

# On the Electronic Impact of Abnormal C4-Bonding in *N*-Heterocyclic Carbene Complexes

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## 1. Computational Details

All geometry optimizations were performed with the ADF program,<sup>[S1]</sup> using a triple  $\zeta$  basis set with polarization functions, the local density approximation (LDA) in the Vosko-Wilk-Nusair parameterization<sup>[S2]</sup> with nonlocal corrections for exchange (Becke88)<sup>[S3]</sup> and correlation (Perdew86)<sup>[S4]</sup> included in a selfconsistent manner, and the analytical gradient method of Versluis and Ziegler.<sup>[S5]</sup>

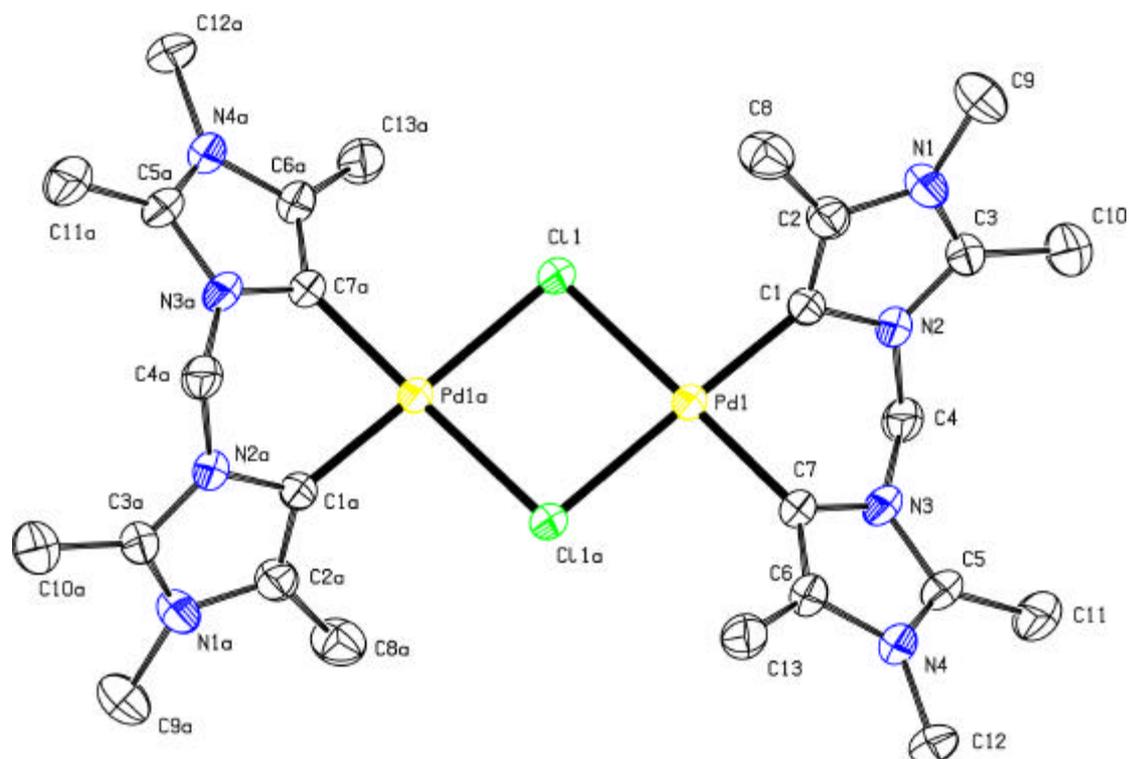
The Pd–Ag bond was analyzed with ADF's established energy decomposition into an orbital interaction ( $\Delta E_{oi}$ ), a steric interaction ( $\Delta E_{steric}$ ), and a preparation energy ( $\Delta E_{prep}$ ), where the latter term results from preparation of the fragments for interaction by deforming them from their equilibrium structure to the geometry and electronic state they acquire in the complex:

$$\Delta E_{bond} = \Delta E_{oi} + \Delta E_{steric} + \Delta E_{prep}$$

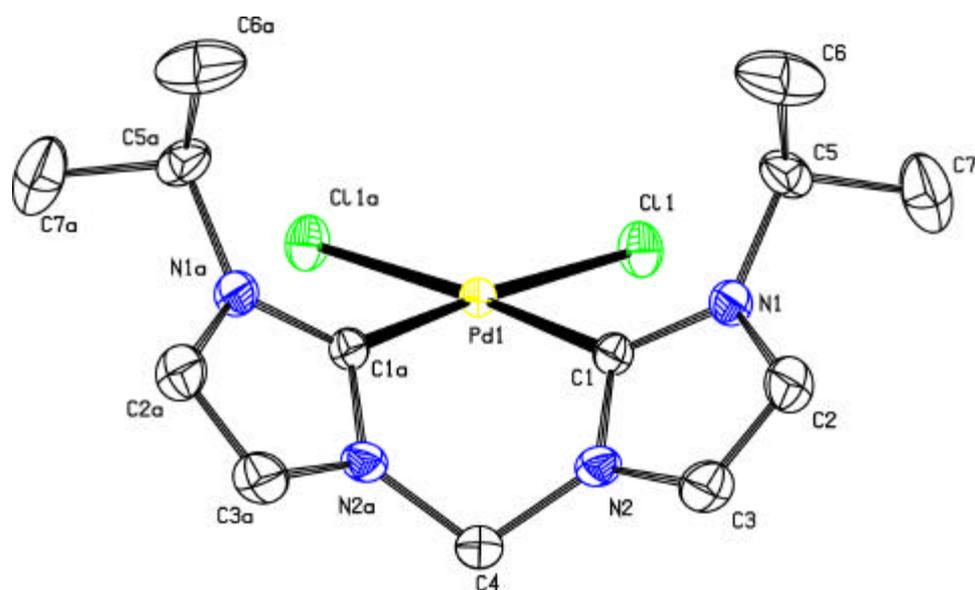
$\Delta E_{steric}$  represents the interaction between the prepared fragments when they are put – with unchanged electron densities – at the positions they occupy in the complex.  $\Delta E_{oi}$  accounts for HOMO–LUMO interactions between occupied orbitals on one moiety with unoccupied orbitals on the other and polarization (empty/occupied orbital mixing on the same fragment). The molecular geometry was adapted to  $C_s$  symmetry in order to distinguish the  $\sigma$  and  $\pi$  part of these interactions.

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- S1 a) C. Fonseca-Guerra, O. Visser, J. G. Snijders, E. J. Baerends, In METECC-95; Clementi, E., Corongiu, C., Eds.; STEFF; Cagliari, Italy, 1995; p. 307; b) Baerends, E. J.; Ellis, D. J.; Ros, P. *Chem. Phys.* **1973**, 2, 41.
- S2 S. H. Vosko, L. Wilk, M. Nusair, *Can. J. Phys.* **1992**, 99, 84.
- S3 A. D. Becke, *Phys. Rev. A* **1988**, 38, 3098.
- S4 Perdew, J. P. *Phys. Rev. B* **1986**, 33, 8822.
- S5 a) L. Fan, L. Versluis, T. Ziegler, E. J. Baerends, W. Raveneck, *Int. J. Quantum. Chem.; Quantum. Chem. Symp.* **1988**, S22, 173; b) L. Versluis, T. J. Ziegler, *J. Chem. Phys.* **1988**, 322, 88. b) Morokuma, K. *J. Chem. Phys.* 1971, 1236. Ziegler, T.; Rauk, A.; *Inorg. Chem.* 1979, 18, 1755. Ziegler, T.; Rauk, A.; *Theor. Chim. Acta* 1977, 46, 1. c) T. Ziegler, A. Rauk, *Inorg. Chem.* **1979**, 18, 1755.

## 2. Solid State Structures of **9'** and **13**



**Figure S1.** ORTEP representation of **9'**, the pseudo-polymorph of **9** (50% probability, solvent molecules, non-coordinating  $\text{BF}_4^-$  anion and hydrogens omitted for clarity). Selected bond lengths ( $\text{\AA}$ ): Pd1–C1 1.973(5), Pd1–C7 1.983(5), Pd1–Cl1 2.3964(12), Pd1–Cl1a 2.4099(13), Pd1 $\cdots$ Pd1a 3.5570(5); selected bond angles (deg): C1–Pd1–C7 84.5(2), C11–Pd1–C11a 84.52(4).



**Figure S2.** ORTEP representation of **13a** (50% probability, co-crystallized DMSO molecule and hydrogens omitted for clarity). Selected bond lengths ( $\text{\AA}$ ): Pd1–C1 1.973(2), Pd1–Cl1 2.3593(6), C1–N1 1.345(3), C1–N2 1.354(3), N1–C2 1.384(3), N2–C3 1.383(3), C2–C3 1.339(4); selected bond angles (deg): C1–Pd1–Cl1a 84.39(13), C11–Pd1–Cl1a 90.08(3), C1–Pd1–Cl1 92.70(7), C1–Pd1–Cl1a 175.94(8), N1–C1–N2 105.2(2).

**Crystal structure determinations.** Suitable single crystals were mounted on a Stoe Mark II-Imaging Plate Diffractometer System (Stoe & Cie, 2002) equipped with a graphite-monochromator. Data collection was performed using Mo-K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) with a nominal crystal to detector distance of 70 mm (for **13a**) and 135 mm (for **9'**), respectively. The structures were solved by direct methods using the program SHELXS-97 and refined by full matrix least squares on  $F^2$  with SHELXL-97.<sup>[S6]</sup> All hydrogen atoms were included in calculated positions and treated as riding atoms using SHELXL-97 default parameters. All non-hydrogen atoms were refined anisotropically. For all structures, a semi-empirical absorption correction was applied using MULscanABS as implemented in PLATON03.<sup>[S7]</sup> Complex **9'** contained one half complex cation and two half-occupied BF $_4^-$  anions per asymmetric unit. One of the BF $_4^-$  anions shared its place with a water molecule (occupancy 0.5). Complex **13a** contained one half complex molecule and one half DMSO molecule per asymmetric unit. Both molecules are lying on symmetry centers which results in 4 molecules per unit cell.

Details on data collection and refinement parameters are collected in Table S1.

Crystallographic data (excluding structure factors) for the structures have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 717915 and 717916. Copies of the data can be obtained free of charge on application to CCDS, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (int.) +44-1223-336-033; E-mail: deposit@ccds.cam.ac.uk].

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S6 G. M. Sheldrick, *Acta Cryst. A*, **2008**, *64*, 112.

S7 A. L. Spek, *J. Appl. Cryst.*, **2003**, *36*, 7.

**Table S1. Crystallographic Data for Complexes 9' and 13a**

	<b>9'</b>	<b>13a</b>
color, shape	light yellow needle	colourless block
crystal size/mm	0.45 × 0.25 × 0.15	0.45 × 0.40 × 0.35
empirical formula	C <sub>26</sub> H <sub>40</sub> B <sub>2</sub> Cl <sub>2</sub> F <sub>8</sub> N <sub>8</sub> Pd <sub>2</sub> × H <sub>2</sub> O	C <sub>13</sub> H <sub>20</sub> Cl <sub>2</sub> N <sub>4</sub> Pd × C <sub>2</sub> H <sub>6</sub> OS
Fw	940.00	487.76
T/K	173(2)	173(2)
crystal system	monoclinic	orthorhombic
space group	<i>P</i> 2 <sub>1</sub> / <i>n</i> (No. 14)	<i>Pnma</i> (No. 62)
unit cell		
<i>a</i> /Å	7.4740(4)	11.2406(8)
<i>b</i> /Å	17.0090(7)	15.8359(12)
<i>c</i> /Å	15.9800(10)	11.5964(10)
<i>b</i> /deg	99.841(5)	90
<i>V</i> /Å <sup>3</sup>	2001.57(18)	2064.2(3)
<i>Z</i>	2	4
<i>D</i> <sub>calc</sub> /g cm <sup>-3</sup>	1.560	1.569
<i>μ</i> /mm <sup>-1</sup> (Mo-K <sub>α</sub> )	1.101	1.269
no. total, unique reflections	27034, 5407	15576, 2080
<i>R</i> <sub>int</sub>	0.0577	0.0688
transmission range	0.693–0.912	0.657–0.731
no. parameters, restraints	223, 8	115, 0
<i>R</i> , <sup>a</sup> <i>R</i> <sub>w</sub> , <sup>b</sup>	0.0557, 0.1764	0.0288, 0.0713
GOF	1.036	1.092
min, max resid density/e Å <sup>-3</sup>	-1.302, 2.004	-0.840, 0.945

<sup>a</sup>  $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$  for all  $I > 2\sigma(I)$

<sup>b</sup>  $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum (w(F_o^4))]^{1/2}$