

Simple Route to the Doubly *ortho*-Palladated Azobenzenes: Building Blocks for Organometallic Polymers and Metallomesogens

Manda Ćurić,* Darko Babić, Aleksandar Višnjevac, and Krešimir Molčanov

Institute Ruđer Bošković, Bijenička c. 54, HR-1000 Zagreb, Croatia

Received May 11, 2005

A new class of doubly cyclopalladated complexes, $\{\text{PdCl}(\text{dmf})\}_2(\mu\text{-azb})$ (**1**) and $\{\text{PdCl}(\text{dmf})\}_2(\mu\text{-aazb})$ (**2**), has been prepared in dimethylformamide (dmf) by reaction of azobenzene (azb) and 4-aminoazobenzene (aazb), respectively, with an excess of $\text{PdCl}_2(\text{CH}_3\text{CN})_2$ complex. Recrystallization of **1** and **2** in dimethyl sulfoxide (dmsO) yields complexes $\{\text{PdCl}(\text{dmsO})\}_2(\mu\text{-azb})$ (**3**) and $\{\text{PdCl}(\text{dmsO})\}_2(\mu\text{-aazb})$ (**4**), respectively. The crystal structures of **1** and **4** have been determined by X-ray diffraction. All complexes are characterized by ^1H and ^{13}C NMR spectra and elemental analysis. In both crystal structures, solvent molecules are bound to palladium through oxygen atoms and oriented *trans* to carbon. In view of greater preference of palladium to nitrogen and sulfur atoms, the experimental structures were rationalized by quantum-chemical calculations and confirmed as the most stable isomers.

of synthetic and stereochemical studies of cyclopalladation with azobenzenes was reported.⁷ However, only four examples of dimetalated azobenzene-containing transition metals (Ni, Mn, Pd, and Ir) are known.⁸ The dimetalated complexes of azobenzene with Pd(II) and Ni(II) have been reported without detailed structural characterization.^{8a,c} There is an increasing interest in multiply cyclopalladated complexes, since such compounds have interesting structural and electronic properties and may serve as precursors to organometallic polymers and metallomesogens.⁹ Here, we report on the synthesis of doubly cyclopalladated complexes with azobenzene (azb) and 4-aminoazobenzene (aazb) and their structures obtained by X-ray analysis and NMR spectroscopy. The experimental investigation was complemented by quantum-chemical calculations in order to provide rational explanation of their structures.

Reaction of azobenzenes with an excess of $\text{PdCl}_2(\text{CH}_3\text{CN})_2$ in dmf at room temperature gives the new complexes $\{\text{PdCl}(\text{dmf})\}_2(\mu\text{-azb})$ (**1**) and $\{\text{PdCl}(\text{dmf})\}_2(\mu\text{-aazb})$ (**2**), which by recrystallization in dmsO, form complexes $\{\text{PdCl}(\text{dmsO})\}_2(\mu\text{-azb})$ (**3**) and $\{\text{PdCl}(\text{dmsO})\}_2(\mu\text{-aazb})$ (**4**), respectively. The excess is needed since chlorides released by the cyclopalladation inactivate Pd complexes by forming chloropalladate species^{7c} which do not undergo cyclopalladation in dmf. All complexes are stable in air and are soluble in solvents of coordinating ability, i.e., dmf, dmsO, CH_3CN , $\text{C}_5\text{H}_5\text{N}$. The coordinated molecules dmf or dmsO are easily washed away with H_2O , CH_3OH or CH_2Cl_2 , CH_3CN , $\text{C}_5\text{H}_5\text{N}$,

Cyclopalladation reactions of azobenzenes and the other N-donor ligands have attracted enormous interest. Palladocycles have been proven useful in organic synthesis,¹ catalysis,² photochemistry,³ and in the design of the metallomesogens⁴ and bioactive compounds.⁵ After the first preparation of cyclopalladated azobenzene⁶ in 1965, a large number

* To whom correspondence should be addressed. E-mail: curic@irb.hr.

- (1) (a) Ryabov, A. D. *Synthesis* **1985**, 233. (b) Pfeffer, M. *Recl. Trav. Chim. Pays-Bas* **1990**, 109, 567.
- (2) (a) Navarro, R.; Urriolabeitia, E. P.; Cativiela, C.; Diaz-de-Villegas, M. D.; Lopez, M. P.; Alonso, E. *J. Mol. Catal.* **1996**, 105, 111. (b) Bergbreiter, D. E.; Osburn, P. L.; Liu, Y. S. *J. Am. Chem. Soc.* **1999**, 121, 9531.
- (3) (a) Dupont, J.; Pfeffer, M.; Spencer, J. *Eur. J. Inorg. Chem.* **2001**, 1917. (b) Wakatsuki, Y.; Yamazaki, H.; Grutsch, P. A.; Santhanam, M.; Kutal, C. *J. Am. Chem. Soc.* **1985**, 107, 8153.
- (4) (a) Schwarz, R.; Gliemann, G.; Jolliet, P. H.; Von Zalevsky, A. *Inorg. Chem.* **1989**, 28, 309. (b) Bruce, D. W.; *J. Chem. Soc., Dalton Trans.* **1993**, 2983. (c) Lyndon, D. P.; Rourke, J. P. *Chem. Commun.* **1997**, 1741. (d) Ghedini, M.; Pucci, D.; Crispini, A.; Barberio, G. *Organometallics* **1999**, 18, 2116. (e) Ghedini, M.; Pucci, D.; Crispini, A.; Barberio, G.; Aiello, I.; Barigelletti, F.; Gessi, A.; Francescangeli, O. *Appl. Organomet. Chem.* **1999**, 13, 565.
- (5) (a) Navarro-Ranniger, C.; Lopez-Solera, I.; Perez, J. M.; Masaguer, J. R.; Alonso, C. *Appl. Organomet. Chem.* **1993**, 7, 57. (b) Higgins, J. D. *J. Inorg. Biochem.* **1993**, 49, 149. (c) Navarro-Ranniger, C.; Lopez-Solera, I.; Gonzales, V. M.; Perez, J. M.; Alvarez-Valdez, A.; Martin, A.; Raithby, P. R.; Masaguer, J. R.; Alonso, C. *Inorg. Chem.* **1996**, 35, 5181.
- (6) Cope, A. C.; Siekman, R. W. *J. Am. Chem. Soc.* **1965**, 87, 3272.

- (7) (a) Ryabov, A. D. In *Perspectives in Coordination Chemistry*; Williams, A. F., Floriani, C., Merbach, A. E., Eds.; Verlag Helvetica Chimica Acta: Basel, VCH: Weinheim, New York, Basel, Cambridge, 1992; p 271. (b) Ryabov, A. D.; Kuz'mina, L. G.; Dvortsova, N. V.; Stufkens, D. J.; van Eldik, R. *Inorg. Chem.* **1993**, 32, 3166. (c) Ćurić, M.; Babić, D.; Marinić, Ž.; Paša-Tolić, Lj.; Butković, V.; Plavec, J.; Tušek-Božić, Lj. *J. Organomet. Chem.* **2003**, 687, 85.
- (8) (a) Bennet, R. L.; Bruce, M. I.; Goodall, B. L.; Stone, G. A. *Aust. J. Chem.* **1974**, 27, 2131. (b) Bruce, M. I.; Liddell, M. J. Snow, M. R.; Tiekink, E. R. T. *Aust. J. Chem.* **1988**, 41, 1407. (c) Siedle, A. R. *J. Organomet. Chem.* **1981**, 208, 115. (d) Zambrano, C. H.; Sharp, P. R.; Barnes, C. L. *Organometallics* **1995**, 14, 3606.
- (9) (a) Sumbly, J. C.; Steel, P. J. *Organometallics* **2003**, 22, 2358. (b) Chakladar, S.; Paul, P.; Mukherjee, A. K.; Dutta, S. K.; Nanda, K. K.; Podder, D.; Nag, K. *J. Chem. Soc., Dalton Trans.* **1992**, 3119. (c) Loeb, S. J.; Shimizu, G. K. H. *J. Chem. Soc., Chem. Commun.* **1993**, 1395. (d) Rourke, J. P.; Lyndon, D. P.; Slater, J. W. *J. Organomet. Chem.* **2002**, 645, 246.

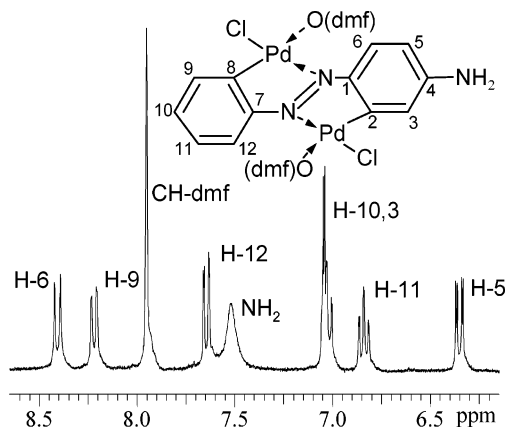


Figure 1. ^1H NMR spectrum of complex **2** in $\text{DMSO-}d_6$.

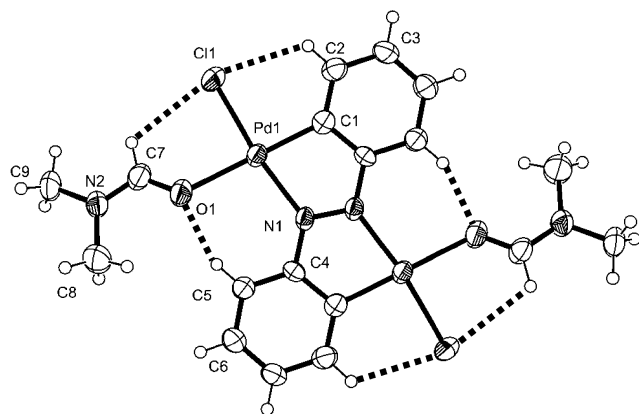


Figure 2. ORTEP drawing of **1**. Ellipsoids are scaled at the 50% probability level. Possible hydrogen bonds (depicted by dotted lines): $\text{C}(5)\text{--H}\cdots\text{O}(1)$ 2.956, 1.942 Å, 155°; $\text{C}(2)\text{--H}\cdots\text{Cl}(1)$ 3.184, 2.557 Å, 116°; and $\text{C}(7)\text{--H}\cdots\text{Cl}(1)$ 3.196, 2.574 Å, 115°.

etc. resulting in the formation of new complexes. In contrast to few known dimetalated azobenzenes with transition metals (Ni, Mn, Pd, and Ir),⁸ the synthesis of these new dipalladated azobenzene complexes is very simple.

The results of chemical analysis are consistent with formulation of these complexes as doubly cyclopalladated compounds. The ^1H NMR spectra show four (for **1** and **3**) and seven (for **2** and **4**) different aromatic protons, confirming the loss of two hydrogens and formation of two five-member rings (Figure 1, also see Supporting Information). The structures of doubly cyclopalladated complexes were also confirmed by ^{13}C NMR spectra (see Supporting Information). Although there are three (for **1** and **3**) or four (for **2** and **4**) possible isomers, differing in the orientation of solvent molecules and Cl atoms toward the Pd–C bond, only one set of signals was observed in the NMR spectra of the complexes. This indicates high selectivity of the double cyclopalladation reaction of azobenzenes.

According to X-ray structures of **1** and **4** (Figures 2 and 3),¹⁰ each Pd is centered in a considerably distorted square-planar environment (angles from 79° to 101°, Table 1). Both

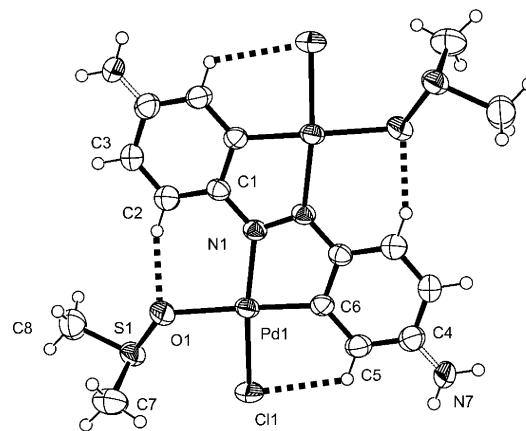


Figure 3. ORTEP drawing of **4**. Ellipsoids are scaled at the 50% probability level. Possible hydrogen bonds (depicted by dotted lines): $\text{C}(2)\text{--H}\cdots\text{O}(1)$ 2.956, 1.971 Å, 150° and $\text{C}(5)\text{--H}\cdots\text{Cl}(1)$ 3.237, 2.594 Å, 117°.

Table 1. Geometries of the Pd Coordination Sphere in **1** and **4**

	1	4
Pd1–Cl1/Å	2.2944(14)	2.3153(16)
Pd1–N1/Å	2.067(5)	2.055(5)
Pd1–C/Å	1.937(5)	1.952(6)
Pd1–O1/Å	2.192(4)	2.178(5)
Cl1–Pd1–N1/°	171.48(13)	172.41(14)
Cl1–Pd1–C/°	93.42(15)	94.35(18)
Cl1–Pd1–O1/°	87.08(11)	87.14(13)
N1–Pd1–C/°	78.9(2)	79.3(2)
N1–Pd1–O1/°	100.93(17)	99.84(18)
C–Pd1–O1/°	174.84(19)	170.2(2)

complexes reveal perfect planarity of the central Pd–azobenzene part, with most deviations in the outer part of the coordination sphere of the Pd atom. Although Pd(II) generally shows a preference for nitrogen and sulfur and a relatively small affinity for oxygen, the dmf and dmsO molecules are coordinated through an O atom and oriented trans to carbon in both complexes. The Pd–C bond lengths (Table 1) are shorter than values predicted from their covalent radii but similar to values found for monopalladated derivative.¹¹ The Pd–O bond lengths are significantly longer than the sum of covalent radii for oxygen and palladium, indicating the strong trans influence of the Pd–C bond.¹² The Pd–N and Pd–Cl bond lengths in both crystal structures are in agreement with the sums of covalent radii. The X-ray structures of **1** and **4** include possible intramolecular hydrogen bonds, as indicated in Figures 2 and 3.

Both complexes crystallize in the monoclinic space group $P2_1/c$, with closely related cell axes and crystal packing governed by weak van der Waals interactions. The molecules are arranged into parallel layers along the crystallographic a axis, roughly 4 Å apart. Complex **1** has molecular C_i symmetry and lies on the crystallographic inversion center at the midpoint of the N=N bond. Despite of lacking molecular C_i symmetry, complex **4** lies also on the crystal-

(10) CCDC-270786 and CCDC-270787 contain the supplementary crystallographic data for **1** and **4** in this paper. The data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, U.K. (fax: +44 1223 336033, e-mail: data_request@ccdc.cam.ac.uk).

(11) Armentano, S.; Crispini, A.; De Muno, G.; Ghedini, M. *Acta Cryst.* **1991**, *C47*, 968.

(12) (a) Rüttimann, S.; Bernardinelli, G.; Williams, A. F. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 392. (b) Vicente, J.; Chichote, M. T.; Lagunas, M. C.; Jones, P. G.; Bembek E. *Organometallics* **1994**, *13*, 1243. (c) Vicente, J.; Areas, A.; Bautista, D.; Jones, P. G. *Organometallics* **1997**, *16*, 2127. (d) Vicente, J.; Abad, J. A.; Förtsch, W.; Jones, P. G.; Fisher, A. K. *Organometallics* **2001**, *20*, 2704.

lographic inversion center at the midpoint of the N=N bond. This is possible due to the structural disorder resulting in two opposite orientations of the molecule over the inversion center, with the $pp = 0.5$. In such a way, molecular pseudo- C_i symmetry is introduced. This disorder is responsible for a somewhat ill-refined C4–N7 bond (1.251(12) Å).

Additional characterization of **1–4** was done by quantum-chemical calculation. In this way, the obtained isomers were compared with other conceivable isomers and their absence has been rationalized. With Pd atoms covalently bound to aromatic carbons and coordinated by azo-nitrogens, different arrangements of Cl atoms and solvent molecules in the coordination shell are possible. Basically, Cl atoms could be cis or trans to carbon, and the solvent molecule (dmso or dmf) could be bound via oxygen or the second heteroatom (sulfur or nitrogen). In principle, each arrangement can be realized separately on both sides of azobenzene, resulting in 10 possible isomers. Their relative energies indicate whether the obtained crystal structures correspond to the most stable isomer, or some other factors, e.g., crystal packing or preparation conditions, govern the spatial arrangement of species in the coordination sphere. The computational method and the basis set were chosen by preliminary calculations of geometry for isomers determined by X-ray diffraction. The results obtained with RHF/DFT methods and two basis sets are tabulated in the Supporting Information. The greatest deviations were found for the bonds around Pd atoms and, in complex **4**, for S=O and C–NH₂ bonds. Pd–C and Pd–Cl bond lengths were improved by DFT and/or larger basis set. The Pd–N bond length was improved only by DFT, while the larger basis set had a small countereffect. The opposite was true with the S=O bond. On the other hand, the Pd–O bond length got worsened both by DFT and larger basis set. A discrepancy with the C–NH₂ bond length was present in all cases. Since the experimental length also remarkably deviates from known data,¹³ we have assumed that it is an artifact caused by pseudosymmetry in the crystallographic structure. On the basis of the average results and practical computational limitations, the DFT method and the larger basis set were chosen for all subsequent calculations.

In each isomer, the position of the solvent molecule is governed by bonding to the Pd atom and by interactions Cl–H(dmf) and O(or N/S)–H(phenyl), possibly having hydrogen-bond character. However, these interactions can be realized in more than one conformation. We have searched for only symmetric C_2 and C_i conformations of complexes **1** and **3** and the conformations of **2** and **4** derived from the symmetric **1** and **3** by attaching an NH₂ group. The isomers with different arrangements around Pd atoms are expected to have intermediate energies, as confirmed by calculations for isomers of **3** (see Supporting Information). Energies of isomers of **1–4** are shown in Table 2. With a single exception (azb/dmso, *trans*-S–Pd–C), two conformations

Table 2. Calculated Energies for Isomers of **1–4** with Equal Configurations around Both Pd Atoms (in kcal/mol), Relative to the Most Stable One^a

	<i>trans</i> - O–Pd–C	<i>cis</i> - O–Pd–C	<i>trans</i> - (N,S)–Pd–C	<i>cis</i> - (N,S)–Pd–C
azb/dmf	0.00 (C_2)	+11.09 (C_2)	n/a	+47.89 (C_2)
	+0.32	+11.21		+47.52 (C_i)
aazb/dmf	0.00	+11.31	n/a	+46.31
	+0.30	+11.45		+45.83
azb/dmso	0.00 (C_2)	+9.13 (C_2)	+17.97 (C_2)	+15.49 (C_2)
	+0.26 (C_i)	+9.17		+16.82 (C_i)
aazb/dmso	0.00	+9.36	+16.30	+13.58
	+0.25	+9.38	+16.41	+13.68

^a Numbers in the same cell correspond to different conformations.

were found for each configurational isomer. The conformations are close in energy with most differences less than 1 kcal/mol. The most stable structures correspond to those experimentally obtained. The isomers next higher in energy have exchanged positions of the Cl atom and the solvent molecule; complete *trans* → *cis* reconfiguration destabilizes the structure by approximately 10 kcal/mol. The isomers with solvent bound by the other heteroatom are even less stable, particularly with dmf. An isomer with the Pd–N(dmf) bond *trans* to carbon could not be obtained, as all attempted geometry optimizations finished with the solvent bound by an O atom. The reasons for remarkably higher energy of isomers with Pd–N(dmf) and Pd–S(dmso) bonds are of a steric nature, as evidenced by marked deviation from planarity and almost tetrahedral arrangement around the Pd atom.

In summary, we have presented synthesis and structures of a novel class of doubly cyclopalladated azobenzenes containing solvent molecules that can be easily replaced by other ligands, with a potential application in designing organometallic polymers and metallomesogens. The computational results indicate that structures with solvent molecules bound by oxygen atoms to the Pd atom in a *trans*-to-carbon position are the most stable ones and that the molecular structures in the solid state are determined solely by properties of isolated molecules. With great certainty, the structures of complexes **2** and **3** can be presumed to have the same coordination around the Pd atom as in the complexes **1** and **4**, respectively.

Acknowledgment. This work was financially supported by The Ministry of Science, Education and Sport of the Republic of Croatia (Grant No. 0098035). The calculations were performed on the Isabella cluster at SRCE, Zagreb. Discussions with Dr. Ivanka Matijasevic and Dr. Ivan Ljubic are gratefully acknowledged.

Supporting Information Available: Experimental procedures, computational details and archived computational results, crystal structure data of **1** and **4** (Table S3 and CIF files), and NMR data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

(13) Allen, F. H. *Acta Crystallogr.* **2002**, *B58*, 380.