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A Defined N-Heterocyclic Carbene Complex for the Palladium-Catalyzed Suzuki Cross-Coupling of Aryl Chlorides at Ambient Temperatures**

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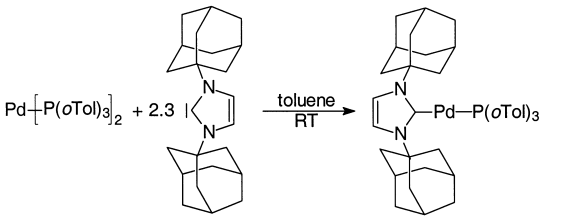
Dedicated to Prof. Dr. Gottfried Huttner on the occasion of his 65th birthday

The Suzuki cross-coupling reaction, which involves the coupling of aryl boronic acid with an organohalide, has proven to be a versatile tool in organic synthesis.[1] Recent developments have led to catalysts based on sterically demanding, basic phosphanes allowing even the conversion of unreactive aryl chlorides.[2] Nevertheless, these reactions still proceed very slowly at room temperature.[3] As N-heterocyclic carbenes (NHC) are sometimes better ligands than phosphanes in homogeneous catalysis,[4] they were also tested in cross-coupling chemistry.[5–7] However, for the effective activation of aryl chlorides the known NHC-based catalysts require temperatures above 80 °C to yield reasonable activities. We now report on palladium(0) catalysts for the Suzuki cross-coupling at *ambient temperatures.*

Recently we established a synthetic procedure for homoleptic bis(NHC)-complexes of palladium(0) by ligand exchange in bis(tri-*ortho*-tolylphosphane)palladium(0) (**1a**).[6] The catalytic activity of these complexes strongly depends on the steric bulk of the NHC ligand. 1,3-Bisadamantylimidazolin-2-ylidene (**2**), as one of the most bulky NHC ligands,[8] represents a good candidate for palladium(0) catalysts of high activities in the Suzuki cross-coupling. However, even in presence of an excess of **2** only one phosphane ligand of **1a** was exchanged, which resulted in the formation of complex **3a** [Eq. (1)].



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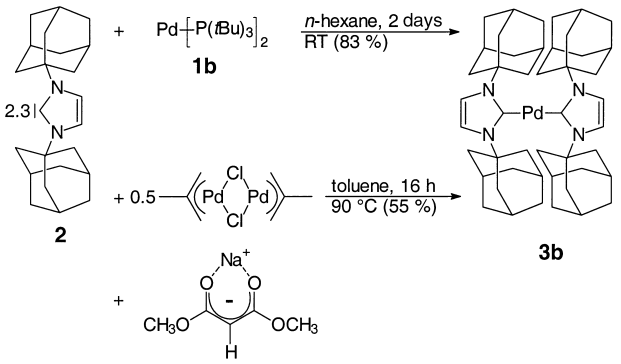
Supporting information for this article is available on the WWW under http://www.angewandte.com or from the author.

There is only one other example of an isolated mixed NHC-phosphane complex of palladium(0) in the literature.[9] Furthermore, **3a** is the first NHC-complex to catalyze the Suzuki cross-coupling of 4-chlorotoluene with phenylboronic acid at ambient temperature (20% conversion). Therefore, it was desirable to prepare the homoleptic palladium(0) complex **3b** as a potential catalyst. Screening various bis(phosphane)palladium(0) precursor complexes led to bis(tri-*tert*-butylphosphane)palladium(0) (**1b**) as the ideal starting material to form **3b** (83% yield, Scheme 1). Compound **3b** also resulted from the in situ reduction of $[\{(\eta^3\text{-}C_3H_5)PdCl\}_2]$ in the presence of **2** at 90 °C (55% yield).[10] This alternative procedure circumvents the use of the expensive starting material **1b**.[11]



Scheme 1. Methods for the synthesis of **3b**.

Crystals suitable for X-ray diffraction studies were obtained from a diethyl ether solution at ambient temperature (Figure 1).[12] The C-Pd-C angle is 180° and the NHC planes are twisted by 95.6(2)°. Therefore the palladium center is sterically encumbered.

Nevertheless, **3b** is a highly active catalyst in the Suzuki cross-coupling of aryl chlorides at room temperature (Table 1). For example, 4-chlorotoluene is coupled to phenyl

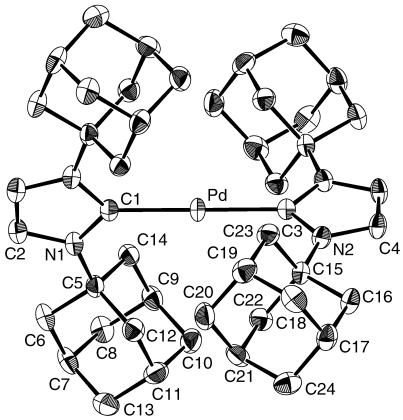
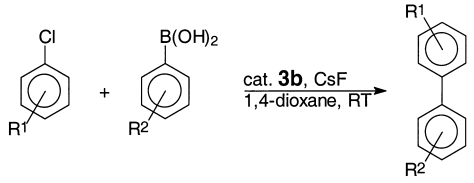


Figure 1. ORTEP[13] drawing of the molecular structure of **3b** in the solid state. Thermal ellipsoids are set at the 50% probability level. Hydrogen atoms are omitted for clarity. Symmetry code: ($' \equiv -x, y, 0.5 - z$). Selected bond lengths [Å] and angles [°]: Pd-C1 2.076(5), Pd-C3 2.084(5), N1-C1 1.375(5), N1-C2 1.376(6), N1-C5 1.493(5), N2-C3 1.371(5), N2-C4 1.374(6), N2-C15 1.489(6), C2-C2′ 1.322(7), C4-C4′ 1.322(7); C1-Pd-C3 180.00, Pd-C1-N1 128.3(2), Pd-C3-N2 128.2(2), N1-C1-N1′ 103.4(4), N2-C3-N2′ 103.7(4).

Table 1. Suzuki cross-coupling of aryl chlorides with catalyst **3b**.[a]



Entry	R^1	R^2	t	[%][b]
1	4-CH_3	H	20 min	97[c]
2	4-CH_3	H	2 h	75
3	4-CH_3	H	24 h	57[d]
4	4-CH_3	H	6 h[e]	> 99
5	4-OCH_3	H	6 h[e]	> 99
6	4-CF_3	H	2 h	95
7	4-CF_3	H	6 h[e]	> 99
8	3-CH_3	H	2 h	80
9	3-CH_3	H	24 h	93
10	4-CF_3	3-OCH_3	24 h	97
11	4-$COCH_3$	3-OCH_3	24 h	95
12	4-CH_3	3-OCH_3	24 h	80

[a] 1.0 equivalent aryl chloride, 1.5 equivalents aryl boronic acid, 2.0 equivalents CsF, 3 mol% **3b**, 1,4-dioxane, RT unless otherwise stated. [b] GC-yield using diethyleneglycol-di-*n*-butyl ether as the internal standard. [c] At 80 °C. [d] At low catalyst loading with 0.1 mol% **3b**. [e] Reaction time not minimized.

boronicacid in the presence of 3 mol% of **3b** and two equivalents of CsF in 97% yield at 80 °C within 20 minutes (entry 1). At room temperature, the same result is obtained after 6 hours (entry 4). The starting turnover frequency (TOF)[14] of 1100 [mol product mol Pd^{-1} h^{-1}] in entry 1 and the turnover number (TON) of 573 [(mol product) (mol Pd)$^{-1}$ h^{-1}] (entry 3) are the highest reported to date for aryl chlorides under these conditions, thus illustrating the activity of catalyst **3b**. The use of 1,4-dioxane as well as two equivalents of CsF gives the best results. Other solvents such as toluene, diethyl ether, or THF give lower conversions. Regarding the salt additive, moderate conversions could still be detected with the use of Cs_2CO_3 while KF was less effective.

Sterically unhindered aryl chlorides can be converted with high to quantitative yields. The reaction time depends on the substituents in the *para* position of the aryl chloride and varies from 2–6 hours (Table 1, entries 4–7). Activated, electron-poor aryl chlorides react nearly quantitatively within 2 hours (Table 1, entry 6) whereas the deactivated ones need 6 hours for a similar conversion (entry 5). The substituents on the aryl boronic acid have an even greater effect on the reaction rates. While *meta* substitution can be compensated by electronically activated aryl chlorides (entries 10, 11), *ortho* substituents both in the aryl chlorides and in the boronic acids are less tolerable. Because of the bulky NHC ligands, sterically less demanding substrates react especially rapidly with the palladium center.

No induction period was observed in these catalytic reactions. However, since palladium black precipitates during the conversion, we cannot exclude that active clusters of the type $[Pd_n(NHC)_m]$ ($n > 0.5m$) are formed.

In conclusion, we have developed a synthetic route to mixed and homoleptic palladium(0) complexes with sterically demanding N-heterocyclic carbene ligands. The homoleptic complex **3b** catalyzes the Suzuki cross-coupling and exhibits

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the highest TON with aryl chlorides at room temperature reported so far. Various *para* and *meta* substituted substrates can be quantitatively converted within a few hours.

Experimental Section

3b: **1b** (1000 mg, 1.81 mmol) was dissolved in *n*-hexane (30 mL). A solution of **2** (1400 mg, 4.16 mmol) in *n*-hexane (30 mL) was added. The mixture was stirred at ambient temperature for 24–48 h during which a yellow solid precipitated. After filtration and drying in vacuo the product was obtained as an analytically pure bright yellow solid. X-ray suitable crystals were obtained by recrystallization from diethyl ether. Yield: 1177 mg, 1.51 mmol, 83 %; m.p. >285 °C (decomp.); ^{1}H NMR (400 MHz, [D$_8$]toluene, 25 °C): $\delta = 1.47-1.80$ (m, 24 H, CH_2 of C$_{10}$H$_{15}$), 2.06–2.12 (m, 12 H, CH of C$_{10}$H$_{15}$), 3.05 (s, 24 H, CH_2 of C$_{10}$H$_{15}$), 6.69 (s, 4 H, NCHCHCH$_2$N); ^{13}C{^{1}H} NMR (100.5 MHz, [D$_8$]toluene, 25 °C): $\delta = 31.0$, 36.8, 44.0 (*C*$_{10}$H$_{15}$), 57.2 (ipso-*C* of C$_{10}$H$_{15}$), 112.7 (NCHCHCH$_2$N), 191.8 (NC*N*); CI-MS: *m*/*z* (%): 778 (3) [*M*$^+$], 336 (100) [NHC$^+$], 281 (33), 207 (27), 203 (40); elemental analysis calcd (%) for C$_{46}$H$_{64}$N$_4$Pd (779.44): C 70.88, H 8.28, N 7.19; found: C 70.80, H 8.24, N 7.22.

Alternative synthesis: **2** (343 mg, 1.02 mmol), [(η^3-C$_3$H$_5$)PdCl]$_2$ (100 mg, 0.254 mmol), and sodium dimethylmalonate (78 mg, 0.506 mmol) were suspended in toluene (30 mL) in a Schlenk tube. The stirred mixture was heated at 90 °C for 16 h after which the solution was brown. After cooling to room temperature, the mixture was filtered to remove some free palladium metal and the solution was concentrated. Crystallization at −50 °C yielded the product as bright yellow solid. Yield: 219 mg, 0.28 mmol, 55 %.

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[11] Current prices according to *STREM* catalogue 2001–2003: **1b** (2 g): 752 €; allylpalladium chloride dimer (2 g): 123 €.

[12] X-ray structure for **3b**·**H$_2$O**: bright yellow crystals, C$_{46}$H$_{64}$N$_4$OPd, crystal dimensions $0.38 \times 0.32 \times 0.24$ mm; $M_r = 797.45$; monoclinic, space group *C*2/*c* (no. 15), $a = 23.436(2)$, $b = 13.213(1)$, $c = 12.999(1)$ Å, $\beta = 104.645(9)^\circ$, $V = 3894.5(6)$ Å^3, $Z = 4$, $\lambda(\mathrm{Mo_{K\alpha}}) = 0.71073$ Å, $\mu = 0.518$ mm^{-1}, $\rho_{calcd} = 1.360$ g cm^{-3}, $T = 199(1)$ K, $F(000) = 1696$. Preliminary examination and data collection were carried out on a Stoe IPDS area detecting diffraction system at the window of a rotating anode (Nonius, FR591). The unit cell parameters were obtained by full-matrix least-squares refinement of 4977 reflections. A total number of 23284 reflections were collected (θ_{max}: 25.66°, exposure time: 300 s per image, 310 images, $\Delta\phi$: 1.0°, dx: 70.0 mm). After merging ($R_{int} = 0.0860$) a sum of 3527 (all data) independent reflections remained and were used for all calculations. 2307 of them were observed data with $I > 2\sigma(I)$. The structure was solved by direct methods (SIR-92)[15] and refined by full-matrix least-squares on F^2 (SHELXL-97).[16] All non-hydrogen atoms of the asymmetric unit were refined anisotropically. All hydrogen atoms were located in the difference Fourier map and refined with individual isotropic temperature parameters, except those located at the water oxygen. They were calculated in ideal positions (riding model). $R1 = 0.0451$ (observed data), $wR2 = 0.1185$ (all data), GOF = 0.934, 365 parameters, $\Delta\rho_{max/min} = 1.11/-0.97$ e Å^{-3}. No correction for decay and absorption was applied. CCDC-175167 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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X-Ray Structural Characterization of a Monoorganotin Acid**

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Dedicated to Sir John Meurig Thomas on the occasion of his 70th birthday

The hydrolysis of monoorganotin trihalides has been a topic of interest in the chemistry of tin for a long time. Methylstannonic acid [Me(Sn(OH)O] was first reported in 1922.[1] It was proposed that monoorganotin acids exist either as cyclic trimers or as chainlike hydroxytin ethers; however, these structural elements could not be confirmed unambiguously.[2] Functionalized organotin compounds are used in organic synthesis[3] and catalytic reactions.[4] Very recently Chandrasekhar et al. synthesized a hexaferrocene–tin–oxygen cluster containing a *cyclo*-tristannoxane-like structure by the reaction of *n*-butylstannonic acid with ferrocene monocarboxylic acid.[5] Basic hydrolysis of diorganotin dihalides also yields tin–oxygen heterocycles,[6, 7] which show no additional sub-

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