The Pd(II) Complex of a N,N'-Diallylbenzimidazol-2-ylidene Ligand

F. Ekkehardt Hahn, Christian Holtgrewe, and Tania Pape

Institut für Anorganische und Analytische Chemie, Westfälische Wilhelms-Universität Münster, Corrensstraße 8, D-48149 Münster, Germany

Reprint requests to Prof. Dr. F. E. Hahn. E-mail: fehahn@uni-muenster.de

Z. Naturforsch. **59b,** 1051 – 1053 (2004); received June 30, 2004

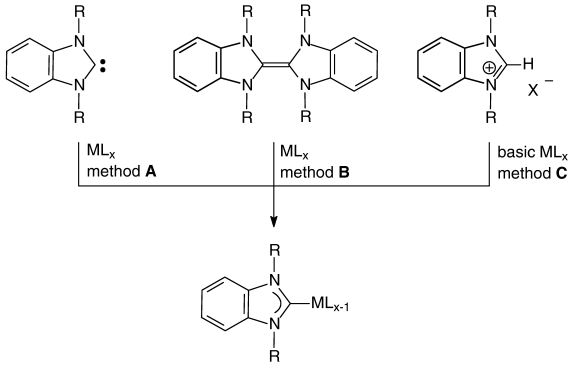
The palladium(II) dicarbene complex *trans*-[$PdBr_2(L)_2$], **2** (L = 1,3-di-(2-propenyl)-benzimidazol-2-ylidene) was synthesized from 1,3-di-(2-propenyl)-benzimidazolium bromide **1** and $Pd(OAc)_2$ by *in situ* deprotonation. The X-ray structure analysis revealed a mononuclear complex with a palladium(II) center coordinated in a square-planar fashion by the two carbene functions and two bromo ligands.

Key words: Benzimidazol-2-ylidene, Palladium(II), Crystal Structure, Allyl Groups

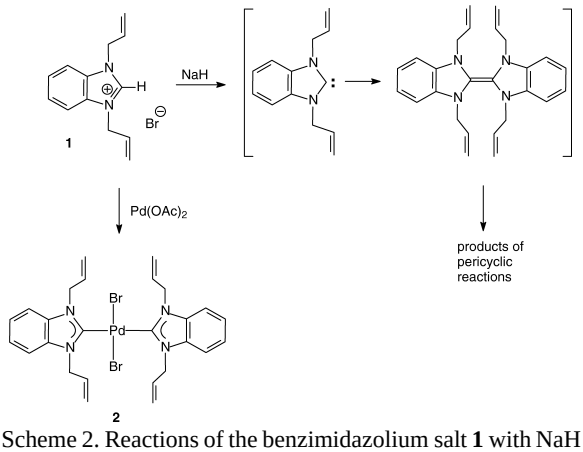
Introduction

Complexes of N-heterocylic carbenes have attracted much interest in the fields of coordination chemistry and homogenous catalysis [1]. Various synthetic procedures for the generation of complexes with benzannulated N-heterocyclic carbene ligands have been reported. These include the reaction of the stable free carbene with a transition metal complex [2, 3] (method **A**) and the cleavage of N,N-bridged [4] and unbridged [5] dibenzotetraazafulvalenes (method **B**) with coordinatively unsaturated transition metal complexes. Alternatively, benzimidazolium salts react with complexes containing basic ligands like $Pd(OAc)_2$ [6] or Ag_2O [7] under *in situ* deprotonation and formation of the complex containing benzimidazol-2-ylidene ligands (method **C**, Scheme 1). In addition to these methods, the preparation of complexes with benzannulated N-heterocyclic carbene ligands from complexes with β-functionalized phenyl isocyanides has been reported [8].

We became interested recently in the coordination chemistry of benzannulated N-heterocyclic carbene ligands which bear N-allyl substituents. After formation of a carbene complex the allyl substituents of the ligand are capable to coordinate to the metal center leading to a coordination environment made up from different sp^2-carbon donors [9]. Free benzimidazol-2-ylidenes dimerize unless protected with sterically demanding N-substituents [4a, 5c]. In case of N-allyl substituted derivatives the C=C double bond of the resulting dibenzotetraazafulvalene reacts with the double bond of the allyl group in a series of pericyclic reactions (Scheme 2) [10]. This rules out methods **A** and **B** (Scheme 1) for the preparation of complexes with N-



Scheme 1. Preparation of benzimidazol-2-ylidene complexes.



Scheme 2. Reactions of the benzimidazolium salt **1** with NaH or $Pd(OAc)_2$ to give **2**.

allyl substituted benzimidazol-2-ylidenes. To avoid the rearrangement reactions only the *in situ* deprotonation (method **C**) can be applied for the preparation of complexes with N-allyl substituted benzimidazol-2-ylidene ligands. We report here the synthesis of the N-allyl substituted benzimidazolium salt **1** and its reaction with $Pd(OAc)_2$ giving complex **2** the molecular structure of which is presented (Scheme 2).

Experimental Section

All manipulations were performed in an atmosphere of dry argon by standard Schlenk techniques. Solvents were dried by standard methods and freshly distilled prior to use.

1,3-Di-(2-propenyl)-benzimidazolium bromide (**1**): Benzimidazole (7.0 g, 60 mmol) is dissolved in ethanol (100 ml). To this solution solid sodium hydrogencarbonate (5.04 g, 60 mmol) and allyl bromide (21.8 g, 180 mmol) are added. The reaction mixture is heated under reflux for 24 h. The volume of the solution is then reduced to 20 ml and the precipitated NaBr is removed by filtration of the hot solution. The filtrate is cooled to 4 °C for 24 h upon which compound **1** crystallizes as colorless needles. Yield: 11.0 g (39 mmol, 65%). ^{1}H NMR (200.131 MHz, $CDCl_3$, ppm): $\delta = 10.97$ (s, 1 H, NC*H*N), 7.65 (m, 2 H, Ar-*H*), 7.48 (m, 2 H, Ar-*H*), 5.97 (m, 2 H, CH_2CH=CH_2), 5.29 (dm, 2 H, $^3J_{HH} = 17.2$ Hz, CH_2CH=C*H*$_{trans}$), 5.23 (dm, 2 H, $^3J_{HH} = 10.2$ Hz, CH_2CH=C*H*$_{cis}$), 5.15 (dm, 4 H, $^3J_{HH} = 6.01$ Hz, CH_2CH=CH_2). – ^{13}C NMR (50.3 MHz, $CDCl_3$, ppm): $\delta = 141.3$ (CH_2CH=CH_2), 130.9 (NCHN), 129.7, 126.9, 121.6 (Ar-*C*), 113.5 (CH_2CH=CH_2), 49.7 (CH_2CH=CH_2). – $C_{13}H_{15}N_2Br$ (279.18): calcd. C 55.93, H 5.42, N 10.03; found C 55.65, H 5.12, N 9.87.

trans-[PdBr$_2$(1,3-di-(2-propenyl)-benzimidazol-2-ylidene)] (**2**): A suspension of **1** (556 mg, 2.0 mmol) and $Pd(OAc)_2$ (224 mg, 1.0 mmol) in THF (20 ml) is refluxed for 72 h. The white precipitate is filtered off and washed with methanol. The reaction product can be recrystallized from refluxing DMSO. Colorless, air-stable crystals of **2** suitable for an X-ray diffraction analysis are obtained by slow cooling of a saturated DMSO solution from 90 °C to room temperature. Yield: 450 mg (0.68 mmol, 68%). ^{1}H NMR (200.1 MHz, [D$_6$]-DMSO, ppm): $\delta = 7.48$ (m, 2 H, Ar-*H*), 7.35 (m, 2 H, Ar-*H*), 5.99 (m, 2 H, CH_2CH=CH_2), 5.38 – 5.53 (m, 4 H, CH_2CH=CH_2), 5.12 (m, 4 H, CH_2CH=CH_2). – MALDI-MS: $m/z = 662.5$ [M$^+$], 582.4 [M$^+$-Br]. – $C_{26}H_{28}N_4Br_2Pd$ (662.74): calcd. C 47.12, H 4.26, N 8.45; found C 46.91, H 4.01, N 8.24.

X-ray structure determination of **2**: Colorless prisms of **2** are obtained by recrystallization from DMSO. Formula $C_{26}H_{28}N_4Br_2Pd$, $M = 662.74$, colorless crystal $0.17 \times 0.10 \times 0.04$ mm^3, $a = 10.5855(6)$, $b = 9.5968(6)$, $c = 12.9721(8)$ Å, $\beta = 93.4400(10)^\circ$, $V = 1315.42(14)$ Å^3, $\rho_{calcd} = 1.673$ g cm^{-3}, $\mu = 3.764$ mm^{-1}, empirical absorption correction ($0.5671 \le T \le 0.8640$), $Z = 2$, monoclinic, space group $P2_1/n$ (No. 14), $\lambda = 0.71073$ Å, $T = 173(2)$ K, ω and φ scans, 14788 reflections collected ($\pm h$, $\pm k$, $\pm l$) in the range $4.8 \le 2\theta \le 60.0^\circ$, 3814 independent ($R_{int} = 0.0325$) and 3344 observed reflections [$I \ge 2\sigma(I)$], 207 refined parameters, $R = 0.0260$, $wR2 = 0.0629$, max. residual electron density 1.263 (-0.430) e Å^{-3}, anisotropic displacement parameters for all non-hydrogen atoms, hydrogen atom positions identified and refined. X-ray intensities were measured using a Bruker AXS Apex diffractometer equipped with a rotating anode. Structure solution with SHELXS-97 [11] by heavy atom methods and refined with SHELXL-97 [12].

Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 242971. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: int. code +44(1223)336-033, e-mail: deposit@ccdc.cam.ac.uk].

Results and Discussion

1,3-Di-(2-propenyl)-benzimidazolium bromide **1** was synthesized in a one pot reaction by heating benzimidazole and two equivalents of allyl bromide in ethanol in the presence of $NaHCO_3$ [13]. The benz-

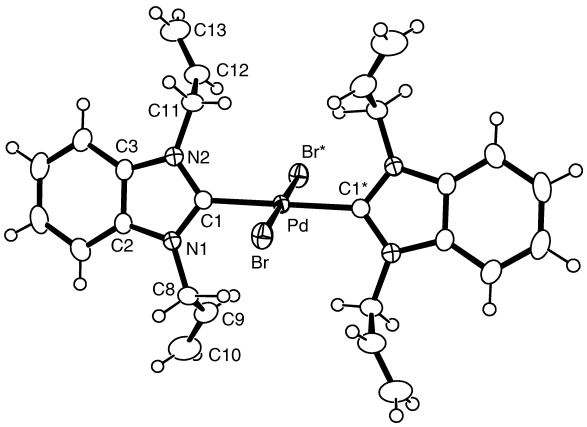


Fig. 1. Molecular structure of complex *trans*-[$PdBr_2(L)_2$], **2**. Hydrogen atoms have been omitted. Selected bond lengths [Å] und angles [°]: Pd-Br 2.4274(2), Pd-C1 2.019(2), N1-C1 1.348(2), N1-C2 1.398(2), N1-C8 1.463(3), N2-C1 1.352(2), N2-C3 1.392(2), N2-C11 1.464(3), C2-C3 1.381(3), C8-C9 1.493(3), C9-C10 1.299(4), C11-C12 1.489(4), C12-C13 1.305(4); Br-Pd-C1 89.07(5), Br-Pd-C1* 90.93(5), C1-N1-C2 110.4(2), C1-N1-C8 124.8(2), C2-N1-C8 124.7(2), C1-N2-C3 110.5(2), C1-N2-C11 124.5(2), C3-N2-C11 124.9(2), Pd-C1-N1 125.75(13), Pd-C1-N2 127.57(14), N1-C1-N2 106.5(2).

imidazolium salt **1** is slightly hygroscopic and soluble in chlorinated hydrocarbons, hot alcohols and water. The ^{1}H NMR spectrum shows the resonance for the NC*H*N proton as a singlet with a characteristic downfield shift at $\delta = 10.97$ ppm. The hydrogen atoms at the C=C double bond appear at $\delta = 5.79$, 5.29 and 5.23 ppm with the typical $^3J_{HH}$ coupling constants for the *cis* ($^3J_{HH} = 10.2$ Hz) and *trans* ($^3J_{HH} = 17.2$ Hz) protons.

The synthesis of the carbene complex **2** was carried out *via in situ* deprotonation of the benzimidazolium salt **1** with $Pd(OAc)_2$ [6] to avoid the side reactions occurring with the free carbene (Scheme 2). Complex **2** is a white powder, which is stable against air and moisture. It is only soluble in hot DMSO and DMF. Therefore no ^{13}C NMR spectrum could be recorded. In the ^{1}H NMR spectrum the signals corresponding to the hydrogen atoms of the allyl groups in **2** are not significantly shifted compared to **1**, indicating that the allyl groups are not coordinated to the palladium center. Attempts to enforce this coordination by halide abstraction with silver salts did not yield any identifiable products.

The molecular structure of complex **2** is depicted in Fig. 1. The palladium atom resides on a crystallographic inversion center and is coordinated in an almost perfect square-planar fashion in a *trans*-configuration. The Pd-C bond length (2.019(2) Å) is longer than observed for Pd^{II} complexes with two benzimidazol-2-ylidenen ligands in *cis*-configuration (1.987(4) and 1.990(8) Å [6]). As seen with other square-planar dicarbene complexes of palladium, the plane of the carbene ligand (C1/N1/C2/C3/N2) is oriented almost perpendicular (74.4°) to the Pd/C1/C1*/Br/Br* plane.

Acknowledgements

We thank the Fonds der chemischen Industrie and the BMBF for a predoctoral fellowship for Christian Holtgrewe.

[1] a) W. A. Herrmann, C. Köcher, Angew. Chem. **109**, 2256 (1997); Angew. Chem. Int. Ed. Engl. **36**, 2162 (1997); b) T. Weskamp, V. P. W. Böhm, W. A. Herrmann, J. Organomet. Chem. **600**, 12 (2000); c) W. A. Herrmann, Angew. Chem. **114**, 1343 (2002); Angew. Chem. Int. Ed. **41**, 1290 (2002); d) D. Bourissou, O. Guerret, F. P. Gabbaï, G. Bertrand, Chem. Rev. **100**, 39 (2000).

[2] F. E. Hahn, L. Wittenbecher, R. Boese, D. Bläser, Chem. Eur. J. **5**, 1931 (1999).

[3] F. E. Hahn, T. von Fehren, R. Fröhlich, Z. Naturforsch. **59b**, 348 (2004).

[4] a) F. E. Hahn, L. Wittenbecher, D. Le Van, R. Fröhlich, Angew. Chem. **112**, 551 (2000); Angew. Chem. Int. Ed. **39**, 541 (2000); b) F. E. Hahn, T. von Fehren, L. Wittenbecher, R. Fröhlich, Z. Naturforsch. **59b**, 541 (2004).

[5] a) F. E. Hahn, T. von Fehren, L. Wittenbecher, R. Fröhlich, Z. Naturforsch. **59b**, 544 (2004); b) F. E. Hahn, L. Wittenbecher, M. Kühn, T. Lügger, R. Fröhlich, J. Organomet. Chem. **617/618**, 629 (2001); c) E. Cetinkaya, P. B. Hitchcock, H. Kücükbay, M. F. Lappert, S. Al-Juaid, J. Organomet. Chem. **481**, 89 (1994).

[6] F. E. Hahn, M. Foth, J. Organomet. Chem. **585**, 241 (1999).

[7] H. M. J. Wang, I. J. B. Lin, Organometallics, **17**, 972 (1998).

[8] a) F. E. Hahn, V. Langenhahn, N. Meier, T. Lügger, W. P. Fehlhammer, Chem. Eur. J. **9**, 704 (2003); b) M. Tamm, F. E. Hahn, Coord. Chem. Rev. **182**, 175 (1999); c) M. Basato, F. Benetello, G. Facci, R. A. Michelin, M. Mozzon, S. Pugliese, P. Sgarbossa, S. M. Sbovata, A. Tassan, J. Organomet. Chem. **689**, 454 (2004).

[9] a) M. Tamm, F. E. Hahn, Inorg. Chim. Acta **288**, 47 (1999); b) S.-T. Liu, K. R. Reddy, Chem. Soc. Rev. **28**, 315 (1999).

[10] F. E. Hahn, C. Holtgrewe, T. Pape, Eur. J. Org. Chem., in preparation.

[11] G. M. Sheldrick, SHELXS-97, Acta Crystallogr. **A46**, 467 (1990).

[12] G. M. Sheldrick, SHELXL-97, Universität Göttingen (1997).

[13] E. A. Groreshnik, D. Schollmeyer, M. G. Mys'kiv, O. V. Pavl'uk, Z. Anorg. Allg. Chem. **626**, 1016 (2000).