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Repetitive Application of Perfluoro-Tagged Pd Complexes for Stille Couplings in a Fluorous Biphasic System**

Siegfried Schneider and Willi Bannwarth*

The recovery and reuse of expensive catalysts is an important topic in catalytic processes. Thus, in homogeneous catalysis the use of liquid biphasic systems has attracted a great deal of attention. Examples include the aqueous biphasic Ruhrchemie/Rhône-Poulenc process,[1] catalytic reactions in supercritical carbon dioxide,[2] catalysis in molten salts,[3] and use of fluorous biphasic systems (FBS).[4]

In the FBS concept, first reported by Horváth and Rábai,[5] owing to the perfluorinated ligands on the organometallic catalyst it is soluble in a fluorous phase (e.g. n-C_6F_{14}, C_7F_{16}, $C_6F_{13}Br$, $CF_3C_6F_{11}$). The reaction is carried out in a two-phase mixture consisting of a perfluorinated solvent and an organic solvent (toluene, hexane, acetonitrile). Such a two-phase system often becomes homogeneous at elevated temperature. Lowering the temperature after reaction leads to reformation of the two phases; the organic phase contains the product, the fluorous phase the catalyst to be reused.

This new concept has been applied to a number of catalytic reactions such as hydroformylation of alkenes,[5] oligomerization of ethylene,[6] hydroboration of alkenes,[7] oxidation of aldehydes,[8] thioethers,[8] and alkanes,[9] epoxidations,[8, 10–12] Wacker oxidation of alkenes,[13] rhodium-catalyzed carbenoid reaction,[14] palladium-catalyzed allylic nucleophilic substitution,[15] cross-coupling of arylzinc bromides with aryl iodides,[16] and the Heck reaction.[17]

Here, we report on the synthesis of three new fluoro-tagged bis-triphenylphosphanepalladium complexes and their application to the Stille cross-coupling reaction,[18] with the goal of reusing the catalyst for subsequent cross-couplings.

Fluoro-tagged phosphanes **1a–c** were synthesized with slight modifications of the original procedures[16, 19] (Scheme 1a, b). Replacement of the iodine substituent of *m*- or *p*-iodoaniline by the perfluoro tag followed by bromination of the diazonium intermediate delivered the corresponding bromobenzene with the fluoro tag in the *m*- or *p*-position, respectively. Br–Li exchange and reaction with PCl_3 yielded the desired phosphanes **1a** and **1b**. To the best of our knowledge, **1b** has not been reported in the literature. Phosphane **1c** was prepared starting from 1,4-dibromobenzene (Scheme 1b). Reaction of the corresponding Grignard compound with $C_8F_{17}CH_2CH_2I$ was applied to introduce the perfluoro tag. Br–Li exchange and reaction with PCl_3 led to

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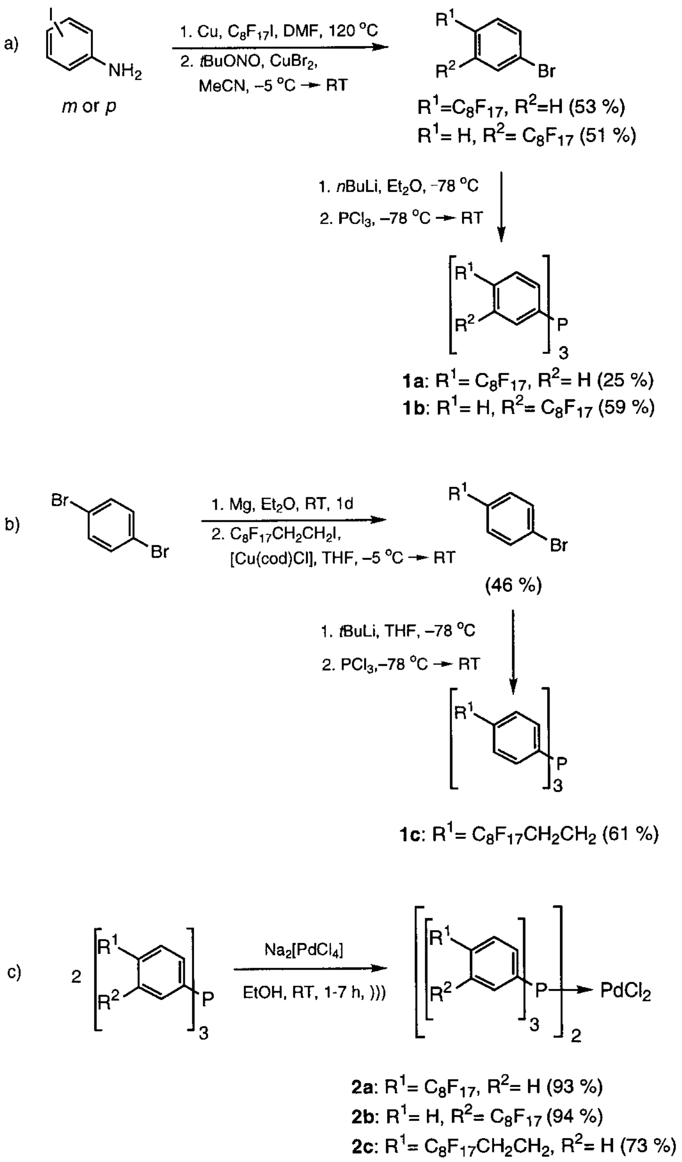


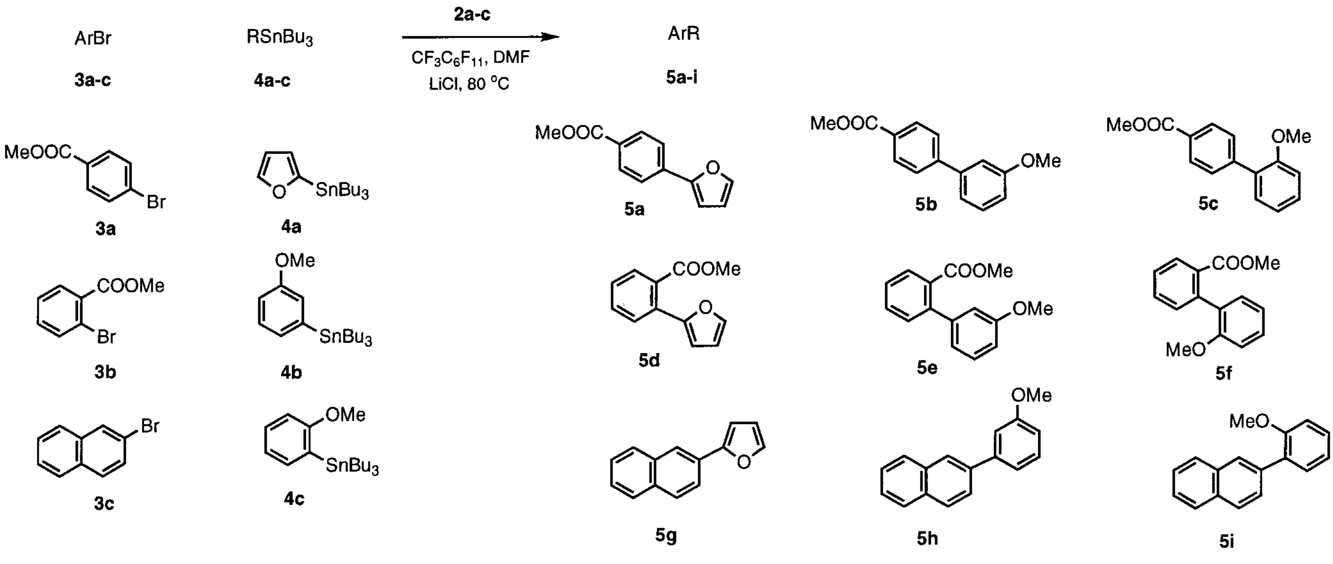
Scheme 1. Synthesis of the ligands **1a–c** and the complexes **2a–c**. cod = 1,5-cyclooctadiene.

phosphane **1c**. The Br–Li exchange was carried out with *t*BuLi since reaction with *n*BuLi led to a severe decrease in the yield of **1c**.

The perfluoro-tagged phosphanes **1a–c** are much more sensitive than unsubstituted triphenylphosphane towards oxidation by air as demonstrated by kinetic studies (^{31}P NMR). The oxidation sensitivity decreased in the order **1a** > **1b** > **1c**. The rate of oxidation was dependent on the position of the fluoro tag (cf. **1a** and **1b**), the *p*-isomer **1a** is oxidized faster than the *m*-isomer **1b**. These observations are in agreement with results obtained with trifluoromethyl-substituted triphenylphosphanes.[20]

The perfluoro-tagged Pd complexes **2a–c** were prepared according to Scheme 1c.[21] Complex formation was carried out at room temperature with a mixture of $Na_2[PdCl_4]$ and the corresponding fluoro-tagged triphenylphosphane in ethanol under sonication (1–7 h). All three complexes were not air-sensitive and were easy to handle.

The perfluoro-tagged Pd complexes were evaluated in Stille couplings according to Scheme 2. Treatment of three different aryl bromides (**3a–c**) with three different tin compounds (**4a–c**) under standardized conditions in the presence of 1.5 mol% of catalyst **2a–c** led to the desired products **5a–i**. The reactions were carried out in a mixture of DMF and perfluoromethylcyclohexane according to Figure 1. This approach led to an easy recycling of the catalyst which was then reapplied to the same type of Stille coupling under identical conditions. The results are outlined in Table 1. The yields are either based on yields of isolated products or alternatively, if yields were lower, on ^1H NMR spectroscopically determined yields (by comparison of signal intensities of expected product and of the pertinent aryl bromide and the tin compound as starting materials). The results obtained indicate that the perfluoro-tagged Pd complexes **2a–c** were generally suitable for Stille couplings in a solvent system consisting of perfluoromethylcyclohexane in DMF. The yields from the C–C coupling reactions were high for all three complexes except when the stannane **4c** was applied as starting material. This was probably due to steric hindrance encountered during



Scheme 2. Stille coupling with the catalysts **2a–c**.

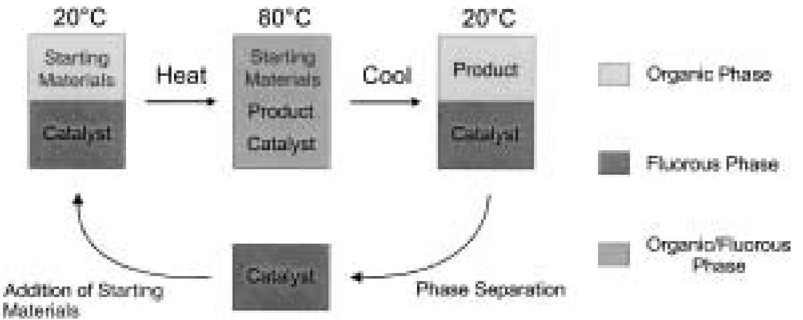


Figure 1. Principle of recycling of the perfluoro-tagged catalysts.

Table 1. Yields of Stille coupling products obtained by employing perfluoro-tagged Pd complexes **2a**–**c** (reaction times and yields of second and third run in parentheses).

Entry	ArBr	Stannane	Cat.	*t* [h]	Product	Yield [%]
1a	**3a**	**4a**	**2a**	3 (8, 8)	**5a**	94 (88, 82)
1b			**2b**			86 (88, 88)
1c			**2c**			98 (79, 84)
2a	**3a**	**4b**	**2a**	3 (8, 8)	**5b**	86 (73, 84)
2b			**2b**			90 (55, 78)
2c			**2c**			81 (78, 81)
3a	**3a**	**4c**	**2a**	16 (24)	**5c**	71 (35)
3b			**2b**			68 (26)
3c			**2c**			68 (50)
4a	**3b**	**4a**	**2a**	3 (8, 8)	**5d**	68 (36, 37)
4b			**2b**			66 (26, 13)
4c			**2c**			81 (75, 61)
5a	**3b**	**4b**	**2a**	3 (8, 8)	**5e**	98 (71, 88)
5b			**2b**			98 (87, 63)
5c			**2c**			94 (93, 96)
6a	**3b**	**4c**	**2a**	24 (24)	**5f**	82 (Spur)
6b			**2b**			55 (Spur)
6c			**2c**			70 (70)
7a	**3c**	**4a**	**2a**	3 (8, 8)	**5g**	90 (89, 76)
7b			**2b**			84 (78, 79)
7c			**2c**			91 (93, 95)
8a	**3c**	**4b**	**2a**	3 (8, 8)	**5h**	74 (67, 55)
8b			**2b**			63 (62, 32)
8c			**2c**			74 (64, 66)
9a	**3c**	**4c**	**2a**	20 (24, 24)	**5i**	49 (43, 44)
9b			**2b**			39 (10, 10)
9c			**2c**			50 (58, 49)

coupling in the *o*-position. Longer reaction times were necessary in these reactions to obtain decent yields.

Furthermore, the complexes can be reused after phase separation according to Figure 1. Longer reaction times were employed in run 2 and 3 to compensate for the loss of activity of the catalysts. When relatively low yields were obtained in the first run, the decrease in the yield for the following runs was more drastic for complexes **2a** and **2b** than for **2c**. Recycling of the complexes was not efficient when stannane **4c** was used.

In a further set of experiments we applied the catalysts **2a**–**c** in repetitive Stille couplings according to Figure 1 leading to **5a**. Identical reaction times were used for all runs (3 h). As can be deduced from Figure 2 the complexes were recycled five times. All three complexes afforded comparable yields in all the runs and only a slight decrease in yield was observed for all three complexes from run 1 to run 6.

The presented three new perfluoro-tagged Pd complexes are suitable as catalysts in Stille couplings in a fluorous biphasic system. They can be recycled and reused after phase separation so that they can be applied up to six times without significant reduction in yield. For all three complexes the yields in these experiments were nearly identical.

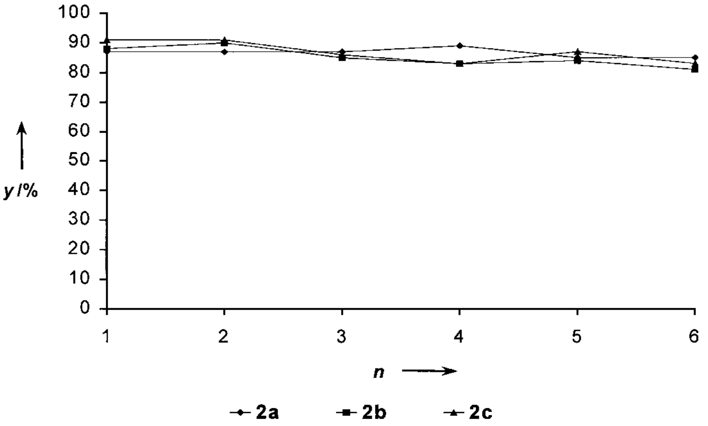


Figure 2. Yields of **5a** after reuse of the catalysts **2a**–**c**. *n*: number of run; *y*: yield. The yields in the first run are not identical with those in Table 1 because they were determined in a different set of experiments.

Experimental Section

1b: *n*BuLi (6.00 mL of a 1.6 M solution in *n*-hexane) was added over 1 h to a stirred solution of 1-bromo-3-(1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluorooctyl)benzene (5.00 g, 8.70 mmol) in anhydrous Et_2O (30 mL) under argon at −78 °C. After the mixture had been stirred for 2 h, PCl_3 (7.25 mL of a 0.40 M solution in diethyl ether) was added dropwise. The mixture was allowed to warm up to room temperature overnight. The mixture was hydrolyzed with a saturated NH_4Cl solution (15 mL) and extracted with diethyl ether (3 × 20 mL). The combined organic layers were dried over $MgSO_4$ and evaporated to dryness. The residue was taken up in a small amount of diethyl ether and filtered over silica with *n*-hexane as solvent. After evaporation phosphane **1b** (2.60 g, 59 %) was obtained. M.p. 84–86 °C; ^{31}P NMR (80 MHz, $CDCl_3$): $\delta = -5.7$; ^1H NMR (200 MHz, $CDCl_3$): $\delta = 7.35$ (d, $J = 6.2$ Hz, 3H); 7.54–7.65 (m, 9H); elemental analysis (%) for $C_{42}H_{12}F_{51}P$ (1516.43): calcd: C 33.27, H 0.80; found: C 33.28, H 0.83.

1a: M.p. 92–95 °C; ^{31}P NMR (80 MHz, $CDCl_3$): $\delta = -5.6$; ^1H NMR (200 MHz, $CDCl_3$): $\delta = 7.41$ (t, $J = 7.5$ Hz, 6H); 7.60 (d, $J = 7.8$ Hz, 6H); elemental analysis (%) for $C_{42}H_{12}F_{51}P$ (1516.43): calcd: C 33.27, H 0.80; found: C 33.55, H 0.97.

1c: M.p. 89–91 °C; ^{31}P NMR (80 MHz, $CDCl_3$): $\delta = -7.1$; ^1H NMR (200 MHz, $CDCl_3$): $\delta = 2.24$–2.50 (m, 6H, CH_2), 2.87–2.96 (m, 6H, CH_2), 7.17–7.37 (m, 12H, aryl-H).

2a: A suspension of the phosphane **1a** (1.05 mmol) and $Na_2[PdCl_4]$ (0.500 mmol) in ethanol was sonicated for 7 h under argon. The color changed from red-brown to yellow. The yellow precipitate was filtered off, washed with water, ethanol, diethyl ether, and dried (Yield: 93 %). M.p. 186–187 °C. ^{31}P NMR (80 MHz, $CDCl_3$): $\delta = 23.6$; elemental analysis (%) for $C_{84}H_{24}F_{102}P_2PdCl_2$ (3210.20): calcd: C 31.43, H 0.75, Cl 2.21; found: C 31.20, H 0.80, Cl 2.06.

The complexes **2b** and **2c** were prepared analogously. **2b**: Yield: 94 %. M.p. 134–136 °C; ^{31}P NMR (80 MHz, $CDCl_3$): $\delta = 25.0$; elemental analysis (%) for $C_{84}H_{24}F_{102}P_2PdCl_2$ (3210.20): calcd: C 31.43, H 0.75, Cl 2.21; found: C 31.52, H 0.81,Cl 2.19.

2c: Yield 73 %. M.p. 182–184 °C; ^{31}P NMR (80 MHz, $CDCl_3$): $\delta = 22.0$; ^1H (200 MHz, $CDCl_3$): $\delta = 2.06$ (m, br. 12H); 2.59 (m, br. 12H); 7.06 (m, br.

12H); 7.81 (m, br. 12H); elemental analysis (%) for $C_{96}H_{48}F_{102}P_2PdCl_2$ (3378.50): calcd: C 34.13, H 1.43, Cl 2.10; found: C 33.91, H 1.46, Cl 2.37.

General coupling procedure (**5a**): To a suspension of catalyst **2c** (10.1 mg, 0.003 mmol) in perfluoromethylcyclohexane (1.2 mL) was added under argon a solution of methyl 4-bromobenzoate **3a** (43.0 mg, 0.200 mmol), tributylstannylfuran **4a** (85.7 mg, 0.240 mmol), and LiCl (8.5 mg, 0.200 mmol) in DMF (1 mL). The mixture was heated at 80 °C for 3 h. After cooling to room temperature the two phases were separated and the fluorous phase was washed with DMF (3 × 1 mL). The fluorous phase containing the catalyst was removed and used as such for the next run. For isolation of product **5a** water (7.5 mL) was added to the DMF layer. After extraction with diethyl ether (4 × 2 mL), the combined diethyl ether solutions were evaporated. The residue was taken up in diethyl ether (1 mL) and aqueous KF solution (5 mL) was added. After the mixture had been stirred overnight, it was extracted with diethyl ether (4 × 2 mL), and the combined diethyl ether layers were passed through a plug consisting of Alox (2 g; neutral, Act. II-III) and silica (4 g). The filtrate was evaporated yielding the desired product **5a** (36.8 mg; 91 %).

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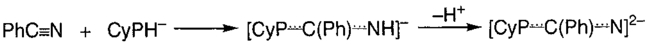
A Li_{10} Cage Containing the $[C_6H_{11}P{\cdots}C(Ph){\cdots}N]^{2-}$ Ion: Umpolung in the Oligomerization of a Nitrile[**]

Neil Feeder, Yvonne G. Lawson, Paul R. Raithby, Jeremy M. Rawson, Alexander Steiner, Jody A. Wood, Anthony D. Woods, and Dominic S. Wright[*]

Studies of oligomeric imido alkali metal complexes $[\{(R')RC{=}NLi\}_n]$, which are readily prepared by the equimolar reactions of organoalkali metal reagents R′M (M = Li–Cs) with organic nitriles ($RC{\equiv}N$), have been fundamental in the development of structural models for a host of related alkali metal complexes.[1] In contrast to the wealth of knowledge concerning the reaction characteristics of organoalkali metal reagents with nitriles,[1, 2] only a few studies have investigated the analogous addition reactions with alkali metal phosphides RR′PM.[3] Surprisingly, although alkali metal complexes containing $[R^1P{\cdots}C(R^2){\cdots}NR^3]^-$ monoanions have been prepared and structurally characterized previously, to our knowledge there are no reports of dianions of the type $[R^1P{\cdots}C(R^2){\cdots}N]^{2-}$. Our interest in the latter stems from their potential application as precursors for the synthesis of main group heterocycles.

Accordingly, we carried out the reaction of CyPHLi (Cy = C_6H_{11}) with $PhC{\equiv}N$, followed by deprotonation of the presumed intermediate anion $[CyP{\cdots}C(Ph){\cdots}NH]^-$ [3b] with *n*BuLi (Scheme 1; see Experimental Section). The product of this reaction, however, is the cage complex **1** containing not only the desired dianion $[CyP{\cdots}C(Ph){\cdots}N]^{2-}$ but also the trianion $[H(PhCN)_3(CyP)_2]^{3-}$, in which C–C bond formation between two PhCN molecules has occurred (Scheme 2). The observation of umpolung (polarity reversal) in the reaction forming this trianion contrasts with the normal mode of oligomerization of nitriles, which involves "head-to-tail" C–N



$$PhC{\equiv}N + CyPH^- \longrightarrow [CyP{\cdots}C(Ph){\cdots}NH]^- \xrightarrow{-H^+} [CyP{\cdots}C(Ph){\cdots}N]^{2-}$$

Scheme 1.

$$[\{\{[CyPC(Ph)N]Li_2\}\{[H(PhCN)_3(CyP)_2]Li_3\}(thf)_3\}_2] \cdot 2\,C_6H_5CH_3 \cdot 2\,THF \qquad \mathbf{1}$$

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