

# The Pd(II) Complex of a Bidentate Di(benzimidazol-2-ylidene) Ligand

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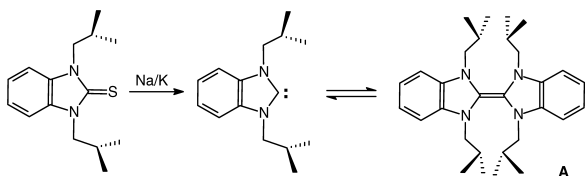
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The pale yellow palladium(II) dicarbene complex *cis*-[PdI<sub>2</sub>(L)], **2** (L = 1,3-bis-(3-neopentylbenzimidazol-2-ylidene)-2,2-dimethylpropane) was synthesized by the reaction of PdI<sub>2</sub> with an N1,N1'-2,2'-dimethylpropane-bridged dibenzotetraazafulvalene **1** in tetrahydrofuran. The X-ray structure analysis revealed a mononuclear complex with a palladium(II) center coordinated in a slightly distorted square-planar fashion by the bidentate carbene ligand and two iodo ligands.

**Key words:** Carbene Ligand, Palladium(II), Crystal Structure

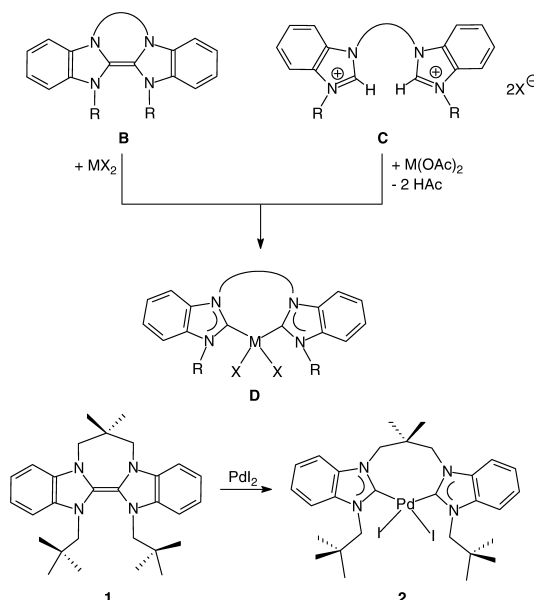
## Introduction

Stable N-heterocyclic carbenes have found widespread applications in coordination chemistry and catalysis [1]. They have been employed as ligands in organometallic chemistry throughout the periodic table. Electron-rich olefins of the enetetramine type (R<sub>2</sub>N)<sub>2</sub>C=C(NR<sub>2</sub>)<sub>2</sub> are a potential source of carbene ligands in organometallic chemistry [1b, 2]. They were first explored by the groups of Wanzlick [3] and Wiberg [4]. A special case of enetetramines are the dibenzotetraazafulvalenes **A**, which can be obtained by reductive desulfurization of benzimidazol-2-thiones [5], a method established by Kuhn [6] for imidazol-2-thiones. We have obtained stable benzannulated N-heterocyclic carbenes and their dimers, the dibenzotetraazafulvalenes [7], and observed an equilibrium between the free carbene and the enetetramine for selected N,N'-substituents [8] (Scheme 1).



Scheme 1. Synthesis of free benzannulated carbenes and dibenzotetraazafulvalenes.

It is also possible to synthesize N1,N1'-alkylbridged dibenzotetraazafulvalenes of type **B** [8] (Scheme 2). Molecules of type **A** [9] or **B** react with coordina-



Scheme 2. Preparation of complexes with chelating dicarbene ligands.

tively unsaturated transition metal complexes to give complexes of type **D** with a chelating dicarbene ligand [8]. Complexes of type **D** can also be obtained by reactions of N1,N1'-alkylbridged bis(benzimidazolium) salts **C** with transition metal acetates [10]. We report here on the reaction of the N1,N1'-C<sub>3</sub>-bridged dibenzotetraazafulvalene **1** with PdI<sub>2</sub> to give the dicarbene complex **2** (Scheme 2).

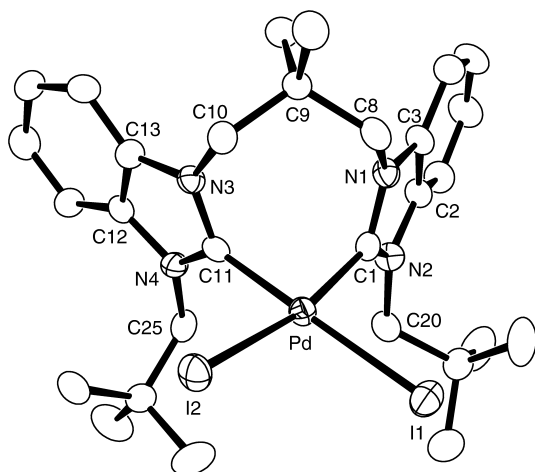


Fig. 1. Molecular structure of complex  $[\text{PdI}_2(\text{L})]$ , **2**. Hydrogen atoms have been omitted. Selected bond lengths [Å] and angles [°] for molecule A [B]: Pd–I1 2.6465(5) [2.6724(5)], Pd–I2 2.6615(5) [2.6411(5)], Pd–C1 1.988(5) [1.988(5)], Pd–C11 1.983(5) [1.982(5)], N1–C1 1.354(6) [1.355(6)], N1–C3 1.397(6) [1.397(6)], N1–C8 1.468(6) [1.463(6)], N2–C1 1.348(6) [1.348(6)], N2–C2 1.390(6) [1.396(7)], N2–C20 1.459(6) [1.467(6)], N3–C10 1.467(6) [1.466(6)], N3–C11 1.345(6) [1.342(6)], N3–C13 1.398(6) [1.402(6)], N4–C11 1.353(6) [1.353(6)], N4–C12 1.399(6) [1.397(6)], N4–C25 1.455(6) [1.483(6)]; I1–Pd–I2 93.12(2) [91.16(2)], I1–Pd–C1 94.14(14) [166.34(14)], I1–Pd–C11 178.91(14) [87.37(14)], I2–Pd–C1 166.36(15) [96.29(14)], I2–Pd–C11 87.97(14) [176.88(14)], C1–Pd–C11 84.8(2) [84.6(2)], Pd–C1–N1 119.8(4) [118.9(3)], Pd–C1–N2 132.0(4) [133.1(4)], N1–C1–N2 107.4(4) [106.8(4)], Pd–C11–N3 123.1(4) [121.5(3)], Pd–C11–N4 129.3(4) [130.6(4)], N3–C11–N4 107.5(4) [107.8(4)].

## 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. The dibenzotetraazafulvalene **1** was prepared according to a published procedure [8].

*cis*- $[\text{PdI}_2(1,3\text{-bis-(3-neopentylbenzimidazol-2-ylidene)-2,2-dimethylpropane})]$  **2**: A solution of **1** (290 mg, 0.652 mmol) in THF (20 ml) was treated with  $\text{PdI}_2$  (260 mg, 0.722 mmol) at room temperature. The reaction mixture was stirred for 14 h and the solvent was removed under reduced pressure. The residue was dissolved in dichloromethane (30 ml) and filtered. Pale yellow crystals of  $\mathbf{2} \cdot \text{CH}_2\text{Cl}_2$ , suitable for an X-ray diffraction analysis, were obtained from a concentrated dichloromethane solution at 0 °C. Yield: 110 mg (0.136 mmol, 21%) of solvent-free **2**.  $^1\text{H}$  NMR (200 MHz,  $[\text{D}_6]\text{DMSO}$ , ppm):  $\delta$  = 7.64–6.89 (m, 8 H, Ar-H), 5.61 (d, 2 H,  $\text{NCH}_2$ ), 4.81 (d, 2 H,  $\text{NCH}_2$ ), 4.49 (d, 2 H,  $\text{NCH}_2$ ), 4.03 (d, 2 H,  $\text{NCH}_2$ ), 1.21 (s, 18 H,  $\text{C}(\text{CH}_3)_3$ ), 0.72

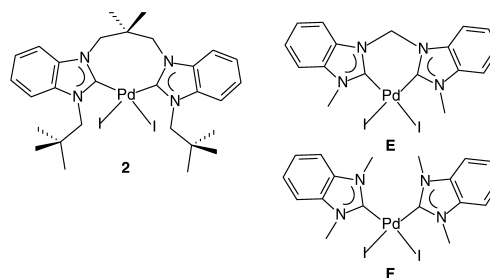
(s, 6 H,  $\text{C}(\text{CH}_3)_2$ ). –  $^{13}\text{C}$  NMR (50.3 MHz,  $[\text{D}_6]\text{DMSO}$ , ppm):  $\delta$  = 134.5, 132.7, 132.0, 122.8, 113.8, 111.8 (Ar-C), 59.5 ( $\text{NCH}_2$ ), 53.2 ( $\text{NCH}_2$ ), 35.0 ( $\text{C}(\text{CH}_3)_3$ ), 33.3 ( $\text{C}(\text{CH}_3)_2$ ), 30.0 ( $\text{C}(\text{CH}_3)_3$ ), 26.6 ( $\text{C}(\text{CH}_3)_2$ ), the  $\text{C}(\text{NR}_2)_2$  resonance was not observed.

*X-ray structure determination of  $\mathbf{2} \cdot \text{CH}_2\text{Cl}_2$* : Formula  $\text{C}_{30}\text{H}_{42}\text{N}_4\text{I}_2\text{Pd}$ ,  $M$  = 889.78, light yellow crystal  $0.15 \times 0.07 \times 0.05$  mm<sup>3</sup>,  $a$  = 11.480(1),  $b$  = 23.691(1),  $c$  = 24.715(1) Å,  $V$  = 6721.8(7) Å<sup>3</sup>,  $\rho_{\text{calcd.}}$  = 1.758 g cm<sup>−3</sup>,  $\mu$  = 25.74 cm<sup>−1</sup>, empirical absorption correction (0.699 ≤  $T$  ≤ 0.882),  $Z$  = 8, orthorhombic, space group  $P2_12_12_1$  (No. 19),  $\lambda$  = 0.71073 Å,  $T$  = 198 K,  $\omega$  and  $\phi$  scans, 60307 reflections collected ( $\pm h, \pm k, \pm l$ ),  $[(\sin \theta)/\lambda]$  = 0.71 Å<sup>−1</sup>, 19671 independent ( $R_{\text{int}}$  = 0.057) and 15288 observed reflections [ $I \geq 2\sigma(I)$ ], 720 refined parameters,  $R$  = 0.047,  $wR^2$  = 0.073, max. residual electron density 1.00 (−0.85) e Å<sup>−3</sup>, refined as racemic twin (Flack parameter 0.207(14)), two independent molecules (connected by inversion symmetry) in the asymmetric unit, hydrogens calculated and refined as riding atoms. The data set was collected with Nonius KappaCCD diffractometer, equipped with a rotating anode generator Nonius FR591. Programs used: data collection COLLECT [11], data reduction Denzo-SMN [12], absorption correction SOR-TAV [13], structure solution SHELXS-97 [14], structure refinement SHELXL-97 [15], graphics ORTEP [16]. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC 232669. 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

The reaction of palladium(II) iodide with one equivalent of the dibenzotetraazafulvalene **1** causes cleavage of the C=C double bond in **1** and yields complex **2** with a chelating bidentate carbene ligand as a pale yellow solid (Scheme 2). Complex **2** is stable in air and water.

The X-ray structure analysis reveals a slightly distorted square-planar coordination geometry around the



Scheme 3. Dicarbene complexes with bridged and unbridged carbene ligands.

palladium atom (Fig. 1) for both molecules of **2** in the asymmetric unit.

The palladium(II) center is coordinated by one bidentate C<sub>3</sub>-bridged dicarbene ligand and two terminal iodo ligands in *cis*-fashion. The C-Pd-C-angle in **2** (84.8(2)° and 84.6(2)°) is only slightly larger, than observed in the C<sub>1</sub>-bridged derivative **E** (83.7(3)°) but much smaller than in the unbridged dicarbene complex **F** (91.3(2)°) (Scheme 3) [10]. The bridging of the carbene units causes the C-Pd-C angle to shrink, but the length of these bridges (C<sub>1</sub> vs C<sub>3</sub>) appears to have almost no effect on this angle.

The length of the bridge between the carbene units is, however, significant for the angles between the planes of the carbene units (five-membered ring C-N-C-C-N) and the PdI<sub>2</sub>C<sub>2</sub> plane. In the unbridged derivative **E** these angles measure 83.1° and 79.8° and thus the carbene planes are oriented almost perpendicular to the PdI<sub>2</sub>C<sub>2</sub> plane [10]. Similar values for these angles are found in **2** (82.7° and 83.6°). In the C<sub>1</sub> bridged derivative **F**, however, the angles between the carbene planes and the PdI<sub>2</sub>C<sub>2</sub> plane measure 54.4° and 51.8° [10]. It appears, that the strain build up by shortening of the bridge between two benzannulated carbene units

does not primarily change the C-Pd-C angle, but instead leads to variations in the angles between the carbene planes and the PdI<sub>2</sub>C<sub>2</sub> plane by a rotation around the Pd-C axis. A shortening of the bridge causes these interplanar angles to shrink and thus leads to a flattening of the whole complex.

The Pd-C<sub>carbene</sub> bond lengths in **2** fall in the range between 1.982(5) and 1.988(5) Å. They are identical within experimental error to the values observed for **E** and **F** (range 1.987(4) Å to 1.991(7) Å) and very similar to those of complexes with chelating bis(imidazol-2-ylidene) ligands [17]. If the proposed (d→p) backbonding [18] exists in square-planar complexes with N-heterocyclic carbene ligands, its magnitude and therefore the M-C<sub>carbene</sub> bond lengths should depend on the angle between the metal coordination plane and the carbene plane. The molecular parameters for **2**, **E** and **F** do not support the existence of backbonding between the carbene ligand and the metal center.

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