

# Molecular Structures and Catalytic Activity of Palladium Complexes Derived from Lutidine-bridged Bis(benzimidazolin-2-ylidene) Ligands

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Dedicated to Prof. Helgard G. Raubenheimer on the occasion of his 65<sup>th</sup> birthday

Reaction of lutidine-bridged dibenzimidazolium dibromides **1–4** with palladium acetate gives pincer-type palladium complexes of the type [Pd(L)Br]Br [**5**]Br–[**8**]Br. Crystals suitable for an X-ray diffraction study have been obtained by slow evaporation of the solvent from dichloromethane/methanol solutions of [**7**]Br and [**8**]Br. The crystal structure of [**7**]<sup>+</sup> reveals a pincer topology of the cationic complex with a distorted square-planar coordination geometry at the metal center. From a solution of complex [**8**]Br, a dinuclear byproduct [**9**]<sup>+</sup> was obtained with two bis(benzimidazolin-2-ylidene) ligands coordinating in a bridging fashion. The pincer-type palladium complexes [**5**]Br–[**8**]Br were tested as precatalysts in Suzuki coupling reactions.

**Key words:** Heterocyclic Carbene Complexes, Palladium(II) Complexes, Pincer Complexes

## Introduction

Stable N-heterocyclic carbenes and particularly their metal complexes have recently attracted attention owing to their application in various homogeneous catalytic processes [1]. Several procedures for the preparation of complexes with benzimidazolin-2-ylidene ligands have been reported. Such complexes can be obtained by reaction of a transition metal complex with the free carbene [2] or by cleavage of the olefinic C=C double bond of dibenzotetraazafulvalenes with a coordinatively unsaturated transition metal complex [3]. In addition, complexes with benzimidazolin-2-ylidene ligands can be prepared by reaction of benzimidazolium salts with transition metal complexes like Pd(OAc)<sub>2</sub> [4], [Ir(μ-OMe)(cod)]<sub>2</sub> [5] or Ag<sub>2</sub>O [6] via an *in situ* deprotonation of the benzimidazolium salts followed by complex formation. Finally, complexes with benzannulated N-heterocyclic carbene ligands are obtained by intramolecular cyclization of coordinated β-functionalized isocyanides giving the NH,NH-stabilized carbene ligands which are easily N,N'-dialkylated [7].

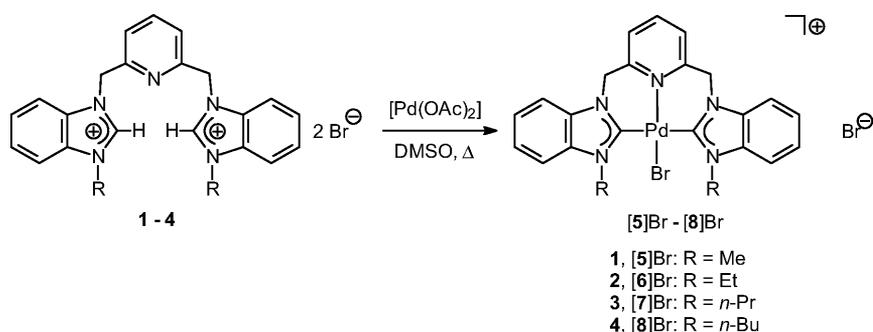
We became interested in the coordination chemistry and application in catalysis of pincer-type complexes with a benzimidazolin-2-ylidene donor function as a carbene source due to the intermediate position of this

type of N-heterocyclic carbene between the saturated imidazolidin-2-ylidene and the ubiquitous unsaturated imidazolin-2-ylidene [1, 2]. We have described some palladium pincer complexes derived from lutidine-[**8a**] or phenylene-bridged [**8b**] bis(benzimidazolin-2-ylidene) ligands. These complexes have been tested as precatalysts in Heck-type coupling reactions.

Here we present an additional molecular structure of a pincer complex with a lutidine-bridged bis(benzimidazolin-2-ylidene) ligand. In addition, the unusual molecular structure of a dinuclear complex with a pincer-type ligand bridging two metal centers is described. The catalytic activity of the pincer complexes in Suzuki coupling reactions is also discussed.

## Results and Discussion

We recently prepared the lutidine-bridged bis(benzimidazolin-2-ylidene) ligands **1–4** and reported the synthesis of their pincer-type palladium complexes [**5**]Br–[**8**]Br [8a]. These complexes were obtained by *in situ* deprotonation of the dibenzimidazolium salts with palladium acetate in good yield (Scheme 1). This method is similar to the published procedure for the preparation of lutidine-bridged dicarbene palladium complexes with imidazolin-2-ylidene donors [9]. Complexes [**5**]Br–[**8**]Br have been completely charac-



Scheme 1. Synthesis of pincer-type palladium complexes [5]Br-[8]Br.

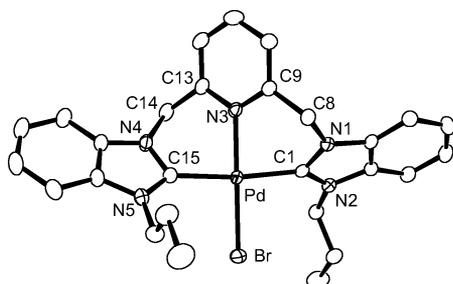
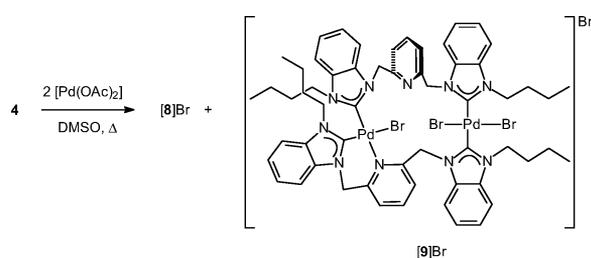


Fig. 1. Molecular structure of the cation [7]<sup>+</sup> in [7]Br·2MeOH. Hydrogen atoms have been omitted for clarity. Displacement ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (deg): Pd–C1 2.025(2), Pd–C15 2.027(3), Pd–N3 2.048(2), Pd–Br 2.411(4), C1–N1 1.352(3), C1–N2 1.350(3), C15–N4 1.353(3), C15–N5 1.345(3); Br–Pd–N3 179.16(6), Br–Pd–C1 93.06(7), Br–Pd–C15 94.58(7), N3–Pd–C1 87.12(9), N3–Pd–C15 85.21(9), C1–Pd–C15 171.98(10), N1–C1–N2 106.7(2), N4–C15–N5 106.6(2), N1–C8–C9 111.4(2), N4–C14–C13 109.3(2).

terized by NMR spectroscopy and mass spectrometry. Isolation of the free carbene ligands or their dibenzotetraazafulvalene dimers was not possible because of intramolecular rearrangement processes occurring upon C2 deprotonation as described earlier [10].

Crystals of [7]Br·2MeOH suitable for an X-ray diffraction analysis were obtained by recrystallization of [7]Br from a dichloromethane/methanol solution. The cationic palladium complex [7]<sup>+</sup> exhibits a slightly distorted square-planar coordination geometry (Fig. 1). The Pd–C bond lengths of 2.025(2) Å (Pd–C1) and 2.027(3) Å (Pd–C15) fall in the range previously reported for similar bis(benzimidazolin-2-ylidene) pincer complexes [8] and neutral palladium complexes with two benzimidazolin-2-ylidene ligands in *trans* configuration [4b]. In addition, the Pd–C bond lengths in [7]<sup>+</sup> are similar to equivalent bond parameters found in palladium pincer-type complexes with imidazolin-2-ylidene donor functions [9]. The Pd–C

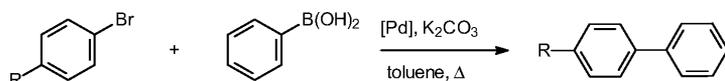


Scheme 2. Synthesis of compound [8]Br and the formation of byproduct [9]Br.

distances in [7]<sup>+</sup> are slightly elongated compared to the values found for neutral palladium complexes with two benzimidazolin-2-ylidene donors in a *cis* configuration [1.987(4)–1.991(7) Å] [4a]. As reported for several other dicarbene pincer complexes, the C–Pd–C bond angle reveals the greatest deviation from a perfect square-planar arrangement of the four donor functions at the metal center [9] owing to the steric constraint imposed by the lutidine spacer group. The bond angles at the bridging methylene carbon atoms remain close to tetrahedral [N1–C8–C9 111.4(2)°, N4–C14–C13 109.3(2)°]. As seen with other benzimidazolin-2-ylidene complexes, the N–C–N angle within the carbene donor expands from about 104° for the free ligand [2a] to about 107° for the coordinated ligand.

Two compounds were obtained upon attempts to crystallize the salt [8]Br (Scheme 2). Apart from the expected mononuclear pincer complex [8]<sup>+</sup> in [8]Br a dinuclear species [9]<sup>+</sup> was obtained as a byproduct (Scheme 2), which had not been detected by NMR spectroscopy prior to the crystallization experiments.

The dinuclear complex [9]<sup>+</sup> contains the potentially tridentate dicarbene ligand acting in a bridging fashion. One palladium atom (Pd1) is surrounded by two benzimidazolin-2-ylidene donors in *trans* orientation in addition to two bromo ligands. The second palladium atom (Pd2) is coordinated by two benzimidazolin-2-

R = H, CHO, C(O)CH<sub>3</sub>

entry	catalyst	mol% cat.	R	time [h]	yield [%]
1	<b>5</b>	0.1	H	24	76
2	<b>6</b>	0.1	H	24	69
3	<b>7</b>	0.1	H	24	70
4	<b>8</b>	0.1	H	24	69
5	<b>5</b>	0.01	H	24	37
6	<b>8</b>	0.01	H	2	48
7	<b>8</b>	0.01	C(O)CH <sub>3</sub>	2	61

Table 1. Pd-Catalyzed Suzuki coupling reaction of phenylboronic acid with aryl bromides.<sup>a</sup>

<sup>a</sup> Reaction conditions: 1.0 mmol of the aryl bromide, 1.2 mmol of phenylboronic acid, 2 mmol K<sub>2</sub>CO<sub>3</sub>, Pd-catalyst and 50 mL of toluene. Yields were determined by gas chromatography.

ylidene donors from different ligands in a *cis* arrangement together with one lutidine nitrogen atom and one bromo ligand. This arrangement leads to two different sets of Pd–C bond lengths in [9]<sup>+</sup>.

The Pd–C bond lengths involving palladium atom Pd1 (Fig. 2) with the *trans* orientation of the carbene donor functions are comparable to those observed in the pincer-type palladium complex [7]<sup>+</sup>. The Pd–C bonds at Pd2 with a *cis* arrangement of the two benzimidazolin-2-ylidene donor functions are shorter [Pd2–C15 1.964(7) Å, Pd–C31 1.988(6) Å] and compare well to the Pd–C bond lengths found in dicarbene complexes with a *cis* arrangement of the carbene donor functions [3b, 4a]. Differences between the metal centers were also observed by comparison of the Pd–Br bond lengths. At Pd1 the two bromo ligands in the *trans* arrangement exhibit Pd1–Br1 and Pd1–Br2 bond lengths of 2.4476(8) and 2.4359(8) Å. The Pd2–Br3 bond [2.4828(9) Å] is longer which reflects the stronger *trans* effect of the carbene donor function compared to the bromo ligand at Pd1. The coordination geometry at the two palladium atoms is best described as distorted square-planar.

We have previously described the catalytic activity of palladium pincer-complexes which were generated *in situ* by reaction of one of the dibenzimidazolium salts **1**–**4** with PdCl<sub>2</sub> in DMF [8a]. Here we report on the catalytic activity of the isolated palladium complexes [5]Br–[8]Br as precatalysts in the Suzuki coupling reaction of bromobenzene and phenylboronic acid. A catalyst loading of 0.1 mol-% gave 69–76% conversion after 24 h in refluxing toluene (Table 1).

The use of a smaller amount of precatalyst [5]Br (0.01 mol-%) yielded only 37% conversion after 24 h. In contrast to [5]Br, the palladium complex [8]Br exhibits higher catalytic activity, with 49% conversion after a reaction time of only 2 h. The coupling

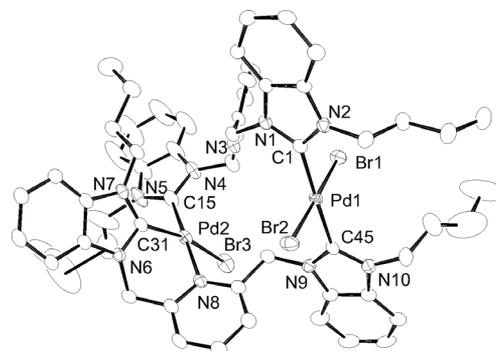


Fig. 2. Molecular structure of the cation [9]<sup>+</sup> in [9]Br·H<sub>2</sub>O·MeOH. Hydrogen atoms, the bromide anion and the solvent molecules have been omitted for clarity. Displacement ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (deg): Pd1–Br1 2.4476(8), Pd1–Br2 2.4359(8), Pd1–C1 2.022(6), Pd1–C45 2.023(6), Pd2–Br3 2.4828(9), Pd2–N8 2.106(5), Pd2–C15 1.964(7), Pd2–C31 1.988(6), C1–N1 1.361(8), C1–N2 1.342(7), C15–N4 1.355(8), C15–N5 1.359(9), C31–N6 1.348(7), C31–N7 1.347(8), C45–N9 1.350(7), C45–N10 1.341(8); Br1–Pd1–Br2 177.90(3), Br1–Pd1–C1 88.6(2), Br1–Pd1–C45 89.8(2), Br2–Pd1–C1 92.1(2), Br2–Pd1–C45 89.5(2), C1–Pd1–C45 178.2(2), Br3–Pd2–N8 93.53(13), Br3–Pd2–C15 87.0(2), Br3–Pd2–C31 165.6(2), N8–Pd2–C15 179.4(3), N8–Pd2–C31 86.4(2), C15–Pd2–C32 93.0(3), N1–C1–N2 106.5(5), N4–C15–N5 107.6(6), N6–C31–N7 106.9(5), N9–C45–N10 105.5(5).

reaction of the more reactive 4-bromoacetophenone and phenylboronic acid proceeds with 61% conversion within 2 h with precatalyst [8]Br. This value is comparable to that of other palladium carbene complexes with benzimidazolin-2-ylidene donor functions. Furthermore, the observed conversion rate is higher than found for neutral pincer-type palladium complexes with xylene-bridged bis(benzimidazolin-2-ylidene) ligands which we reported recently [8b].

We have described an unusual coordination mode of a lutidine-bridged bis(benzimidazolin-2-ylidene) lig-

and leading to a dinuclear palladium complex with two bridging ligands. Both metal centers in this complex are coordinated by two benzimidazolin-2-ylidene donors, but with a different arrangement (*cis* or *trans*) of the carbene donors. Attempts to use the palladium complexes [5]Br–[8]Br as precatalysts in Suzuki-type reactions showed in most cases an acceptable catalytic activity in a range typically observed for neutral dicarbene pincer complexes.

## Experimental Section

The dibenzimidazolium dibromides 1–4 and the dicarbene palladium complexes [5]Br–[8]Br were prepared as previously described [8a].

**General method for the Suzuki coupling:** A two-necked 100 mL flask was fitted with a reflux condenser and charged with an aryl bromide (1.0 mmol), phenylboronic acid (0.144 g, 1.2 mmol) and potassium carbonate (0.276 g, 2.0 mmol). Toluene (50 mL) was added and the suspension was brought to reflux. The desired amount of the palladium complexes [5]Br–[8]Br was dissolved in 1 mL of dichloromethane. This solution was injected into the boiling toluene solution, and the mixture was refluxed for the desired time. The mixture was allowed to cool to r.t. and the organic phase was passed over a short silica gel column. The resulting solution was then analyzed by quantitative GC analysis with a Shimadzu GC-2100 with an Agilent Technologies HP 5 capillary column (30 m).

**X-Ray structure determination of compounds [7]Br·2MeOH and [9]Br·H<sub>2</sub>O·MeOH:** Suitable crystals of [7]Br·2MeOH and [9]Br·H<sub>2</sub>O·MeOH were mounted on a Bruker AXS 2000 CCD diffractometer equipped with a rotating molybdenum anode ( $\lambda = 0.71073 \text{ \AA}$ ) and a CCD area detector. Diffraction data were measured at 153(2) K in the range  $2.4 \leq 2\theta \leq 60.1^\circ$  for [7]Br·2MeOH and  $3.1 \leq 2\theta \leq 55.2^\circ$  for [9]Br·H<sub>2</sub>O·MeOH. Structure solution [11] and re-

finement [12] were achieved with standard Patterson and Fourier techniques. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were added to the structure models in calculated positions.

**Selected crystallographic details for [7]Br·2MeOH:** Formula C<sub>29</sub>H<sub>37</sub>N<sub>5</sub>Br<sub>2</sub>O<sub>2</sub>Pd,  $M = 753.86$ , colourless crystal,  $0.21 \times 0.18 \times 0.11 \text{ mm}^3$ , monoclinic, space group  $P2_1/c$ ,  $a = 17.315(3)$ ,  $b = 9.2733(15)$ ,  $c = 19.470(3) \text{ \AA}$ ,  $\beta = 99.202(3)^\circ$ ,  $V = 3086.0(8) \text{ \AA}^3$ ,  $\rho_{\text{calcd}} = 1.62 \text{ g cm}^{-3}$ ,  $\mu = 3.2 \text{ mm}^{-1}$ , empirical absorption correction (0.5508  $\leq T \leq$  0.7180),  $Z = 4$ , 34191 intensities collected ( $\pm h$ ,  $\pm k$ ,  $\pm l$ ), 8950 independent ( $R_{\text{int}} = 0.0458$ ) and 6878 observed intensities [ $I \geq 2\sigma(I)$ ], 358 refined parameters, residuals for all data  $R = 0.0574$ ,  $wR2 = 0.0880$ , max. residual electron density  $0.91/-0.47 \text{ e \AA}^{-3}$ .

**Selected crystallographic details for [9]Br·H<sub>2</sub>O·MeOH:** Formula C<sub>59</sub>H<sub>72</sub>N<sub>10</sub>Br<sub>4</sub>O<sub>2</sub>Pd<sub>2</sub>,  $M = 1485.71$ , colourless crystal,  $0.24 \times 0.11 \times 0.07 \text{ mm}^3$ , triclinic, space group  $P\bar{1}$ ,  $a = 13.775(2)$ ,  $b = 14.842(2)$ ,  $c = 17.275(2) \text{ \AA}$ ,  $\alpha = 106.779(3)$ ,  $\beta = 93.275(3)$ ,  $\gamma = 104.697(3)^\circ$ ,  $V = 3238.2(8) \text{ \AA}^3$ ,  $\rho_{\text{calcd}} = 1.52 \text{ g cm}^{-3}$ ,  $\mu = 3.0 \text{ mm}^{-1}$ , empirical absorption correction (0.5262  $\leq T \leq$  0.8138),  $Z = 2$ , 31689 intensities collected ( $\pm h$ ,  $\pm k$ ,  $\pm l$ ), 14861 independent ( $R_{\text{int}} = 0.0432$ ) and 9373 observed intensities [ $I \geq 2\sigma(I)$ ], 723 refined parameters, residuals for all data  $R = 0.1037$ ,  $wR2 = 0.1819$ , max. residual electron density  $1.33/-0.79 \text{ e \AA}^{-3}$ .

Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC 629034 for [7]Br·2MeOH and CCDC 629035 for [9]Br·H<sub>2</sub>O·MeOH. Copies of the data can be obtained free of charge via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

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- [1] a) F.E. Hahn, *Angew. Chem. Int. Ed.* **2006**, *45*, 1348; b) D. Bourissou, O. Guerret, F.P. Gabbaï, G. Bertrand, *Chem. Rev.* **2000**, *100*, 39; c) W. A. Herrmann, C. Köcher, *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2162; d) W. A. Herrmann, *Angew. Chem. Int. Ed.* **2002**, *41*, 1290.
- [2] a) F.E. Hahn, L. Wittenbecher, R. Boese, D. Bläser, *Chem. Eur. J.* **1999**, *5*, 1931; b) F.E. Hahn, T. von Fehren, R. Fröhlich, *Z. Naturforsch.* **2004**, *59b*, 348.
- [3] a) F.E. Hahn, L. Wittenbecher, D. Le Van, R. Fröhlich, *Angew. Chem. Int. Ed.* **2000**, *39*, 541; b) F.E. Hahn, T. von Fehren, L. Wittenbecher, R. Fröhlich, *Z. Naturforsch.* **2004**, *59b*, 541; c) F.E. Hahn, T. von Fehren, L. Wittenbecher, R. Fröhlich, *Z. Naturforsch.* **2004**, *59b*, 544; d) F.E. Hahn, T. von Fehren, T. Lügger, *Inorg. Chim. Acta.* **2005**, *358*, 4137.
- [4] a) F.E. Hahn, M. Foth, *J. Organomet. Chem.* **1999**, *585*, 241; b) F.E. Hahn, C. Holtgrewe, T. Pape, *Z. Naturforsch.* **2004**, *59b*, 1051.
- [5] F.E. Hahn, C. Holtgrewe, T. Pape, M. Martin, E. Sola, L. A. Oro, *Organometallics* **2005**, *24*, 2203.
- [6] a) H.M.J. Wang, I.J.B. Lin, *Organometallics* **1998**, *17*, 972; b) F.E. Hahn, M.C. Jahnke, T. Pape, *Organometallics* **2006**, *25*, 5927.
- [7] a) M. Tamm, F.E. Hahn, *Coord. Chem. Rev.* **1999**, *182*, 175; b) F.E. Hahn, V. Langenhahn, N. Meier,

- T. Lügger, W. P. Fehlhammer, *Chem. Eur. J.* **2003**, *9*, 704; c) F. E. Hahn, C. Garcia Plumed, M. Münder, T. Lügger, *Chem. Eur. J.* **2004**, *10*, 6285; d) F. E. Hahn, V. Langenhahn, T. Lügger, T. Pape, D. Le Van, *Angew. Chem. Int. Ed.* **2005**, *44*, 3759.
- [8] a) F. E. Hahn, M. C. Jahnke, V. Gomez-Benitez, D. Morales-Morales, T. Pape, *Organometallics* **2005**, *24*, 6458; b) F. E. Hahn, M. C. Jahnke, T. Pape, *Organometallics* **2007**, *26*, 150.
- [9] E. Peris, R. H. Crabtree, *Coord. Chem. Rev.* **2004**, *248*, 2239.
- [10] a) C. Holtgrewe, C. Diedrich, T. Pape, S. Grimme, F. E. Hahn, *Eur. J. Org. Chem.* **2006**, 3116; b) H. V. Huynh, N. Meier, T. Pape, F. E. Hahn, *Organometallics* **2006**, *25*, 3012.
- [11] G. M. Sheldrick, SHELXS-97, *Acta Crystallogr.* **1990**, *A46*, 467.
- [12] G. M. Sheldrick, SHELXL-97, Program for the Refinement of Crystal Structures, University of Göttingen, Göttingen (Germany) **1997**.