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Neutral Ligands with Exceptional Donor Ability for Palladium-Catalyzed Alkene Hydrogenation**

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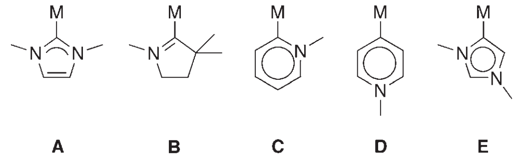
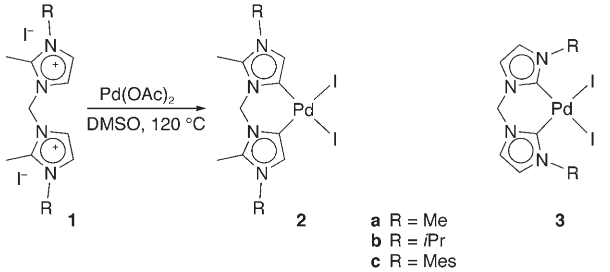
The metal-mediated (catalytic) activation of strong and typically unreactive bonds under mild conditions requires the development of powerful ligand sets. Two particularly useful strategies have been developed during the last few years.[1] The first relies on electron-deficient systems with high-valent early transition metals, often in a d^0 configuration.[2] Such metal centers have been shown to activate unreactive bonds through agostic interactions and subsequent σ-bond metathesis. In a second strategy, electron-rich metal centers are used to promote bond activation through oxidative addition, and late transition metals such as the platinum group metals typically accommodate the required electron density for these reactions.[3] The relative basicity can be further increased by using acidic media[4] and by installing strongly donating nontransferable ligands in the metal coordination sphere.[5]

N-heterocyclic carbenes (NHCs) represent a particularly attractive class of ligands for such applications, since they belong to the class of the strongest neutral donors known to date.[6] Generally, carbenes are bound to the transition metal (M) through the C(2) carbon atom (**A**). Pioneering work has recently shown that the donor power is further enhanced by reducing the number of stabilizing heteroatoms to a single nitrogen atom, such as in **B**[7] or in pyridylidene-type carbenes (**C** and **D**).[8] Similarly, displacing one of the two heteroatoms to a more remote position is expected to impose a higher electron density at the metal center. For example, C(4)-bound carbenes (**E**) were shown to be significantly stronger donors than their classical C(2)-bound homologues.[9]



Here, we have expanded this approach to *cis*-chelating dicarbene systems in which two imidazolium-derived carbenes are unusually coordinated through the C(4) atom (**E**). The coordinated palladium center appears to be highly basic in such a coordination environment and shows—unlike the corresponding C(2)-bound analogue—appreciable catalytic activity in olefin hydrogenation.

Metalation of the C(2)-methylated diimidazolium salt **1** with Pd(OAc)$_2$ in DMSO afforded the C(4)-bound dicarbene palladium diiodide **2** in high yield (Scheme 1). The corresponding BF$_4^-$ salt of **1** failed to yield any metalated product. Formation of an inorganic palladate precursor seems to be essential,[10] presumably since palladation of such imidazolium salts is reminiscent of nucleophilic aromatic substitution. Complexes **2** are highly soluble in polar organic solvents such as DMSO and MeOH, yet only sparingly so in CHCl$_3$. The signal for the metal-bound carbon atom appears in the ^{13}C NMR spectrum around $\delta = 125$ ppm, and hence at considerably higher field than in C(2)-bound NHC palladium complexes (for example, in **3b** $\delta = 160$ ppm).



Scheme 1. Synthesis of palladium dicarbene complexes **2** with C(4) bonding as opposed to C(2) bonding (in **3**). Mes = mesityl = 2,4,6-trimethylphenyl.

A single-crystal X-ray analysis of **2b** unequivocally confirmed the presumed ligand bonding mode (Figure 1).[11] The bite angle of the dicarbene is 83.8(5)°, very similar to that of the analogous C(2)-bound dicarbene complex **3b**.[12] The Pd–C bond lengths in **2b** are 1.932(12) and 1.963(11) Å, which are at the shorter end of the range typically observed for C(2)-bound analogues.[12,13] The Pd–I bonds are slightly longer than in classical carbenes (2.68 Å versus 2.65 Å) and indicate a higher *trans* influence in the C(4)-bound carbenes. Most significantly, the heterocyclic C–C bond in **2b** corresponds to a delocalized double bond (ca. 1.40(2) Å) rather

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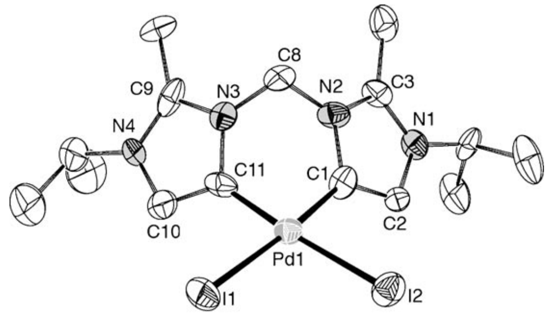
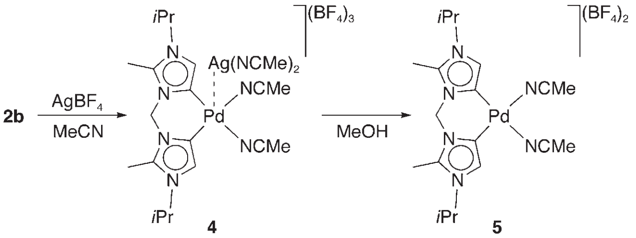


Figure 1. Ortep representation of one of the two crystallographically independent molecules of **2b** (50% probability; H atoms and cocrystallized solvent molecules are omitted for clarity). Selected bond lengths [Å]: Pd1-C1 1.963(11), Pd1-C11 1.937(13), Pd1-I1 2.6797(12), Pd1-I2 2.6812(14), C1-C2 1.388(16), C10-C11 1.41(2).

than a localized C=C bond as observed in C(2)-bound carbenes (typically 1.32 Å).

Complex **2b** is considerably less stable towards acids than the C(2)-bound analogue **3b**. Addition of sulfuric acid induced rapid dissociation of the complex at room temperature and concomitant formation of **1**, presumably as the bisulfate salt. In contrast, complex **3b** is stable for several days under identical conditions. Steric effects may account for this difference in reactivity, as the Pd–C bond is less shielded by the isopropyl groups in **2b**. Furthermore, the increased polarization of the C(4)–Pd bond relative to that of C(2)–Pd enhances the electron density at the Pd center. Accordingly, proton binding may initially occur through the high-lying metal d_{z^2} orbital in **2b**. Subsequent hydrogen migration to the metal-bound carbon atom then cleaves the Pd–C bond to yield **1**.

While we have not succeeded in detecting a metal-bound hydrogen atom spectroscopically, we find support for the feasibility of such a reaction pathway from reactions of **2** with other Lewis acids. For example, complex **2b** rapidly transforms in the presence of $AgBF_4$ (MeCN solution) into the bimetallic complex **4**, which possesses a Pd$\cdots$Ag interaction (Scheme 2). Atomic absorption spectroscopic analysis of amorphous material indicated the presence of equimolar quantities of Ag and Pd. An X-ray diffraction analysis of single crystals[11] revealed the unambiguous formation of an Ag adduct with an unusually short Pd$\cdots$Ag contact of 2.8701(6) Å (Figure 2).[14] Two MeCN solvent molecules and a fluoride ion from BF_4^- complete the formally tetrahedral coordination geometry around the silver nucleus. Removal of the Ag^+ ion to afford the bissolvento complex **5** can be achieved by dissolving the adduct **4** in DMSO or MeOH. These solvents apparently successfully compete with the palladium center as a Lewis base for Ag complexation.



Scheme 2. Formation of the bissolvento complexes **4** and **5**.

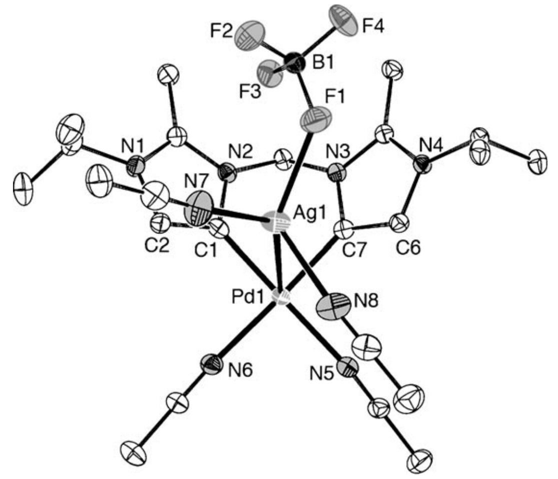


Figure 2. Ortep representation of the dimetallic complex **4** (30% probability; H atoms and two BF_4^- ions are omitted for clarity). Selected bond lengths [Å] and angles [°]: Pd1-Ag1 2.8701(6), Pd1-C1 1.981(5), Pd1-C7 1.972(4), Pd1-N5 2.085(4), Pd1-N6 2.085(4), C1-C2 1.361(7), C6-C7 1.368(6); C1-Pd1-C7 85.95(18), Ag1-Pd1-C1 65.77(13), Ag1-Pd1-C7 68.32(13).

The formation of a silver adduct with **2** but not with **3** suggests there is a higher electron density at the palladium center in C(4)-bound carbene complexes. We have quantified this effect by X-ray photoelectron spectroscopy (XPS, Figure 3). The bonding energies of both the 3d and the 3p palladium electrons in **2** are exceptionally low compared with other palladium(II) complexes,[15] including **3**. This weaker electron bonding reflects the strong donor ability of C(4)-bound carbenes and corroborates previous results obtained from CO vibrations in related iridium(I) complexes.[9]

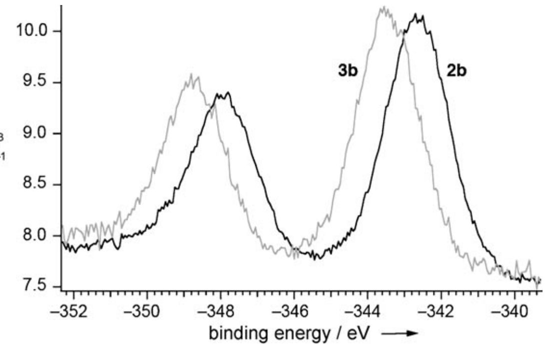
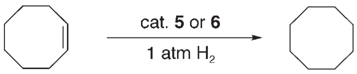


Figure 3. XPS spectra (3d level) of the C(4)-bound dicarbene complex **2b** (black) and its C(2)-bound analogue **3b** (gray).

We have exploited the unique properties of these complexes in catalytic olefin hydrogenation, which involves the activation of H_2 as a key step.[16] Preliminary experiments have been carried out using complexes **2** and **5** as catalyst precursors under mild conditions, that is, at room temperature and 1 atm H_2. The hydrogenation of cyclooctene to cyclooctane [Eq. (1)] is observed with the bissolvento complex **5**, while the neutral homologue **2** was inactive under these



conditions. Comparative experiments have been performed with the bissolvento complex of **3b**, that is, the C(2)-bound complex **6**.[12] Irrespective of the solvent, the conversions are substantially lower with **6** than with the C(4)-bound complex **5** (Table 1, entries 1–5). The hydrogenation of cyclooctene with **5** in polar solvents such as EtOH is complete within less than 5 h. Longer reaction times are required to achieve full conversion when the catalyst loading is reduced below 1 mol% (Table 1, entries 6–8). Catalytic activity essentially ceases at a 0.01 mol% loading. This finding suggests that complex **5** is a true catalyst precursor in this transformation. Computational as well as mechanistic studies are ongoing to elucidate further details of this catalytic reaction.[17]

Table 1: Catalytic hydrogenation of cyclooctene with complexes **5** and **6**.[a]

Entry	Solvent	*t* [h]	cat. loading[b]	Conversion[c] [%]	
				5	**6**
1	MeOH	8 (24)	1%	78 (100)	24
2	EtOH	4.5	1%	100	19
3	THF	8 (24)	1%	50 (100)	9
4	CH_2Cl_2	8 (24)	1%	30 (100)	0
5	toluene	8 (24)	1%	0 (34)	0
6	EtOH	2.5	3%	100	n.d.[d]
7	EtOH	26	0.1%	66	n.d.
8	EtOH	72	0.01%	< 5	n.d.

[a] General conditions: cyclooctene (2.0 mmol), Pd complex (1 mol%), EtOH (6 mL), RT, 1 atm H_2; catalyst precursor **6** is the product from an $AgBF_4$-mediated halide abstraction from **3b** (Scheme 1, see also Ref. [12]). [b] In mol equiv relative to cyclooactene. [c] Determined by GC. [d] Not determined.

In conclusion, we have developed an efficient route to novel complexes comprising highly electron-rich palladium(II) centers. Key to these unique electronic features is a rigid *cis*-chelating, strongly donating, and neutral dicarbene ligand that is bound through C(4) as opposed to C(2), as is normally observed with imidazolium-derived heterocyclic carbenes. The high electron density imparted by this bonding mode affects the stability as well as the catalytic activity of the coordinated metal center and allows for the activation of less reactive bonds such as in H_2. Currently, we are extending this approach to other platinum group metals to target the activation of strong C–H and C–C bonds. Carbene-type ligands bound through the C(4) atom are particularly attractive for designing new catalyst systems for this purpose.

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[1] J. A. Labinger, J. E. Bercaw, *Nature* **2002**, *417*, 507; R. H. Crabtree, *Chem. Rev.* **1995**, *95*, 987.

[2] a) P. L. Watson, *J. Am. Chem. Soc.* **1983**, *105*, 6491; b) M. E. Thompson, S. M. Baxter, A. R. Bulls, B. J. Burger, M. C. Nolan, B. D. Santarsiero, W. P. Schaefer, J. E. Bercaw, *J. Am. Chem. Soc.* **1987**, *109*, 203; c) J. Y. K. Tsang, M. S. A. Buschhaus, P. Legzdins, *J. Am. Chem. Soc.* **2007**, *129*, 5372.

[3] a) A. E. Shilov, G. B. Shul'pin, *Activation and Catalytic Reactions of Saturated Hydrocarbons in the Presence of Metal Complexes*, Kluwer, Dordrecht, **2000**; b) "Activation and Functionalization of C–H Bonds": *ACS Symp. Ser.* **2004**, *885* (Eds.: K. I. Goldberg, A. S. Goldman).

[4] R. A. Periana, D. J. Taube, S. Gamble, H. Taube, T. Satoh, H. Fujii, *Science* **1998**, *280*, 560.

[5] a) R. G. Bergman, *Science* **1984**, *223*, 902; b) C. M. Jensen, *Chem. Commun.* **1999**, 2443; c) I. Göttker-Schnetmann, P. White, M. Brookhart, *J. Am. Chem. Soc.* **2004**, *126*, 1804.

[6] a) D. Bourissou, O. Guerret, F. P. Gabbai, G. Bertrand, *Chem. Rev.* **2000**, *100*, 39; b) W. A. Herrmann, *Angew. Chem.* **2002**, *114*, 1342; *Angew. Chem. Int. Ed.* **2002**, *41*, 1290; c) *N-Heterocyclic Carbenes in Synthesis* (Ed.: S. P. Nolan), Wiley-VCH, Weinheim, **2006**.

[7] a) V. Lavallo, J. Mafhouz, Y. Canac, B. Donnadieu, W. W. Schoeller, G. Bertrand, *J. Am. Chem. Soc.* **2004**, *126*, 8670; b) V. Lavallo, Y. Canac, C. Präsang, B. Donnadieu, G. Bertrand, *Angew. Chem.* **2005**, *117*, 5851; *Angew. Chem. Int. Ed.* **2005**, *44*, 5705; c) V. Lavallo, Y. Canac, A. Dehope, B. Donnadieu, G. Bertrand, *Angew. Chem.* **2005**, *117*, 7402; *Angew. Chem. Int. Ed.* **2005**, *44*, 7236.

[8] a) J. S. Owen, J. A. Labinger, J. E. Bercaw, *J. Am. Chem. Soc.* **2004**, *126*, 8247; b) W. H. Meyer, M. Deetlefs, M. Pohlmann, R. Scholtz, M. W. Esterhuysen, G. R. Julius, H. G. Raubenheimer, *Dalton Trans.* **2004**, 413; c) M. Albrecht, H. Stoeckli-Evans, *Chem. Commun.* **2005**, 4705; d) S. K. Schneider, G. R. Julius, C. Loschen, H. G. Raubenheimer, G. Frenking, W. A. Herrmann, *Dalton Trans.* **2006**, 1226; e) S. K. Schneider, P. Roembke, G. R. Julius, H. G. Raubenheimer, W. A. Herrmann, *Adv. Synth. Catal.* **2006**, *348*, 1862.

[9] a) S. Gründemann, A. Kovacevic, M. Albrecht, J. W. Faller, R. H. Crabtree, *J. Am. Chem. Soc.* **2002**, *124*, 10473; b) A. R. Chianese, A. Kovacevic, B. M. Zeglis, J. W. Faller, R. H. Crabtree, *Organometallics* **2004**, *23*, 2461; c) H. Lebel, M. K. Janes, A. B. Charette, S. P. Nolan, *J. Am. Chem. Soc.* **2004**, *126*, 5046; d) D. Bacciu, K. J. Cavell, I. A. Fallis, L. Ooi, *Angew. Chem.* **2005**, *117*, 5416; *Angew. Chem. Int. Ed.* **2005**, *44*, 5282; e) J. Schütz, E. Herdtweck, W. A. Herrmann, *Organometallics* **2004**, *23*, 6084.

[10] W. A. Herrmann, J. Schwarz, M. G. Gardiner, *Organometallics* **1999**, *18*, 4082.

[11] See the Supporting Information for details of the X-ray crystal structures of **2b** and **4** and of the catalytic experiments.

[12] M. Heckenroth, A. Neels, H. Stoeckli-Evans, M. Albrecht, *Inorg. Chim. Acta* **2006**, *359*, 1929.

[13] a) W. A. Herrmann, J. Schwarz, M. G. Gardiner, M. Spiegler, *J. Organomet. Chem.* **1999**, *575*, 80; b) A. M. Magill, D. S. McGuinness, K. J. Cavell, G. J. P. Britovsek, V. C. Gibson, A. J. White, D. J. Williams, A. H. White, B. W. Skelton, *J. Organomet. Chem.* **2001**, *617*, 546; c) S. Ahrens, A. Zeller, M. Taige, T. Strassner, *Organometallics* **2006**, *25*, 5409; d) T. Scherg, S. K. Schneider, G. D. Frey, J. Schwarz, E. Herdtweck, W. A. Herrmann, *Synlett* **2006**, 2894.

[14] A structure search of the CSD returned only one compound with shorter Ag···Pd interactions: a) Y. Liu, K. H. Lee, J. J. Vittal, T. S. A. Hor, *J. Chem. Soc. Dalton Trans.* **2002**, 2747; see also: b) J. Forniés, A. Martin in *Metal Clusters in Chemistry, Vol. 1*

(Eds.: P. Braunstein, L. A. Oro, P. R. Raithby), Wiley-VCH, Weinheim, **1999**, p. 417.

[15] C. D. Wagner, W. M. Riggs, L. E. Davis, J. E. Moulder in *Handbook of X-ray Photoelectron Spectroscopy* (Ed.: G. E. Mullenberg), Perkin–Elmer, Minnesota, **1979**.

[16] P. Pelagatti in *Handbook of Homogeneous Hydrogenation, Vol. 1* (Eds.: G. de Vries, C. J. Elsevier), Wiley-VCH, Weinheim, **2007**, p. 71.

[17] Different mechanisms are conceivable, including: a) H_2 polarization involving singlet carbenes,[18] b) oxidative addition of H_2 to **5** and formation of an intermediate dicarbene dihydride palladium(IV) species followed by migratory insertion of the π-acceptor ligand into the Pd–H bond;[19] c) carbene insertion into the Pd–H bond and subsequent reductive elimination of an imidazolium group,[20] thus yielding iminium-stabilized Pd nanoparticles as catalytically active species.[21]

[18] G. D. Frey, V. Lavallo, B. Donnadieu, W. W. Schoeller, G. Bertrand, *Science* **2007**, *316*, 439.

[19] D. S. McGuinness, M. J. Green, K. J. Cavell, B. W. Skelton, A. H. White, *J. Organomet. Chem.* **1998**, *565*, 165; D. C. Graham, K. J. Cavell, B. F. Yates, *Dalton Trans.* **2006**, 1768.

[20] D. S. McGuinness, N. Saendig, B. F. Yates, K. J. Cavell, *J. Am. Chem. Soc.* **2001**, *123*, 4029.

[21] a) J. Kiwi, M. Grätzel, *J. Am. Chem. Soc.* **1979**, *101*, 7214; b) S. Klingenhöfer, W. Heitz, A. Greiner, S. Oestreich, S. Föster, M. Antonietti, *J. Am. Chem. Soc.* **1997**, *119*, 10116; c) J. Dupont, R. F. de Souza, P. A. Z. Suarez, *Chem. Rev.* **2002**, *102*, 3667.