	> 98 (> 98)
4	0.1	0.001	86 (45)
Sonogashira			
5	100	2	> 98 (97, 71)
6	10	0.2	> 98 (30, 0)
7	1	0.02	22 (0)
8	0.1	0.002	11 (0)

[a] The yields in parentheses are for the second (and third) runs with the same catalyst.

In the Suzuki reaction (Scheme 1) complete conversions were obtained with catalyst loadings down to 0.01 mol% and the catalyst could be recycled (Table 1, entries 1–3). With 0.001 mol% of catalyst, the yield in the first run was 86% and dropped to 45% in the second run (Table 1, entry 4). This corresponds to a cumulated turnover number (TON) of 131 000.



Scheme 1. Suzuki reactions performed with **3a–c** immobilized on support **1** as catalysts. a) 0.001–1.5 mol% catalyst, DME, 2 M aq. Na_2CO_3, 80 °C.

Further experiments were performed by using 10 mg Pd complex per g FRPSG, and a catalyst loading of 0.1 mol%. The three different complexes **3a–c** were used in the coupling of *para*-nitrobromobenzene and phenylboronic acid. Complexes **3a** and **3b** both have an ethylene spacer separating the perfluoroalkyl chain and the phenyl ring, the perfluoro tag is attached to the *para* or *meta* position, respectively. In complex **3c** an OCH_2 spacer is used. Earlier experiments had shown that spacers between the perfluoroalkyl chain and the aromatic ring are advantageous for the stability of the catalysts.[38]

All three catalysts gave complete conversions and could be recycled without significant decrease of activity (Table 2). Catalyst leaching was assessed for the coupling of *para*-nitrobromobenzene and phenylboronic acid with 0.1 mol% of complex **3a**. Using support **1**, a Pd content of 5.4 ppm in the crude organic product was determined by inductively coupled

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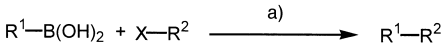
Table 2. Suzuki reactions with complexes **3a–c** immobilized on **1** (see Scheme 1).

Entry	Pd complex	Yield [%][a]
1	**3a**	> 98 (93, 93, 93)
2	**3b**	96 (98, 93, 91)
3	**3c**	> 98 (96, 95, 95)

[a] The yields in parentheses are for the second (third, and fourth) runs with the same catalyst.

plasma mass spectrometry (ICP-MS),[39] which corresponds to 1.8% of the total Pd. In the inorganic residue, which consists mainly of Na_2CO_3, 0.2 ppm of Pd was found, which corresponds to less than 0.1% of the Pd. Thus, less than 1.9% of the catalyst was washed off from FRPSG **1**. In an identical experiment using support **2** a Pd leaching of less than 1.6% was determined. Accordingly, the nature of the fluorous solid support seems to influence the leaching only marginally.

The catalyst **3a** on support **1** was tested with a number of different substrates (Scheme 2, Table 3). Yields were generally high for electron-deficient aryl bromides (Table 3,



Scheme 2. Suzuki reactions with different substrates performed with **3a** immobilized on support **1** as catalyst. X = Br, I. a) 0.1 mol% catalyst, DME, 2 M aq. Na_2CO_3, 80 °C, 15 h.

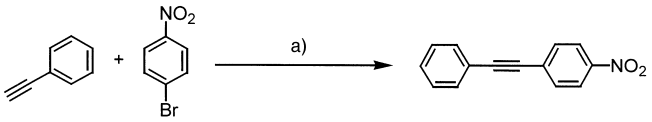
Table 3. Suzuki reactions with different substrates, using 0.1 mol% **3a** on support **1** (see Scheme 2).

Entry	R^1	R^2	Yield [%][a]
1	Ph	4-NO_2-C_6H_4	95 (97, 97)
2	Ph	4-CH_3CO-C_6H_4	> 98 (85, 14)
3	Ph	4-EtOOC-C_6H_4	93 (69, 4)
4	Ph	2-naphthyl	82 (17)
5	Ph	3,4-$F_2C_6H_3$	78 (6, 0)
6	Ph	3,4,5-$F_3C_6H_2$	83 (34, 2)
7	Ph	4-MeO-C_6H_4	48 (2)
8[b]	Ph	4-MeO-C_6H_4	76, (75, 52)
9[c]	Ph	4-MeO-C_6H_4	70, (10, 0)
10[d]	Ph	4-MeO-C_6H_4	73 (4, 0)
11	4-MeO-C_6H_4	4-NO_2-C_6H_4	94 (97, 94)
12	4-MeO-C_6H_4	4-CN-C_6H_4	94 (97, > 98)
13	4-MeO-C_6H_4	4-CH_3CO-C_6H_4	85 (> 98, 29)
14	4-MeO-C_6H_4	4-EtOOC-C_6H_4	72 (56, 19)
15	3-thienyl	4-NO_2-C_6H_4	89 (0)
16	3-thienyl	4-CH_3CO-C_6H_4	61 (0)
17	Cy	4-NO_2-C_6H_4	0 (0)
18	Cy	4-CH_3CO-C_6H_4	0 (0)

[a] The yields in parentheses are for the second (and third) runs with the same catalyst. [b] 4-Iodoanisole was used instead of 4-bromoanisole. [c] 0.3 mol% **3a** was used. [d] 0.2 mol% of the corresponding phosphane was added.

entries 1–6, and 11–15) and for aryl iodides (Table 3, entry 8). For electron-rich *para*-bromoanisole only 48% conversion was achieved (Table 3, entry 7), but higher conversions were obtained with either higher catalyst loading (Table 3, entry 9) or additional phosphane ligand (Table 3, entry 10). Recycling was successful for very reactive substrates (Table 3, entries 1, 11, and 12). For all other substrates a significant decrease of catalyst activity was observed, the decrease being the greater, the less reactive the halide was. With 3-thienylboronic acid high conversions were obtained in the first run, but no conversion was found with recycled catalyst and only the aryl bromide was recovered (Table 3, entries 15 and 16). This complete loss of activity might be due to catalyst poisening by the thiophene. With cyclohexylboronic acid no conversion was observed (Table 3, entries 17 and 18).

In the Sonogashira reaction (Scheme 3) with 2 mol% catalyst high yields were obtained for three successive experiments (Table 1, entry 5). With 0.2 mol% catalyst conversion was still complete, but the yield dropped significantly when the catalyst was reused (Table 1, entry 6). With lower catalyst loadings, conversions were not complete within 14 h and the recovered FRPSG showed no catalytic activity (Table 1, entries 7 and 8).



Scheme 3. Sonogashira reactions performed with complex **3a** immobilized on support **1** as catalyst. a) 0.002–2 mol% catalyst, CuI, DME, nBu$_2$NH, 100 °C, 14 h.

In summary, we could demonstrate the immobilization of perfluoro-tagged palladium catalysts on FRPSG, and their use for Suzuki and Sonogashira cross-coupling reactions. The catalysts showed activities comparable to those found in liquid–liquid FBC. The catalysts were separated from the product by simple decantation. Leaching was as low as 1.9% and 1.6% for **1** and **2**, respectively, and the recovered catalyst could be reused in several instances. Because of the dilution of the catalyst with FRPSG, very small amounts of catalysts could be easily and precisely handled. In contrast to conventional FBC approaches, no fluorous solvent was needed for the reaction and the isolation and recovery of the catalyst. An advantage of our strategy compared to conventional covalent catalyst immobilization is that the same support can be used for different catalysts, without the need for a separate linker unit. Before attachment, the catalyst can be characterized by usual methods. It is also conceivable to adjust the reaction conditions in such a way that the catalyst is detached from the FRPSG during the reaction and re-attached during workup. Further investigations to extend this immobilization strategy to other catalytic systems are currently underway.

Experimental Section

General procedure for Suzuki cross-coupling reactions: A 50 mL Schlenk tube was charged with FRPSG supported catalyst (100 mg), evacuated, and refilled with argon (3×). Stock solutions of the aryl halide (0.3 M in dimethoxyethane (DME), 1.0 mL, 0.3 mmol), the boronic acid (0.33 M in DME (with 4-methoxyphenylboronic acid methanol was used instead), 1.0 mL, 0.33 mmol) and Na_2CO_3 (2 M in water, 1.0 mL, 2.0 mmol) were added. The tube was sealed with a screw cap and shaken at 80 °C for 15 h. The reaction mixture was cooled to 0 °C and the liquid phase was removed under argon with a pipette. The FRPSG was washed with DME (2 × 2 mL), water (2 × 2 mL), and DME (2 × 2 mL). The combined liquid phases were diluted with water (40 mL) and brine (20 mL) and were extracted with *tert*-butyl methyl ether (3 × 20 mL). The combined extracts were concentrated in vacuo, the residue was take up in diethyl ether (2 mL), put on a plug of

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neutral alumina (3 mL, activity 2–3) and eluted with diethyl ether (~14 mL). Evaporation of the solvent gave the product. Yields were determined by ^{1}H NMR integration against a known amount of 1,2-dibromoethane. The immobilized catalyst was reused as such in further experiments.

Determination of catalyst leaching: A 100 mL Schlenk flask was charged with FRPSG supported catalyst (500 mg, 10 mg Pd complex per g FRPSG, 1.48 μmol), 4-bromonitrobenzene (303 mg, 1.50 mmol), and phenylboronic acid (205 mg, 1.68 mmol), evacuated and refilled with argon (3×). DME (10 mL) and Na_2CO_3 (2 M in water, 5.0 mL, 10.0 mmol) were added. The flask was shaken under argon at 80 °C for 15 h, and then the reaction mixture was cooled to room temperature and filtered. The residue was washed with DME (2×10 mL), water (2×10 mL), and again with DME (2×10 mL), and the organic and aqueous filtrates were collected separately. The solvents were removed in vacuo, the resulting solids were powdered, and the Pd content determined by ICP-MS.

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9,9-Dilithiofluorene: The First Crystal-Structure Analysis of an α,α-Dilithiated Hydrocarbon**

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Lithiated hydrocarbons are one of the most important classes of compounds in organoelement chemistry. Many of these compounds have been structurally investigated in solution and the crystalline state, as well;[1–3] di- and oligometallated species earned special interest.[4,5] Dilithiomethane is mentioned as one example here, it is available from the thermolysis of lithium methanide[6,7] and used in many synthetic procedures. A series of oligomeric structures of lithium methanide was investigated with quantum-chemical methods, in which carbon atoms take the coordination number six.[8] In monomeric dilithiomethane the planar coordination of the carbon atom is only less stable than the tetrahedral coordination of the carbon atom by 71 kJ mol^{-1}.[9,10] However, the final structure in solution and of the solid state has not been determined.[11,12] Several substituted derivatives, such as Me_3CCHLi_2, $Me_3SiCHLi_2$,[13] and the title compound 9,9-Dilithiofluorene,[14] have been synthesized, but their structures are not known. It was possible to solve the crystal structures of heteroatom substituted derivatives, such as $PhS(O)(NMe)CLi_2Ph$,[15] $(Me_3SiNPPh_2)_2CLi_2$,[16,17] $(MeO)_2P(O)CLi_2SiMe_3$ (as aggregate with dimethylamide),[18] and $PhSO_2CLi_2(SiMe_3)$,[19] where Li–O and Li–N bonds dominate the structures. The anion $(CHPMe_2NSiMe_3)^{2-}$ together with $BuMe_2SiO^-$ forms the backbone of a Li_{14} cluster.[20] $[\{(Me_3Si)_2CH\}_6Al_2CH_2Li_2]$ was considered as a R_3Al-adduct to CH_2Li_2.[21] Herein, we describe the crystal structure of the 9,9-dilithiofluorene complex **2** [Eq. (1)].

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