Inorg. Chem. **2006**, *45*, 9160–9162

Inorganic Chemistry
Communication

Metal–Metal Bonding in Sterically Frustrated Dipalladium Species

Stefan Deeken,[†] GÜnter Motz,[‡] Viktor Bezugly,[§] Horst Borrmann,[§] Frank R. Wagner,*[,§] and Rhett Kempe*[,†]

Lehrstuhl Anorganische Chemie II, Universität Bayreuth, 95440 Bayreuth, Germany, Lehrstuhl Keramische Werkstoffe, Universität Bayreuth, 95440 Bayreuth, Germany, and Max-Planck-Institut für Chemische Physik fester Stoffe, 01187 Dresden, Germany

Received June 19, 2006

Stoichiometric-deficient lithiation of (2,6-diisopropylphenyl)(4-methylpyridin-2-yl)amine and reaction with $[(cod)PdCl_2]$ (cod = 1,5-cyclooctadiene) yield a dimeric Pd complex. X-ray structural analysis of this complex reveals a very short Pd–Pd distance (2.429 Å). Topological analysis of the electron density and the electron localization function from scalar relativistic density functional theory calculations clearly indicate a Pd(I)–Pd(I) σ-bonding interaction, for which the corresponding occupied localized orbital can be identified.

Group 10 metal complexes stabilized by deprotonated 2-aminopyridines have become an intensively investigated class of compounds since 1998.[1] Because of the flexibility of the binding mode ranging from a strained η^2 coordination—predominantly observed in early-transition-metal and lanthanide complexes—to a bridging binding mode common in late-transition-metal chemistry,[2] two general types of compounds are observed. There are limited reports for the two heavier elements of group 10.[1,3] Amidopalladium complexes are intermediates of the Pd-catalyzed aryl amination[4] and rapidly reductively eliminate amido ligands as deprotonated 2-aminopyridines.[5] Recently, we initiated a research program exploring the reactivity of metal complexes stabilized by sterically demanding aminopyridinato ligands,[6] where we expected to form Pd−Pd-bonded species via steric frustration (Chart 1). Because of the steric bulk of the ligand, only two deprotonated aminopyridines should bind a dinuclear unit (Chart 1, right) and not four as in the thermodynamically stable paddlewheel arrangement (Chart 1, left), which could lead to a Pd−Pd bond. Metal−metal bonding is well documented for Pd complexes.[7] To the best of our knowledge, the shortest ligand-bridged Pd−Pd bond [2.391(2) Å] was described by Cotton and co-workers[8] for a Pd(III) dimeric unit and the shortest nonsupported one [2.4878(7) Å] by Kurasuwa et al.[9] for a Pd(I) dimeric unit of the corner-sharing L_3−Pd(I)−Pd(I)−L_3 type. In this report, we present an unsymmetrical corner-sharing L_2−Pd(I)−Pd(I)−L_3 complex in which the metal−metal bond is supported by deprotonated aminopyridines.

Compound **1** [(2,6-diisopropylphenyl)(4-methylpyridin-2-yl)amine] can be synthesized via Pd-catalyzed aryl amination as previously reported.[6c] The reaction of lithiated **1** with

---

* To whom correspondence should be addressed. E-mail: wagner@cpfs.mpg.de (F.R.W.), kempe@uni-bayreuth.de (R.K.).

[†] Lehrstuhl Anorganische Chemie II, Universität Bayreuth.

[‡] Lehrstuhl Keramische Werkstoffe, Universität Bayreuth.

[§] Max-Planck-Institut für Chemische Physik fester Stoffe.

(1) Spannenberg, A.; Arndt, P.; Kempe, R. *Angew. Chem.* **1998**, *110*, 824−827; *Angew. Chem., Int. Ed.* **1998**, *37*, 832−835.

(2) For review, please see: Kempe, R. *Eur. J. Inorg. Chem.* **2003**, 791−803.

(3) (a) Oskui, B.; Mintert, M.; Sheldrick, W. S. *Inorg. Chim. Acta* **1999**, *287*, 72−81. (b) Schneider, A.; Freisinger, E.; Beck, B.; Lippert, B. *J. Chem. Soc., Dalton Trans.* **2000**, 837−838. (c) Kempe, R.; Noss, H.; Fuhrmann, H. *Chem.*−*Eur. J.* **2001**, *7*, 1630−1636. (d) Su, C.-W.; Chen, J.-D.; Keng, T.-C.; Wang, J.-C. *Inorg. Chem. Commun.* **2001**, *4*, 201−204. (e) Kamar, K. K.; Das, S.; Hung, C.-H.; Castineiras, A.; Kuz'min, M. D.; Rillo, C.; Bartolome, J.; Goswami, S. *Inorg. Chem.* **2003**, *42*, 5367−5375. (f) Mizota, M.; Sakai, K. *Acta Crystallogr., Sect. E* **2004**, *60*, m473−m476. (g) Dogan, A.; Sarkar, B.; Klein, A.; Lissner, F.; Schleid, T.; Fiedler, J.; Zalis, S.; Jain, V. K.; Kaim, W. *Inorg. Chem.* **2004**, *43*, 5973−5980. (h) Chen, T.-R.; Wu, Y.-Y.; Chen, J.-D.; Wang, J.-C. *J. Chin. Chem. Soc. (Taipei)* **2004**, *51*, 1395−1400.

(4) (a) Shekhar, S.; Ryberg, P.; Hartwig, J. F.; Mathew, J. S.; Blackmond, D. G.; Strieter, E. R.; Buchwald, S. L. *J. Am. Chem. Soc.* **2005**, *128*, 3584−3591. (b) Singh, U. K.; Strieter, E. R.; Blackmond, D. G.; Buchwald, S. L. *J. Am. Chem. Soc.* **2002**, *124*, 14104−14114. (c) Alcazar-Roman, L. M.; Hartwig, J. F.; Rheingold, A. L.; Liable-Sands, L. M.; Guzei, I. A. *J. Am. Chem. Soc.* **2000**, *122*, 4618−4630. (d) Beletskaya, I. P.; Bessmertnykh, A. G.; Guilard, R. *Tetrahedron Lett.* **1999**, *40*, 6393−6397. (e) Hartwig, J. F. *Acc. Chem. Res.* **1998**, *31*, 852−860. (f) Louie, J.; Paul, F.; Hartwig, J. F. *Organometallics* **1996**, *15*, 2794−2805.

(5) (a) Wagaw, S.; Buchwald, S. L. *J. Org. Chem.* **1996**, *61*, 7240−7241. (b) Hartwig, J. F. *Synlett* **1996**, 329−340. (c) Schareina, T.; Hillebrand, G.; Kempe, R. *Eur. J. Inorg. Chem.* **2001**, 2421−2426. (d) Schareina, T.; Kempe, R. *Angew. Chem., Int. Ed.* **2002**, *114*, 1591−1601; *Angew. Chem., Int. Ed.* **2002**, *41*, 1521−1523.

(6) (a) Scott, N. M.; Schareina, T.; Tok, O.; Kempe, R. *Eur. J. Inorg. Chem.* **2004**, 3297−3304. (b) Scott, N. M.; Kempe, R. *Eur. J. Inorg. Chem.* **2005**, 1319−1324. (c) Deeken, S.; Proch, S.; Casini, E.; Braun, H. F.; Mechtler, C.; Marschner, C.; Motz, G.; Kempe, R. *Inorg. Chem.* **2006**, *45*, 1871−1879. (d) Noor, A.; Kretschmer, W.; Kempe, R. *Eur. J. Inorg. Chem.* **2006**, in press. (e) Kretschmer, W.; Meetsma, A.; Hessen, B.; Schmalz, T.; Qayyum, S.; Kempe, R. *Chem.*−*Eur. J.* **2006**, in press.

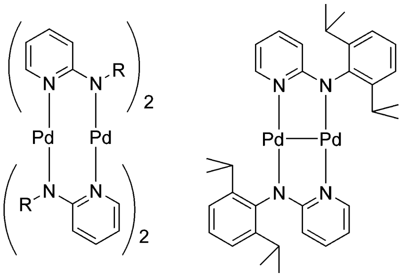
(7) For selected reviews, see: (a) Murahashi, T.; Kurosawa, H. *Coord. Chem. Rev.*. **2002**, *231*, 207−228. (b) Jain, V. K.; Jain, L. *Coord. Chem. Rev.* **2005**, *249*, 3075−3197.

(8) Cotton, F. A.; Gu, J.; Murillo, C. A.; Timmons, D. J. *J. Am. Chem. Soc.* **1998**, *120*, 13280−13281.

(9) Murahashi, T.; Otani, T.; Mochizuki, E.; Kai, Y.; Kurosawa, H.; Sakaki, S. *J. Am. Chem. Soc.* **1998**, *120*, 4536−4537.

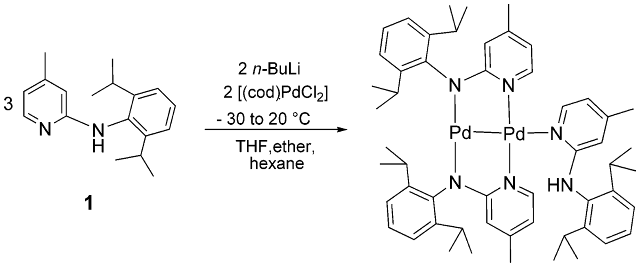
10.1021/ic0610987 CCC: $33.50

Chart 1. Metal−Metal Bond Formation via Steric Frustration[a]



[a] R is a sterically less demanding substituent.

Scheme 1. Synthesis of **2**



2

[(cod)PdCl$_2$] (cod = 1,5-cyclooctadiene) in diethyl ether/tetrahydrofuran at −30 °C results, after workup in hexane, in the formation of **2**, which could be isolated as brown crystals in low yield. After the composition of **2** was identified, 3 equiv of **1** and only 2 equiv of BuLi (Scheme 1), including a long enough reaction time to guarantee complete deprotonation of **1**, were used. Compound **2** was characterized by X-ray crystal structural analysis, NMR, and elemental analysis.

NMR spectroscopy revealed **2** to be a diamagnetic compound in the investigated temperature range. The signal sets of 1 equiv of protonated **1** and 2 equiv of deprotonated **1** were observed. Sharp signals at low temperature indicated that there is no exchange between any of the chemically nonequivalent ligands. The proton NMR singlet at 5.93 ppm results from the N−H function of the aminopyridine ligand. X-ray crystal structural analysis[10] of **2** was performed by using a STOE-IPDS II equipped with an Oxford Cryostream low-temperature unit. Structural solution and refinement was accomplished using *SIR97*,[11] *SHELXL97*,[12] and *WinGX*.[13] The molecular structure of **2** is shown in Figure 1. Pd1 is linearly coordinated by two amido N atoms from deprotonated aminopyridine ligands. It is an example of a low-coordinate Pd center. Pd2 is coordinated by three pyridine N atoms in a T-shaped style. This type of coordination is found in monomeric arylpalladium(II) amido complexes[14] and in dimeric complexes of the corner-sharing L$_3$−Pd(I)−Pd(I)−L$_3$ type, where the two T-shaped ligand arrangements are normally found twisted by about 90°.[7] This twist angle is 18° for **2**. Furthermore, the very short Pd−Pd distance of 2.429 Å should be noted. Because deprotonated aminopyridines are anionic ligands and two of these ligands stabilize **2**, the electronic situation could be described either as a mixed-valence compound, with Pd2 being Pd(0) and Pd1 being Pd(II), or as a metal−metal-bonded dimer with the oxidation state +1 for both metal atoms. Deprotonated 2-aminopyridines show a delocalized binding mode in which the anionic charge is distributed between the two N donor functions.[2] Thus, the coordination of the ligands is not necessarily pointing toward the mixed-valence interpretation.

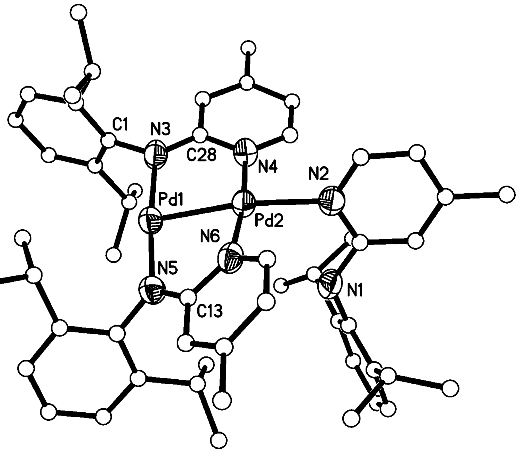


Figure 1. Crystal structure of **2**. Selected bond lengths [Å] and angles [deg]: Pd1−Pd2 2.429(4), N2−Pd2 2.176(3), N3−Pd1 2.001(4), N4−Pd2 2.065(4), N5−Pd1 2.015(3), N6−Pd2 2.047(3); N3−Pd1−Pd2 86.82(10), N5−Pd1−Pd2 88.42(9), N4−Pd2−Pd1 87.56(9), N6−Pd2−Pd1 85.33(8), N2−Pd2−Pd1 169.93(8), N3−Pd1−N5 175.06(13), N6−Pd2−N4 172.67(12), N6−Pd2−N2 93.67(13), N4−Pd2−N2 93.64(13), N5−C13−N6 116.5(4), N3−C28−N4 117.7(4).

Electronic structure calculations were performed to get insight into the bonding situation. The calculation of the electronic structure of **2** was performed at the density functional theory level using the *ADF* program package.[15] The scalar relativistic approach *ZORA*,[16] Becke's gradient-corrected exchange-energy functional,[17] and Lee, Yang, and Parr's[18] gradient-corrected correlation-energy functional (BLYP) were employed. High-quality extended basis sets from the internal library of the *ADF* package were used. The calculations were performed on the basis of the experimental crystal structure data. To investigate the charge distribution and the bonding interaction between the two Pd atoms, the electron density, electron localization function (ELF),[19,20] and localized molecular orbitals on a grid were subsequently calculated from the self-consistent wave function using the program *DGrid*.[21] The topological analysis of ELF and of the electron density according to the Bader's Atoms in

---

(10) CCDC-610354 contains the supplementary crystallographic data for this publication. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html.

(11) Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G. L.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Polidori, G.; Spagna, R. *J. Appl. Crystallogr.* **1999**, *32*, 115−119.

(12) Sheldrick, G. M. *SHELX97, Programs for Crystal Structure Analysis*, release 97-2; Institut für Anorganische Chemie der Universität: Göttingen, Germany, 1998.

(13) Farrugia, L. J. *J. Appl. Crystallogr.* **1999**, *32*, 837−838.

(14) Yamashita, M.; Hartwig, J. F. *J. Am. Chem. Soc.* **2004**, *126*, 5344−5345.

(15) *ADF2005.01*; SCM, Theoretical Chemistry, Vrije Universiteit: Amsterdam, The Netherlands, http://www.scm.com.

(16) van Lenthe, E.; Baerends, E. J.; Snijders, J. G. *J. Chem. Phys.* **1993**, *99*, 4597−4610.

(17) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098−3100.

(18) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785−789.

(19) Becke, A. D.; Edgecombe, K. E. *J. Chem. Phys.* **1990**, *92*, 5397−5403.

(20) Silvi, B.; Savin, A. *Nature (London)* **1994**, *371*, 683−686.

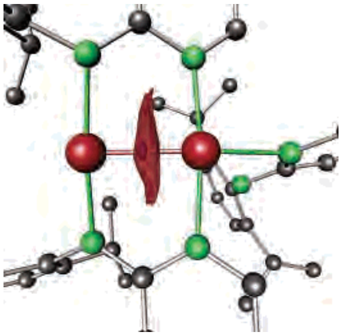


Figure 2. Purple ELF isosurface (isovalue = 0.307) enclosing the maximum between the two Pd atoms. The disk-shaped corresponding ELF basin is shown semitransparent red.

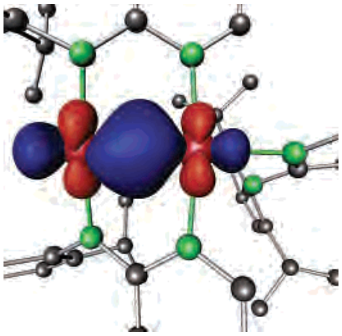


Figure 3. Localized bonding orbital between two Pd atoms: contour surface plots for the orbital values of +0.05 (red) and −0.05 (blue).

Molecules (AIM) scheme[22] was performed using the program *Basin*.[23] AIM partitioning of space into basins of the electron density, which are bound by surfaces of zero flux in a density gradient[22] provides a quantum mechanically based scheme for unique attribution of the electronic charge to atoms in a molecule. It was therefore used in the present study to decide on the question of single valency versus mixed valency of the Pd atoms. The question of chemical bonding was addressed with the topological analysis of ELF. Recently, the topologically relevant kernel of ELF has been recovered from the single-determinant approximation to a general functional of the electronic pair density named the electron localizability indicator, which explicitly contains information about local same-spin electron pairing[24] in a unique way.

The essentially equal populations of 45.7 and 45.5 electrons of Bader's atomic basins for Pd1 and Pd2, respectively, strongly indicate that the two species have the same oxidation state, +1, in the present compound. The small difference in the populations comes from the different ligand environments of the Pd atoms. Topological analysis of ELF reveals a local maximum in the valence region between the two Pd atoms (Figure 2), which is interpreted as a clear sign for covalent bonding between the two metal atoms. The corresponding ELF basin has an electronic population of 0.3 electrons, which is roughly one-third of the value expected for strong σ-bonding transition metal−transition metal interactions [see, e.g., $Re_2(CO)_{10}$].[25] The electronic shell population of the 4th Pd shell is 17.3 and 17.0 electrons for Pd1 and Pd2, respectively, such that about 1 electron is absent with respect to the neutral free atom calculated in an identical manner. The electronic population of the common ELF basin in the valence region has to be equally assigned to both atoms, giving total electron counts of 45.5 and 45.2 electrons, respectively, which corroborates the single-valency scenario. It is worth noting that the Pd−Pd interaction cannot be easily detected from the canonical orbitals because as a result of heavy mixing with ligand p orbitals a unique σ-bonding orbital does not occur. In contrast, the lowest unoccupied molecular orbital corresponds to the Pd1−Pd2 σ^* dd antibonding orbital. Application of the orbital localization procedure according to Foster and Boys[26] to the occupied molecular orbitals provides a localized orbital describing the Pd1−Pd2 σ interaction (Figure 3). From its nodal structure and orientation with respect to the ligands, it should be classified as predominantly a σ $d_{x^2-y^2}d_{x^2-y^2}$ bonding orbital. The dominance of $d_{x^2-y^2}$-mediated Pd−Pd interactions over d_{z^2} ones has been discussed already by Harvey and Murtaza for Pd−Pd interactions in twisted L_3−Pd(I)−Pd(I)−L_3 type complexes.[27] For comparison, geometry optimization of a hypothetical $(py)_3$−Pd−Pd−$(NMe_2)_2$ molecule (within C_{2v} symmetry, py = pyridine, Me = methyl) with localized negative ligand charges has been carried out. It yields a breaking of the Pd−Pd bond and a dissociation of the molecule. This is a clear sign that the nature of the ligand is of primary importance for the Pd−Pd bond formation and the very short distance observed in **2**.

All applied methods to analyze the bonding situation indicate the presence of a covalent bond between two Pd atoms in the investigated compound, leading to a single-valency scenario of Pd in the oxidation state +1.

In conclusion, we showed that steric frustration can lead to metal−metal bonding in the above-mentioned chemistry. The classic paddlewheel structural motif, which is accomplished by deprotonated aminopyridines (and a large variety of similar anionic ligands[28]) in combination with M^{2+} ions, can become metal−metal bonded by restricting the coordination of only two, instead of four, of these anionic ligands for steric reasons. Noteworthy for compound **2** is the corner-sharing untwisted L_2−Pd(I)−Pd(I)−L_3 motif, and it displays a very short metal−metal bond, the shortest observed for Pd(I) in a bimetallic molecule.

Acknowledgment. Financial support from the DFG (Grants SPP 1166 and SPP 1181) and the Fonds der Chemischen Industrie is gratefully acknowledged.

Supporting Information Available: Detailed experimental procedures, details of the calculations, and X-ray crystallographic files (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

IC0610987

---

(21) Kohout, M. *Program DGrid*, version 3.1; Max Planck Institute for Chemical Physics of Solids: Dresden, Germany, 2005.

(22) Bader, R. F. W. *Atoms in Molecules—A Quantum Theory*; Clarendon Press: Glousestershire, U.K., 1995.

(23) Kohout, M. *Program Basin*, version 3.1; Max Planck Institute for Chemical Physics of Solids: Dresden, Germany, 2005.

(24) Kohout, M. *Int. J. Quantum Chem.* **2004**, *97*, 651−658.

(25) Kohout, M.; Wagner, F. R.; Grin, Y. *Theor. Chem. Acc.* **2002**, *108*, 150−156.

(26) Foster, J. M.; Boys, S. F. *Rev. Mod. Phys.* **1960**, *32*, 300−302.

(27) Harvey, P. D.; Murtaza, Z. *Inorg. Chem.* **1993**, *32*, 4721−4729.

(28) Cotton, F. A.; Walton, R. A. *Multiple Bonds between Metal Atoms*, 2nd ed.; Clarendon Press: Oxford, U.K., 1993.