A convenient and efficient procedure for the palladium-catalyzed cyanation of aryl halides using trimethylsilylcyanide

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Dedicated to Professor Ernst Otto Fischer on the occasion of his 85th birthday

Abstract

Benzonitriles are easily accessible from the corresponding aryl bromides in a palladium-catalyzed reaction using trimethylsilylcyanide (TMSCN) as cyanating agent under mild conditions. The key of success for the cyanation protocol is the slow dosage of the TMSCN to the reaction mixture. This new method is applicable to both activated and deactivated aryl and heteroaryl bromides giving the corresponding benzonitriles in good to excellent yields.
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Keywords: Aryl halides; Benzonitriles; Cyanation; Homogeneous catalysis; Palladium; Trimethylsilylcyanide

1. Introduction

Palladium-catalyzed coupling processes of aryl halides are well established methods for carbon−carbon bond formation in organic synthesis on laboratory and industrial scale for fine chemical synthesis [1]. Their generality and broad tolerance of functional groups make these methods especially attractive for the use in natural product synthesis. In addition, a number of currently used industrial fine chemicals might be synthesized by shorter and more selective routes compared to classic stoichiometric organic transformations. Hence, we are interested for some time in the development of palladium-catalyzed coupling reactions of aryl bromides and chlorides to a practical level [2].

Among the different palladium-catalyzed aryl−X refinement reactions the catalytic cyanation of aryl halides (Scheme 1) is somewhat underdeveloped [3]. That is in part surprising because this transformation offers a simple and elegant approach towards substi-

tuted benzonitriles, and the resulting products are of considerable importance as integral part of dyes, natural products, herbicides, agrochemicals, pharmaceuticals, and new active agents [4].

On an industrial scale aryl cyanides are produced mainly via ammoxidation of the corresponding toluenes [5]. In addition, still the classic Rosenmund−von Braun reaction, whereby aryl halides react with stoichiometric amounts of copper(I) cyanide, and the reaction of diazonium salts with copper(I) cyanide (Sandmeyer reaction) are used to a considerable extent. Compared to the latter two methods the transition metal-catalyzed cyanation of aryl halides is an environmentally more friendly procedure and does not lead to the formation of stoichiometric amounts of copper waste. So far, both nickel [6] and palladium complexes [7] have been used as catalyst. Mechanistic studies of the palladium-catalyzed cyanation revealed that cyanide ions deactivate both palladium(II) and palladium(0) species in the catalytic cycle (Scheme 2) [8]. Hence, catalyst productivity is comparably low in cyanation reactions (TON typically 10−50) compared to other palladium-catalyzed coupling reactions (TON 10 000−100 000) [9].
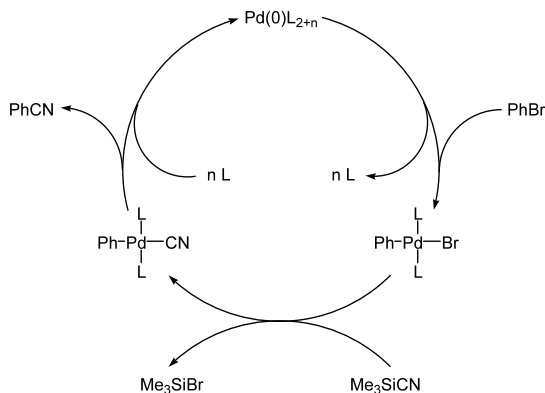
Recently, we have been able to show, that an efficient control of the concentration of dissolved cyanide ions in

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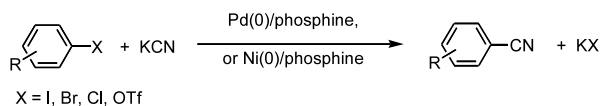
Scheme 1. Palladium- or nickel-catalyzed cyanation of aryl–X.

Scheme 2. Proposed mechanism of the palladium-catalyzed cyanation of bromobenzene using TMSCN as cyanating agent.
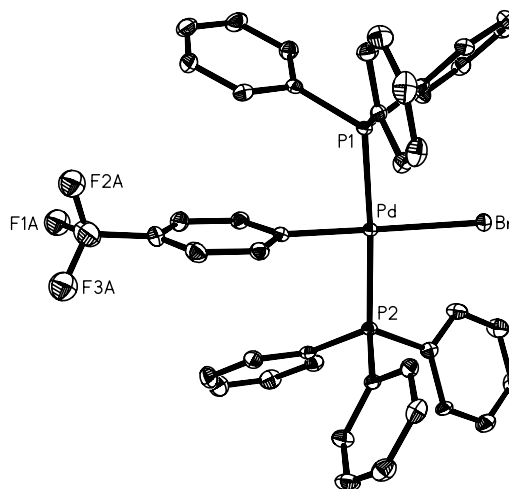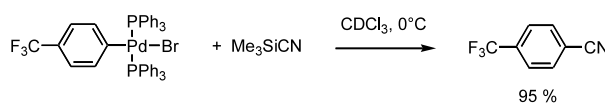

Fig. 1. Crystal structure of **1** [12]. The thermal ellipsoids correspond to 30% probability. Hydrogen atoms have been omitted for clarity. For the disordered CF_3 group the fluorine atoms with highest probability of occupation are shown. Selected bond lengths (Å) and angles (°): Pd–P1 2.331(2), Pd–P2 2.346(2), Pd–Br 2.5244(9), Pd–C 2.012(4); P1–Pd–Br 88.98(5), Br–Pd–P2 94.63(5), P2–Pd–C 89.32(13), C–Pd–P1 87.01(13).

Scheme 3. Stoichiometric reaction of **1** with TMSCN.

solution is required in order to improve catalytic efficiency [8a]. This is difficult to achieve applying solid KCN or NaCN as cyanation agent due to the nature of the reaction mixture (suspension). However, slow addition of acetone cyanohydrin gives improved results [10].

Another interesting 'liquid cyanation reagent' would be trimethylsilylcyanide (TMSCN). TMSCN can easily be handled on laboratory scale and has safety advantages compared to other cyanide sources. To the best of our knowledge there has been no palladium- or nickel-catalyzed cyanation of aryl bromides or aryl chlorides reported in the literature [11].

2. Results and discussion

During attempts to prepare arylpalladium(II) cyano complexes we discovered that *trans*-bromo[4-(trifluoromethyl)phenyl]bis(triphenylphosphine)palladium(II) (**1**) [12] (Fig. 1) reacts readily and highly selectively with TMSCN. The corresponding benzonitrile was obtained in 95% yield even below 0 °C (Scheme 3). Hence, we thought that TMSCN should be an efficient and mild cyanation reagent for a palladium-catalyzed coupling reaction.

Catalytic studies with TMSCN were performed initially using the cyanation of 4-bromobenzotrifluoride (Table 1). Based on our previous investigations [8a,13] we applied catalyst systems based on palladium in the presence of 1,5-bis(diphenylphosphino)pentane (dpppe) and *N,N,N′,N′*-tetramethylethylenediamine as ligands in toluene. As the palladium catalyst *trans*-bromo[4-(trifluoromethyl)phenyl]bis(triphenylphosphine)palla-

dium(II) (**1**), which is supposed to form an active intermediate of the catalytic cycle (Scheme 2) by ligand exchange, was used. Compared to other palladium sources this complex does not require a pre-formation to form an active catalyst species. In all catalytic experiments TMSCN is continuously dosed to the reaction mixture using a syringe pump. In agreement with literature there is no reaction observed using TMSCN under the previously optimized reaction conditions without dosage [14].

However, slow dosage of TMSCN to 4-bromobenzotrifluoride and 2 mol.% of **1** resulted in smooth formation of 4-(trifluoromethyl)benzonitrile. The desired nitrile is obtained in quantitative yield ($\geq 99\%$) without any by-product being observed (Table 1, entry 1). This is the first example of a palladium-catalyzed cyanation of aryl bromides using TMSCN as the cyanide source. Excellent conversion and selectivity was also observed at more convenient reaction conditions (80 °C) and in the presence of 1 mol.% of catalyst (Table 1, entries 2 and 4). However, at 60 °C no full conversion took place (Table 1, entry 3). The use of *trans*-bromo(3-tolyl)bis(triphenylphosphine)palladium(II) (**2**) instead of **1** gave similarly good results.

Next we were interested in the scope and limitation of the new protocol. Table 2 shows some different aryl

Table 1
Use of TMSCN in the palladium-catalyzed cyanation of 4-bromobenzotrifluoride

Entry	Catalyst (mol.%)	Dpppe [mol.%]	Temperature [°C]	Conversion [a] [%]	Yield [a] [%]
1	**1** (2)	2	120	100	≥ 99
2	**1** (2)	2	80	100	≥ 99
3	**1** (2)	2	60	17	15
4	**1** (1)	1	120	100	≥ 99

General conditions: 4-bromobenzotrifluoride (2 mmol), **1**, dpppe and TMEDA (0.4 mmol) were dissolved in toluene (2 ml) under argon. The mixture was heated under stirring, and 1 M TMSCN solution (2.1 ml) was added via syringe pump to the solution (dosage rate: 0.1 ml h^{-1}). After cooling to room temperature 400 μl of diethyleneglycol di-*n*-butylether were added for GC-analysis.

[a] Conversions and yields were determined by GC.

halides, tested in the palladium-catalyzed cyanation using TMSCN in the presence of **1** or **2** as catalyst.

In general, a wide variety of aryl bromides can easily be transformed into the corresponding substituted benzonitriles. Activated aryl bromides, e.g. 4-bromobenzotrifluoride, methyl 4-bromobenzoate, 4′-bromoacetophenone, 4-bromofluorobenzene, 4-bromonitrobenzene, and 4-bromobenzonitrile (Table 2, entries 1–7) gave the desired products in good to very good yield (53–99%). Somewhat surprising, there is no significant difference in reactivity observed when applying non-activated and deactivated aryl bromides. Bromobenzene, 3-bromotoluene, 4-bromotoluene, 3-bromoanisole, and 4-bromoanisole react with TMSCN in good to excellent yield (62–99% yield) to the corresponding nitriles (Table 2, entries 8–13). In case of the reaction of 3-bromotoluene with TMSCN the effect of the P/Pd-ratio was studied. 3-Methylbenzonitrile was obtained in 84% yield in the presence of 2 mol.% Pd and 2 mol.% dpppe (Table 2, entry 9). When the metal content was reduced to 1 mol.% (1 mol.% dpppe) the yield decreased to 65%. However, by decreasing the palladium/phosphine ratio to 1:6 the product was observed in 92% (Table 2, entry 10). Hence, we conclude that it should be possible to even improve the shown product yields by variation of the Pd/P ratio. Apart from aryl bromides we also tested one heteroaryl bromide (3-bromopyridine) and an activated aryl chloride (4-chlorobenzotrifluoride) (Table 2, entries 14, 15). The products were obtained in 68 and 39% yield, respectively. Improved results for the cyanation of aryl chlorides are expected at higher reaction temperature. Unfortunately, the relatively low boiling point of the TMSCN (114–117 °C) prevents the realization of such reactions in standard glassware equipment.

In summary, we have shown that TMSCN reacts readily and selectively with arylpalladium(II) halide complexes to give the corresponding benzonitriles. TMSCN is a mild and easy cyanating agent for the palladium-catalyzed cyanation of aryl halides. Key to success of the catalytic reactions is the dosage of the cyanide via syringe pump to the reaction mixture to prevent catalyst deactivation by excess cyanide ions in solution. The generality of the described procedure has been shown by conversion of a variety of activated, non-activated, and deactivated aryl or heteroaryl bromides into the corresponding benzonitriles.

3. Experimental

3.1. General

All chemicals are commercially available and were used without further purification. Toluene was stored over molecular sieve 4 Å. TMSCN was used as a 1 M solution in toluene. All products were fully characterized after isolation (^{1}H-NMR, ^{13}C-NMR, MS, IR, and elemental analysis) or in the case of commercially available products by comparison of GC–MS data.
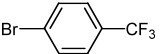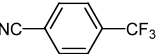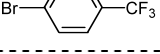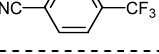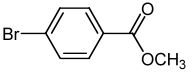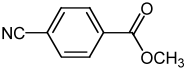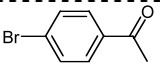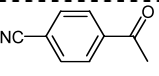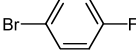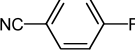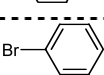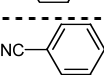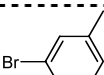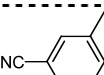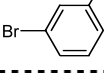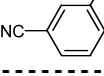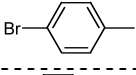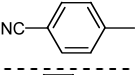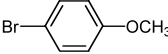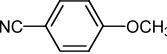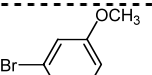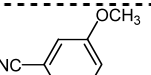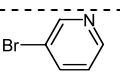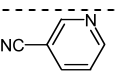
3.2. General procedure

A two necked round bottom reaction flask (25 ml) with condenser was charged with palladium catalyst (0.04 mmol) and dpppe (17.6 mg, 0.04 mmol) and purged with argon. The aryl halide (2 mmol), *N,N,N′,N′*-tetramethylethylenediamine (60 μl; 0.4 mmol), and toluene (2 ml) were added. The reaction mixture was heated to 120 °C and while magnetically stirring a 1 M TMSCN solution (2.1 ml; 2.1 mmol) was dosed via a syringe pump with a dosage rate of 0.1 ml h^{-1} (0.1 mmol h^{-1}). After 21 h the reaction was cooled to room temperature (r.t.), internal standard (diethyleneglycol di-*n*-butylether; 400 μl) was added and the reaction mixture was diluted with dichloromethane. Conversion and yield were determined by GC analysis.

3.3. Oxidative addition products

In a three necked round bottom reaction flask (50 ml) with condenser 5.78 g (5.0 mmol) tetrakis(triphenylphosphine)palladium(0) were placed and purged with argon. The aryl bromide (20 mmol) and toluene (20 ml) were

Table 2
Scope and limitation of the palladium-catalyzed cyanation of aryl halides with TMSCN

Entry	Aryl halide	Product	Catalyst	Conversion[a] [%]	Yield[a] [%]
1	Br—⟨⟩—CF₃	NC—⟨⟩—CF₃	1	100	≥ 99
2			2	100	98
3	Br—⟨⟩—C(O)OCH₃	NC—⟨⟩—C(O)OCH₃	2	87	82
4	Br—⟨⟩—C(O)CH₃	NC—⟨⟩—C(O)CH₃	2	71	56
5	Br—⟨⟩—F	NC—⟨⟩—F	2	83	76
6	Br—⟨⟩—NO₂	NC—⟨⟩—NO₂	2	67	53
7	Br—⟨⟩—CN	NC—⟨⟩—CN	2	100	63
8	Br—⟨⟩	NC—⟨⟩	2	100	≥ 99
9	Br—⟨⟩—CH₃	NC—⟨⟩—CH₃	2	99	84
10[b]			2	100	92
11	Br—⟨⟩—CH₃	NC—⟨⟩—CH₃	2	99	96
12	Br—⟨⟩—OCH₃	NC—⟨⟩—OCH₃	2	70	62
13	Br—⟨⟩—OCH₃	NC—⟨⟩—OCH₃	2	90	89
14	Br—⟨N⟩	NC—⟨N⟩	2	75	68
15[c]	Cl—⟨⟩—CF₃	NC—⟨⟩—CF₃	1	50	39

General conditions: aryl and heteroaryl halide (2 mmol), palladium complex (0.04 mmol), dpppe (0.04 mmol; Pd:P = 1:4) and TMEDA (0.4 mmol) were dissolved in toluene (2 ml) under argon. The mixture was refluxed under stirring, and 1 M TMSCN solution (2.1 ml) was added via syringe pump to the solution (dosage rate: 0.1 ml h⁻¹). After cooling to room temperature 400 μl of diethyleneglycol di-*n*-butylether were added for GC-analysis.
[a] Conversions and yields were determined by GC.
[b] 0.02 mmol palladium complex; 0.04 mmol dpppe (Pd:P = 1:6).
[c] Solvent:xylene; 140 °C.

added and the reaction mixture was stirred at 80 °C for 4 h. After cooling to r.t. the solvent and excess aryl bromide were distilled off the mixture under reduced pressure. The solid residue was washed three times with diethyl ether and the remaining crude product was dissolved in dichloromethane. After addition of pentane the oxidative addition product was obtained in 80–95% yield as colorless crystals.

3.4. Analytical data

3.4.1. trans-Bromo[4-(trifluoromethyl)phenyl]bis-(triphenylphosphine)palladium(II)

^{1}H-NMR (400 MHz, CD₂Cl₂, 297 K): δ 7.52 (m, 12H), 7.38 (m, 6H), 7.29 (m, 12H), 6.76 (d, ^3J(H,H) = 8.1 Hz, 2H), 6.41 (d, ^3J(H,H) = 8.1 Hz, 2H); ^{13}C{^{1}H}-NMR (101 MHz, CD₂Cl₂, 297 K) [15]: δ 136.3 (q,

^3J(C,F) = 5.3 Hz), 135.0 (t, ^1J(C,P) = 6.2 Hz), 131.4 (t, ^2J(C,P) = 22.9 Hz), 130.4 (s), 128.3 (t, ^3J(C,P) = 5.2 Hz), 123.6 (s); ^{31}P-NMR (162 MHz, CD$_2$Cl$_2$, 297 K): δ 24.3; MS (FAB, NBA, *m/z*): 855 [M$^+$ −1], 775, 630, 407, 339, 262; IR (Nujol, cm^{-1}): 3054, 1437, 1322, 1111, 1096, 1069, 745, 693, 519; Anal.: Calc. for C$_{43}$H$_{34}$BrF$_3$P$_2$Pd: C, 60.34; H, 4.00; Br, 9.33; P, 7.24; Pd, 12.43%; Found: C, 60.01; H, 4.27; Br, 9.71; P, 7.25; Pd, 12.12%.

3.4.2. *trans-Bromo(3-tolyl)bis(triphenylphosphine)palladium(II)*

^{1}H-NMR (400 MHz, CDCl$_3$, 297 K): δ 7.49 (m, 12H), 7.30 (m, 6H), 7.23 (m, 12H), 6.55 (m, 1H), 6.14 (m, 3H), 1.52 (s, 3H); ^{31}P-NMR (162 MHz, CD$_2$Cl$_2$, 297 K): δ 24.3.

Acknowledgements

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[12] X-ray data of **1** were collected on a STOE-IPDS diffractometer using graphite monochromated $Mo-K_\alpha$ radiation. The structure was solved by direct methods (SHELXS-86: G.M. Sheldrick, Acta Crystallogr. Sect. A 1990, 46, 467) and refined by full-matrix least-squares techniques against F2 (SHELXL-93). Non-hydrogen atoms (except atoms of disordered groups) were refined anisotropically. The hydrogen atoms were included at calculated positions and refined using the riding model. The fluorine atoms of the CF_3 group were found to be disordered over three different rotational orientations. XP (BRUKER AXS) was used for structure representation. Crystal data for **1**: crystal size $0.4 \cdot 0.3 \cdot 0.3$ mm, colourless prism, space group $P\bar{1}$, triclinic, $a = 10.291(2)$, $b = 11.710(2)$, $c = 18.290(4)$ Å, $\alpha = 84.78(3)$, $\beta = 80.42(3)$, $\gamma = 66.25(3)°$, $V = 1988.6(7)$ Å^3, $Z = 2$, $\lambda_{calc} = 1.571$ g cm^{-3}, 5959 reflections measured, 5959 were independent of symmetry and 4712 were observed ($I > 2\sigma(I)$), R (obsd data) $= 0.040$, wR_2 (all data) $= 0.110$, 485 parameters. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no CCDC-203377. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk).

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[14] 2 mmol aryl halide, 2 mmol cyanide, 0.04 mmol palladium(II) acetate, 0.08 mmol dpppe, 0.4 mmol TMEDA, 2 ml toluene, 160 °C, 16 h, in a pressure tube.

[15] Signals for $Pd-C$, $C-CF_3$ and $C-CF_3$ were not detectable under routine measurement conditions.