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Double HCl elimination and configuration change in the square-planar palladium complex *trans*-[{(Ph₂PC₆H₄CONH)₂C₆H₄}PdCl₂] under Suzuki conditions: Isolation and molecular structure of *cis*-[{(Ph₂PC₆H₄CON)₂C₆H₄}Pd]

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Dedicated to Professor Max Herberhold on the occasion of his 70th birthday

Abstract

The *trans*-configurated square-planar palladium complex *trans*-[{($Ph_2PC_6H_4CONH$)_2C_6H_4}PdCl₂] (1), which catalyzes the Suzuki cross coupling of 4-bromotoluene with phenylboronic acid, was found to react with potassium carbonate in toluene at 90 °C (Suzuki conditions) to give *cis*-[{($Ph_2PC_6H_4CON$)_2C_6H_4}Pd] (2). The single-crystal X-ray structure analysis of **2** reveals the square-planar palladium center to be in a *cis* configuration. The *trans*-*cis* configuration change at palladium is possible because of the elimination of two HCl equivalents in the conversion of **1** into **2**. Both complexes **1** and **2** show approximately the same catalytic performance for Suzuki reactions, suggesting **2** to be the catalytically active species.

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Keywords: Palladium complexes; Suzuki cross-coupling; Square-planar geometry; cis and trans configuration

The Suzuki cross-coupling (Suzuki–Miyaura reaction), catalyzed by various palladium complexes, is among the most powerful synthetic tools for the generation of carbon–carbon bonds [1]. Although many different palladium(II) or palladium(0) complexes catalyze this coupling reaction, significant efforts have been put on the design of suitable ligands that can increase the catalytic activity of the palladium center. Some of the most active Suzuki catalysts are palladium complexes susceptible to *ortho*-metallation or palladacycle formation [2,3]. Still, the best results for the Suzuki cross-coupling of the deactivated and sterically hindered aryl bromide with aryl boronic acid have been obtained by Buchwald and co-

workers [4] with ligands avoiding palladacycles formation. Recently, several palladium(II) complexes containing trans-spanning diphosphine ligands that contain a rigid ligand backbone have been synthesized [5,6]. Thus, trans-[PdCl₂(SPANphos)] reported by van Leeuwen does not show any tendency to *cis-trans* isomerization [5], the complex *trans*- $[PdCl_2-(diphos)]$ (diphos = 2,6-bis(2-((diphenylphosphino)methyl)phenyl)benzene) reported by Protasiewicz [6] has been successfully used as Heck and Suzuki catalyst, in spite of the rigid *trans*-geometry [7]. With the diphosphine Xantphos, developed by van Leeuwen [8] and used as a ligand for Suzuki reaction, palladium complexes with trans-standing alkyl and chloro ligands [9] and with trans-standing aryl and bromo ligands [10] have been isolated and characterized by X-ray crystallography. Since we recently synthesized a square planar

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Table 1

Catalytic turnover numbers (TON), indicating the moles of product formed per mol of catalyst used after 18 h, for the Suzuki cross-coupling of phenylboronic acid with the substrate 4-bromotoluene catalyzed by 1 and 2 in toluene in the presence of K_2CO_3 (2 equivalents with respect to substrate) [12]

<i>T</i> (°C)	Catalyst/substrate	1	2
30	1:1000	280	450
30	1:10000	1350	2000
30	1:100 000	0	0
60	1:1000	1000	1000
60	1:10000	5100	7400
60	1:100 000	33 000	49000
90	1:1000	1000	1000
90	1:10000	7350	8800
90	1:100 000	61 500	71000

trans-palladium complex containing a rigid diphosphine ligand backbone, *trans*- [$\{(Ph_2PC_6H_4CONH)_2C_6H_4\}PdCl_2$] (1) [11], we tested it as a catalyst for Suzuki cross-coupling reactions.

We studied the Suzuki cross-coupling of phenylboronic acid with 4-bromotoluene catalyzed by complex 1 at different temperatures and in different catalyst/substrate ratios. The results compiled in Table 1 show that complex 1 has a medium catalytic performance with respect to known Suzuki catalysts [1–4], the highest catalytic turnover number (TON) being 61500 (catalyst/substrate ratio of 1:100000 at 90 °C) for the cross-coupling with the deactivated substrate 4-bromotoluene.

As we observed a color change from yellow to red during the catalytic reaction, we decided to study the reactivity of **1** towards a base such as K_2CO_3 in toluene under the same conditions (90 °C) as those for the Suzuki cross-coupling reaction but without substrate and phenylboronic acid [13]. Under these conditions we observed the same color change from yellow to red, and from the resulting solution we isolated the complex *cis*-[{(Ph₂PC₆H₄CON)₂-C₆H₄}Pd] (**2**). The conversion of **1** into **2** implies the loss of two molecules of HCl, caused by the action of the base (Scheme 1). The double HCl elimination from **1** is the same reaction already observed for the platinum analogue *trans*-[{(Ph₂PC₆H₄CONH)₂C₆H₄}PtCl₂] which, however, works



Fig. 1. ORTEP view of **2** with thermal ellipsoids at the 50% probability level; hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Pd(1)-P(1) 2.2528(10), Pd(1)-P(2) 2.2481(11), Pd(1)-N(1) 2.032(4), Pd(1)-N(2) 2.069(3), C(7)-O(1) 1.229(5), C(14)-O(2) 1.235(5), C(7)-N(1) 1.356(5), C(14)-N(2) 1.353(5), C(9)-P(1) 1.817(4), C(20)-P(2) 1.823(4). Selected bond angles (°): P(1)-Pd(1)-P(2) 105.44(4), N(1)-Pd(1)-N(2) 82.19(13), P(1)-Pd(1)-N(1) 82.29(10), P(1)-Pd(1)-N(2) 161.74(10), P(2)-Pd(1)-N(1) 172.01(10), P(2)-Pd(1)-N(2) 89.85(10), O(1)-C(7)-N(1) 124.5(4), O(2)-C(14)-N(2) 122.9(4).

already with triethylamine as a base [16], while the palladium complex 1 requires a stronger base such as K_2CO_3 .

Complex 2 was characterized by correct NMR (1 H, 13 C, ³¹P) and mass-spectroscopic data as well as by satisfactory elemental analysis data [13]. Moreover, red crystals of 2. CH₂ Cl₂, suitable for single-crystal X-ray structure analvsis, were obtained by leaving a concentrated dichloromethane solution of the complex standing several days at room temperature [14]. The molecular structure of 2 shows the palladium atom to be in a distorted square-planar geometry, surrounded by two chlorine atoms and two nitrogen atoms in a *cis* coordination geometry, see Fig. 1. The formation of five- and six-membered chelate rings imposes a considerable distortion around the palladium atom. The N-Pd-N angle [82.19(13)°] is acute, whereas the P–Pd–P angle is obtuse by more than 15° [105.44(4)°]. The atoms Pd(1), P(1), P(2), N(1) and N(2) are almost coplanar, with an average deviation of 0.0813 Å; the metal lies out of the plane by 0.1038(13) Å. The Pd–P distances of the *cis* complex 2 are shorter than the Pd–P distances in the trans complex 1 [11] (see Fig. 1).

The isolation of the red complex 2, formed from the yellow complex 1 under Suzuki conditions, suggests 2 to be the active species in Suzuki cross-coupling reactions catalyzed by 1, given the fact that the color of the reaction solution changes from yellow to red during the Suzuki reaction with 1 as a catalyst precursor. We therefore compared the catalytic activities of 1 and 2 for the Suzuki cross-coupling of phenylboronic acid with 4-bromotoluene under the same conditions. The results compiled in Table 1 show that the catalytic turnover numbers of both complexes are comparable, 2 being always slightly more active. This is reasonable, if one assumes that 1 is only a catalyst precursor which has to be transformed under catalytic conditions into the active species 2 by double HCl elimination. As this reaction implies a *trans-cis* configuration change at the palladium center, it appears that the *cis* configuration is the more adequate one for Suzuki activity.

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References

- [1] (a) N. Miyaura, A. Suzuki, Chem. Rev. 95 (1995) 2457-2483;
- (b) S. Kotha, K. Lahiri, D. Kashinath, Tetrahedron 58 (2002) 9633–9695;
 - (c) A. Suzuki, J. Organomet. Chem. 653 (2002) 83-90;
- (d) F. Bellina, A. Carpita, R. Rossi, Synthesis 15 (2004) 2419–2440.
 [2] M. Beller, H. Fischer, W.A. Herrmann, K. Öfele, C. Brossmer, Angew. Chem., Int. Ed. 34 (1995) 1848–1849.
- [3] R.B. Bedford, S.L. Hazelwood (néeWelch), M.E. Limmert, D.A. Albisson, S.M. Draper, P.N. Scully, S.J. Coles, M.B. Hursthouse, Chem. Eur. J. 9 (2003) 3216–3227.

- [4] (a) T.E. Barder, S.D. Walker, J.R. Martinelli, S.L. Buchwald, J. Am. Chem. Soc. 127 (2005) 4685–4696;
 (b) J. Yin, M.P. Rainka, X. Zhang, S.L. Buchwald, J. Am. Chem. Soc. 124 (2002) 1162–1163;
 (c) J.P. Wolfe, R.A. Singer, B.H. Yang, S.L. Buchwald, J. Am. Chem. Soc. 121 (1999) 9550–9561.
- [5] Z. Freixa, M.S. Beentjes, G.D. Batema, C.B. Dieleman, G.P.F. van Strijdonck, J.N.H. Reek, P.C.J. Kamer, J. Fraanje, K. Goubitz, P.W.N.M. van Leeuwen, Angew. Chem., Int. Ed. 42 (2003) 1284– 1287.
- [6] R.C. Smith, J.D. Protasiewicz, Organometallics 23 (2004) 4215– 4222.
- [7] R.C. Smith, C.R. Bodner, M.J. Earl, N.C. Sears, N.E. Hill, L.M. Bishop, N. Sizemore, D.T. Hehemann, J.J. Bohn, J.D. Protasiewicz, J. Organomet. Chem. 690 (2005) 477–481.
- [8] M. Kranenburg, Y.E.M. van der Burgt, Organometallics 14 (1995) 3081–3089.
- [9] P.C.J. Kramer, P.W.N.M. van Leeuwen, Acc. Chem. Res. 34 (2001) 895–904.
- [10] J. Yin, S.L. Buchwald, J. Am. Chem. Soc. 124 (2002) 6043-6048.
- [11] S. Burger, B. Therrien, G. Süss-Fink, Eur. J. Inorg. Chem. (2003) 3099–3103.
- [12] In a Schlenk tube, the catalyst was added (in the molar ratio given in Table 1) to a solution of 138 mg (0.5 mmol) of $K_2CO_3 \cdot 1.5 H_2O$, 91 mg (0.75 mmol) of phenylboronic acid and 0.5 mmol of the aryl bromide in 5 mL of toluene. Then, the mixture was heated to the desired temperature (Table 1) and stirred for 18 h. After cooling, the solution was filtrated over a small silica gel column, then the silica gel was eluted with ether (20 mL). The filtrate was analyzed by GC.
- [13] A solution of complex 1 (0.050 g, 0.058 mmol) and K₂CO₃ (1.2 g, 8.56 mmol) in toluene (10 mL) was stirred at 90 °C, until the yellow solution turned dark red (~3 h). Then the solvent was evaporated *in vacuo*, and the product was purified by column chromatography on silica gel using acetone as an eluant (red fraction, yield 50%). ¹H NMR (400 MHz, CDCl₃): $\delta = 8.68-8.65$ (m, 2H), 7.75–7.72 (m, 2H), 7.57(t, *J* = 7.5 Hz, 2H), 7.43–7.40 (m, 4H), 7.24 (t, *J* = 7.5 Hz, 2H), 7.21–7.13 (m, 16H), 6.82–6.73 (m, 4H). ³¹P NMR (81 MHz, CDCl₃): $\delta = 26.77$ (s). ¹³C NMR (100 MHz, CDCl₃): $\delta = 164.86$, 146.53, 133.88, 133.82, 133.76, 132.19, 131.58, 129.31, 129.26, 129.20, 128.78, 128.24, 124.87, 122.43. Masse: ESI-*m*/*z* = 811 [M + Na]⁺. Anal. Calcd.: C, 66.97; H, 4.09; N, 3.55 Found: C, 66.75; H, 4.23; N, 3.41.
- [14] **2**·**CH**₂**Cl**₂: C₄₅H₃₄Cl₂N₂O₂P₂Pd, $M = 873.98 \text{ g mol}^{-1}$, trigonal, $R\bar{3}$, $a = 44.266(2), c = 11.6026(4) \text{ Å}, V = 19689.1 (15) \text{ Å}^3, T = 153(2) \text{ K},$ Z = 18, $D_c = 1.327 \text{ g cm}^{-3}$, μ (Mo- K α) = 0.656 mm⁻¹, 35624 reflections measured, 8040 unique ($R_{int} = 0.0855$) which were used in all calculations. $R_1 [I > 2\sigma(I)] = 0.0513$, $wR_2 (F^2) = 0.1061$ (all data). The intensity data were collected on a Stoe Mark II-Image Plate Diffraction System [15] equipped with a two-circle goniometer and using Mo-K\alpha graphite monochromated radiation ($\lambda = 0.71073$ Å). Image plate distance 135 mm, ω rotation scans 0–146° at ϕ 0°, step $\Delta \omega = 1.0^{\circ}$, exposures of 9 min per image, 20 range 1.70–51.55°, d_{\min} – $d_{\text{max}} = 23.995 - 0.817$ Å. The structure was solved by direct methods using the program SHELXS-97 [16] and refined by full matrix least squares on F^2 with SHELXL-97 [17]. The hydrogen atoms were included in calculated positions and treated as riding atoms using SHELXL-97 default parameters. All non-hydrogen atoms were refined anisotropically, using weighted full-matrix least-squares on F^2 . A semi-empirical absorption correction was applied using the MULscanABS routine in PLATON [18]; transmission factors: $T_{\min}/T_{\max} = 0.80681/0.93560$. All attempts to refine the disordered molecule of CH₂CL₂ failed. Therefore, the SQUEEZE instruction in PLATON [18] was used to calculate the potential solvent accessible area in the unit cell; 4925.7 Å³ were calculated containing 1012 electrons. Therefore, 18 CH₂Cl₂ molecules per unit cell were included in all further calculations. The figure was drawn with ORTEP [19]. CCDC-602847 contains the supplementary crystallographic data for

this structure. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44 1223 336 033; E-mail:deposit@ccdc.cam.ac.uk].

- [15] Stoe, X-Area V1.26 & X-RED32 V1.26 Software, Stoe & Cie GmbH, Darmstadt, Germany, 2005.
- [16] G.M. Sheldrick, SHELXS-97 Program for crystal structure determination, Acta Cryst. A46 (1990) 467–473.
- [17] G. Sheldrick, SHELXL-97, Universität Göttingen, Göttingen, Germany, 1999.
- [18] A.L. Spek, J. Appl. Cryst. 36 (2003) 7-13.
- [19] L.J. Farrugia, J. Appl. Cryst. 30 (1997) 565.