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

Marion Heckenroth, Evelyne Kluser, Antonia Neels, and Martin Albrecht*

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 d⁰ 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—analogous 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 BF₄⁻/C₀ 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 CHCl₃. The signal for the metal-bound carbon atom appears in the ¹³C NMR spectrum around δ = 125 ppm, and hence at considerably higher field than in C(2)-bound NHC palladium complexes (for example, in 3b δ = 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.](image)

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 than a single one, with the Pd–C bond lengths in 2b being 1.932(12) and 1.963(11) Å, which are considerably shorter than those of classical carbenes (2.68 Å versus 2.65 Å).
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<sub>2</sub> 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<sub>4</sub> (MeCN solution) into the bimetallic complex 4, which possesses a Pd–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 of 2 revealed the unambiguous formation of an Ag adduct with an unusually short Pd–Ag contact of 2.8701(6) Å (Figure 2). Two MeCN solvent molecules and a fluoride ion from BF<sub>4</sub>– complete the formally tetrahedral coordination geometry around the silver nucleus. Removal of the Ag<sup>+</sup> 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.

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, 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.

We have exploited the unique properties of these complexes in catalytic olefin hydrogenation, which involves the activation of H<sub>2</sub> as a key step. 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<sub>2</sub>. The hydrogenation of cyclooctene to cyclo-
octane [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. 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

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<th>cat. loading[a]</th>
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<td>EtOH</td>
<td>72</td>
<td>0.01%</td>
<td>5 (n.d.)</td>
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[a] General conditions: cyclooctene (2.0 mmol), Pd complex (1 mol%), EtOH (6 mL), RT, 1 atm H₂; catalyst precursor 6 is the product from an AgBF₄-mediated halide abstraction from 3b (Scheme 1, see also Ref. [12]). [b] In mol equiv relative to cyclooctene. [c] Determined by GC. [d] Not determined.

Table 1: Catalytic hydrogenation of cyclooctene with complexes 5 and 6.

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]

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 H₂. 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.

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

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Different mechanisms are conceivable, including: a) H₂ polarization involving singlet carbenes [18] b) oxidative addition of H₂ 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]


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General Synthesis of 2
A mixture of [Pd(OAc)$_2$] (2.0 mmol) and 1 (2.0 mmol) was stirred in DMSO (5–10 mL) at 50°C for 2h and at 110°C for another 3h. Addition of CH$_2$Cl$_2$ (20 mL) followed by Et$_2$O (50 mL) initiated precipitation of the product. Repetition of the precipitation (2x) gave the product as an off-white solid.

Analytical data for 2a: Yield: 1.05 g, 93% (recrystallized from MeOH/Et$_2$O). $^1$H NMR (500 MHz, [D$_6$]DMSO, 25°C, TMS): δ 7.06 (s, 2H; H$_{im}$), 6.08 (s, 2H; CH$_2$), 3.66 (s, 6H; NCH$_3$), 2.65 (s, 6H; C(CH$_3$); $^{13}$C[$^1$H] NMR (125 MHz, [D$_6$]DMSO, 25°C, TMS): δ 142.2 (C$^2$), 123.1 (C$_{carbene}$), 121.0 (C$^5$), 59.7 (CH$_2$), 34.0 (NCH$_3$), 9.7 (CH$_2$); Elem. anal. calcd. for C$_{11}$H$_{16}$I$_2$N$_4$Pd (563.85): C 23.40, H 2.86, N 9.93; found: C: 23.45, H 2.89, N 9.82.

Analytical data for 2b: Yield: 1.17 g, 95% (recrystallized from DMSO/MecN/Et$_2$O). $^1$H NMR (500 MHz, [D$_6$]DMSO, 25°C, TMS): δ 7.16 (s, 2H; H$_{im}$), 6.08 (s, 2H; CH$_2$), 4.55 (sept, $^3$J$_{HH} = 6.8$ Hz, 2H; CHMe$_2$), 2.71 (s, 6H; CH$_3$), 1.37 (d, $^3$J$_{HH} = 6.8$ Hz, 12H; CH(C$_3$)$_2$); $^{13}$C[$^1$H] NMR (125 MHz, [D$_6$]DMSO, 90°C, TMS): δ 140.7 (C$^2$), 121.9 (C$_{carbene}$), 118.7 (C$^5$), 59.4 (CH$_2$), 49.1 (CHMe$_2$), 22.1 (C(CH$_3$)$_2$), 9.9 (CH$_3$); Elem. anal. calcd. for C$_{15}$H$_{24}$I$_2$N$_4$Pd (619.91): C 28.21, H 3.90, N 9.03; found: C: 28.44, H 3.76, N 8.70.

Analytical data for 2c: Yield: 1.22 g, 72% (recrystallized from MeCN/Et$_2$O). $^1$H NMR (500 MHz, [D$_6$]DMSO, 25°C, TMS): δ 7.14 (s, 4H; H$_{mes}$), 7.06 (s, 2H; H$_{im}$), 6.28 (s, 2H; CH$_2$), 2.47 (s, 6H; C(CH$_3$)), 2.32 (s, 6H, ArCH$_3$), 1.98 (s, 12H, ArCH$_3$); $^{13}$C[$^1$H] NMR (50 MHz, [D$_3$]MeCN, 25°C, TMS): δ 142.5 (C$^2$), 140.0 (C$_{aryl}$), 134.7 (C$_{aryl}$), 130.8 (C$_{aryl}$), 129.3 (C$_{aryl}$), 123.5 (C$_{carbene}$), 121.7 (C$^5$), 60.5 (CH$_2$), 20.6 (ArCH$_3$), 16.9 (ArCH$_3$), 9.9 (CH$_3$).

Synthesis of 4
A mixture of 2b (0.45 g, 0.7 mmol) and AgBF$_4$ (0.42 g, 2.2 mmol) was stirred in MeCN (20 mL) at RT for 18 h. After filtration through Celite, the product was precipitated by the addition of Et$_2$O (80 mL). Subsequent washing by addition of MeCN (20 mL) followed by reprecipitation with Et$_2$O (80 mL) gave 4 (0.61 g, 98%). Recrystallization by slow diffusion of Et$_2$O into a saturated solution of 4 in MeCN gave analytically pure material. $^1$H NMR (360 MHz, [D$_3$]MeCN, 25°C, TMS): δ 7.04 (s, 2H; H$_{im}$), 5.84 (s, 2H; CH$_2$), 4.51 (sept, $^3$J$_{HH} = 6.6$ Hz, 2H; CHMe$_2$), 2.59 (s, 6H; CH$_3$), 1.44 (d, $^3$J$_{HH} = 6.6$ Hz, 12H; CH(CH$_3$)$_2$); $^{13}$C[$^1$H] NMR (50 MHz, [D$_3$]MeCN, 25°C, TMS): δ 143.2 (C$^2$), 127.8 (C$_{carbene}$), 121.0 (C$^5$), 60.4 (CH$_2$), 51.3 (CHMe$_2$), 22.4 (C(CH$_3$)$_2$), 10.6 (CH$_3$); Elem. anal. calcd. for C$_{25}$H$_{36}$AgBF$_4$I$_2$N$_8$Pd (899.29): C 30.72, H 4.03, N 12.46; found: C: 30.85, H 4.17, N 12.32.

Synthesis of 5
Complex 4 (0.61 g, 0.68 mmol) was dissolved in MeOH (20 mL). Addition of Et$_2$O (80 mL) gave a precipitate which was isolated by filtration. Repetition of the precipitation (2x) followed by recrystallization from MeCN/Et$_2$O gave 5 as an off-white solid (0.42 g,
93%). $^1$H NMR (360 MHz, $[\text{D}_6]$DMSO, 25°C, TMS): $\delta$ 7.09 (s, 2H; $H_m$), 6.06 (s, 2H; CH$_2$), 4.57 (sept, $^3J_{HH} = 6.5$ Hz, 2H; CHMe$_2$), 2.70 (s, 6H; CH$_3$), 1.39 (d, $^3J_{HH} = 6.5$ Hz, 12H; CH(C$_H_3$)$_2$); $^{13}$C($^1$H) NMR (50 MHz, $[\text{D}_6]$DMSO, 25°C, TMS): $\delta$ 141.8 (C$_2$), 127.0 (C$_{carbon}$), 118.7 (C$_3$), 59.5 (CH$_3$), 49.4 (CHMe$_2$), 22.0 (C(CH$_3_2$)), 9.8 (CH$_3$); Elem. anal. calcd. for C$_{19}$H$_{30}$B$_2$F$_8$N$_6$Pd (622.51): C 36.66, H 4.86, N 13.50; found: C: 36.69, H 4.97, N 13.40.

General procedure for alkene hydrogenation

A solution of catalyst precursor (12 mg, 20 $\mu$mol) and olefin (2.0 mmol) in EtOH (6 mL) was saturated with H$_2$ for 4 min and stirred at RT under an atmosphere of H$_2$ (1 bar). Samples (0.1 mL) were withdrawn at regular time intervals and filtered through a short pad of SiO$_2$ and analyzed by GC-MS (volatile substrates) or by $^1$H NMR.

Crystallographic details

Crystal data for $2b$: C$_{15.25}$H$_{25.25}$I$_{2}$N$_4$O$_{0.375}$Pd, $M_r$ = 630.84, monoclinic $C2/c$, $a = 22.406(3)$, $b = 16.037(2)$, $c = 25.188(4)$, $\beta = 101.64(2)$, $V = 8865(2)$, $Z = 16$, $\rho_{\text{calc}} = 1.891$ g cm$^{-3}$, $\mu(\text{MoK}_\alpha) = 0.71073$ Å, $T = 173(2)$ K, 23299 reflections collected, 8700 independent ($R(int) 0.1550$), full-matrix least-squares refinement on $F^2$, $R_1 = 0.0383$, $wR_2 = 0.0615$ for $I > 2\sigma(I)$, 0 restraints and 408 refined parameters. The compound crystallised with two independent Pd(II) complex molecules, one methanol and one water molecule in the asymmetric unit. All atom positions of the methanol and the water molecule are half occupied, the water molecule lies on a special position.

Crystal data for $4$: C$_{23}$H$_{36}$AgB$_3$F$_{12}$N$_8$Pd, $M_r$ = 899.30, monoclinic $P2_1/n$, $a = 19.5940(16)$, $b = 7.6372(4)$, $c = 24.462(2)$, $\beta = 104.977(7)$, $V = 3489.9(4)$, $Z = 4$, $\rho_{\text{calc}} = 1.712$ g cm$^{-3}$, $\mu(\text{MoK}_\alpha) = 0.71073$ Å, $T = 173(2)$ K, 43337 reflections collected, 6219 independent ($R(int) 0.0396$), full-matrix least-squares refinement on $F^2$, $R_1 = 0.0469$, $wR_2 = 0.1237$ for $I > 2\sigma(I)$, 20 restraints and 433 refined parameters.

CCDC-603583 ($2b$) and CCDC-645302 ($4$) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.