A PALLADIUM (II) COMPLEX CONTAINING IMIDAZOLE MOIETIES. SYNTHESIS AND STRUCTURAL EXAMINATION

Alexandrina D. Tanase,[a] Eberhardt Herdtweck,[a] Wolfgang A. Herrmann,[a,*] and Fritz E. Kühn [b,*]

[a] Department of Chemistry, Chair of Inorganic Chemistry, Technische Universität München, Lichtenbergstraße 4, 85747, Garching, Germany (E-mail: wolfgang.herrmann@ch.tum.de)

[b] Department of Chemistry, Molecular Catalysis, Technische Universität München, Lichtenbergstraße 4, 85747, Garching, Germany, (E-mail: fritz.kuehn@ch.tum.de)

Abstract – *trans*-[PdCl$_2$(NCyIm)$_2$] was prepared through a route involving the corresponding silver precursor. 3-cyclohexyl-1-picolylimidazolium salt and Ag$_2$O give a *trans*-[Ag(NCyIm)$_2$]$^+$ species with the imidazole ring bound at the N1 atom, not at the C2 atom.

Transition metal complexes bearing N-heterocyclic carbene (NHC) ligands have been known for many years[1] and have emerged as new types of ligands in homogeneous catalysis mostly during the past decade.[2,3] The combination of chelate and pincer effects of such carbenes has provided novel types of catalysts.[4] Significant innovations have been made in the synthesis and investigation of palladium (II) complexes bearing chelating nitrogen ligands. A number of these complexes has been found to be highly active for important organic reactions, e. g. the Heck coupling reaction or the ethylen/CO copolymerization.[5] Previous studies have been primarily devoted to cyclometallated palladium complexes incorporating imine, amine, oxime, or oxazoline[6] moieties. Several neutral and cationic palladium(II) complexes have been reported, incorporating *N*-coordinated bis- and tris-imidazole chelates that were found to be catalytically active in the Heck reaction of 4-bromoacetophenone with N-butyl acrylate.[5] An example of a mixed imidazolylidene-imidazole palladium complex and its application in the Sonogashira coupling reaction has also been reported.[7]

Monomethyl and dimethyl Pd(II) complexes of bridged bisimidazole and mixed imidazole-N-heterocycle

(py, pz) ligands have been prepared by Canty et al. and their dynamic behavior has been studied with variable temperature NMR spectroscopy.[8] Potentially hemilabile carbene ligands containing both strong and weak donor groups have found widespread use in homogeneous catalysis. The hemilabile part in such ligands is capable of reversible dissociation from the metal center. Such dynamic behavior is known to produce vacant coordination sites that allow complexation of substrates during the catalytic cycle, at the same time the strong donor moiety remains connected to the metal center.[9]

The synthesis and structural characterization of a Pd (II) complex **3** bearing imidazole moieties is reported in the present work. The corresponding Pd (II) complexes of N-functionalized heterocyclic carbene ligands **5**, **6** have been synthesized through a route involving carbene transfer from an Ag (I), carbene precursor.

RESULTS AND DISCUSSION

The N-functionalized imidazolium bromide salt **1** was prepared by reacting the corresponding halide with 1-cyclohexylimidazole according to Scheme 1. Attempts to prepare the free carbene by deprotonation of the imidazolium salt failed due to the high acidity of the methylene protons in **1.** The yellow solid obtained was characterized by analytical and spectroscopic methods.

Scheme 1

R= Cy; X = Br

1 (63 % yield)
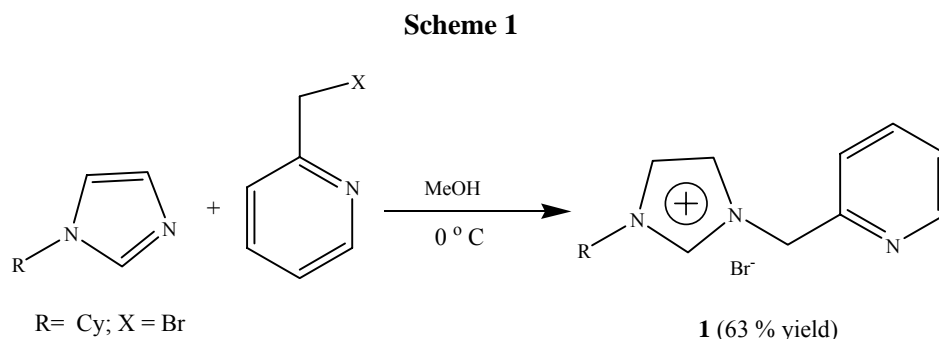
While attempting to prepare a palladium (II) complex from the picolylimidazolium salt **1** by transmetallation of the corresponding silver complex, an *trans*-[Ag(NCyIm)$_2$]$^+$ species was isolated, with the imidazole rings unexpectedly bound directly to the N1 atom (Figure 1 and Scheme 2). The ^{1}H NMR data of the silver complex **2** show equivalent cyclohexyl and imidazole protons, but no signal corresponding to the methylene linker group was detected. It was at first considered that the compound obtained could be a result of the unreacted 1-cyclohexylimidazole present in the original ligand precursor **1**, but this possibility was excluded by elemental analysis and mass spectrometry. The formation of **2** in refluxing CH$_2$Cl$_2$ for 2 days, however, requires a C-N bond cleavage of the ligand precursor **1**.

It was observed that under mild conditions in N-heterocyclic carbene precursors a cleavage of their C-N bonds occurs, yielding the alkylimidazole fragments.[7,10] The formation of the bisimidazole silver complex **2**, is in contrast to previous studies on C-H bond activation in imidazolium systems, which have so far

always, led to the usual C2 carbenes silver complexes.[9,11] Occasionally, the Ag_2O reagent can give unexpected products in its reaction with an imidazolium salt, therefore quite some care needs to be taken to verify if the desired reaction has indeed occurred.

Scheme 2. Synthesis of Ag^I and Pd^{II} Complexes [a]
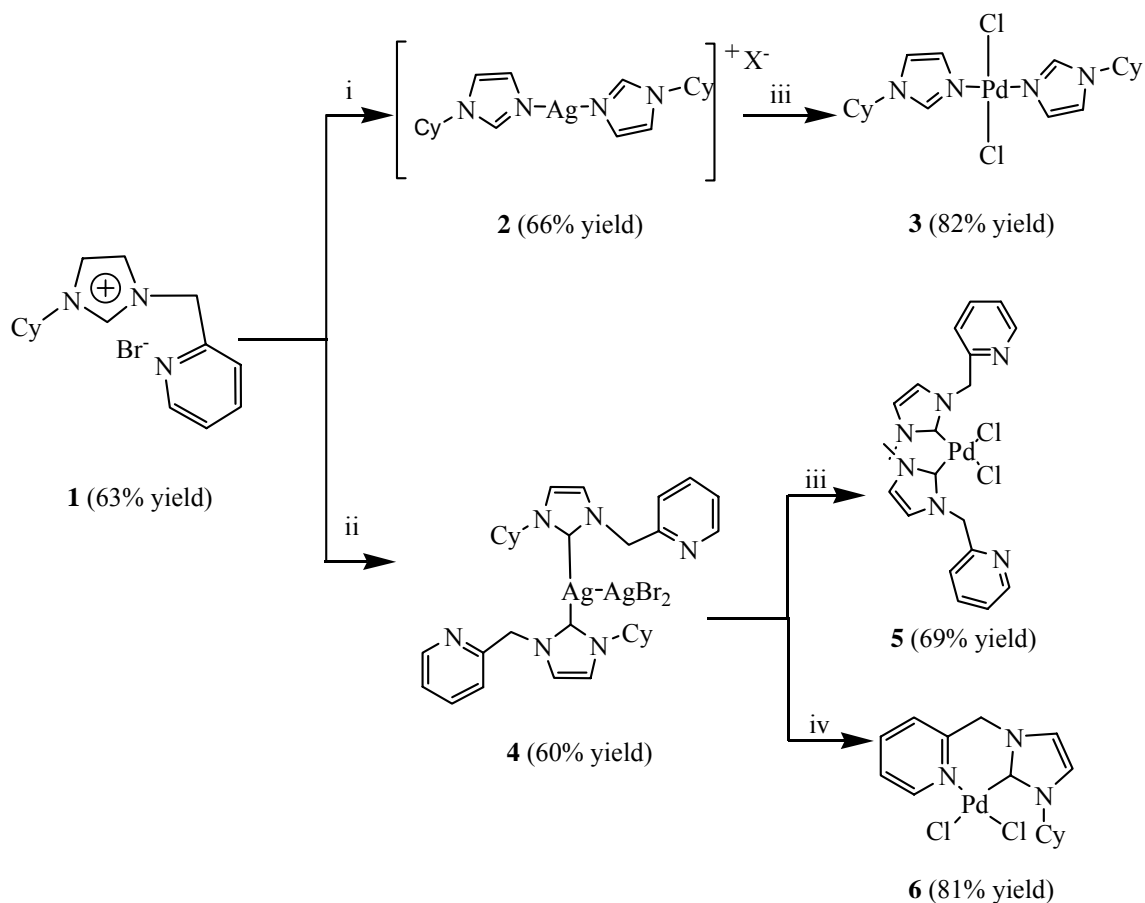
^{a} Reagents: (i) Ag_2O, CH_2Cl_2, reflux 40 °C, 2 days; (ii) Ag_2O, CH_2Cl_2, rt, 2 h; (iii) $PdCl_2(CH_3CN)_2$, CH_2Cl_2, 1h; (iv) 2 $PdCl_2(COD)$, CH_2Cl_2, 40 min.

The silver complex **2** reacts smoothly with the Pd(II) precursor $PdCl_2(MeCN)_2$ to yield the corresponding *trans*-[$PdCl_2(NCyIm)_2$] palladium complex **3**. In a typical reaction the Ag complex was stirred with the Pd precursor in CH_2Cl_2 solution for 1 h before being filtered to remove the precipitated AgBr. Subsequent workup of the solution afforded the complex in 82 % yield. The crystal structure of **3** has been determined by X-ray diffraction analysis. The ORTEP drawing of **3** is shown in (Figure 1).
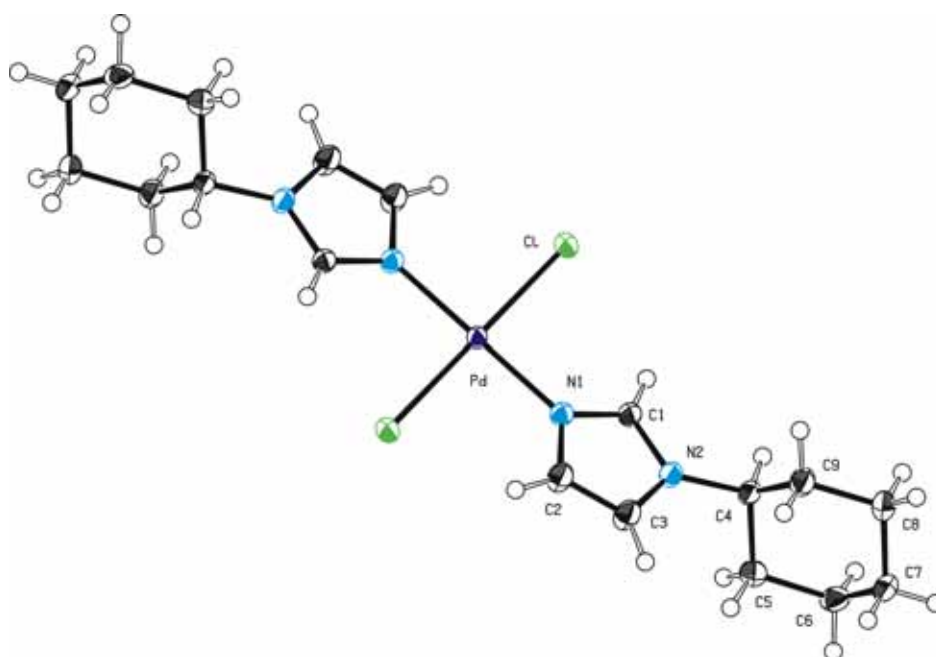
Figure 1. ORTEP style reprezentation of compound **3** in the solid state. Thermal ellipsoids are drawn at the 50 % probability level. The molecule shows a crystallographic C_i symmetry and an operator for generating equivalent atoms of (1-x, 1-y, 1-z).

The complex consists of monomeric $Pd(NCyIm)_2Cl_2$ units. Most of the crystal structures of corresponding dihalide-bis(1-alkylimidazole)-palladium(II) indicate that in the solid state the *trans* isomer crystallizes preferentially, where as the two imidazole ligands are coordinated *trans* to each other at the palladium center. The imidazole ligands were found to coordinate to the metal through the electronic 'pair' of the N1. The Pd atom in **3** is coordinated in a square-planar fashion to the Cl and N atoms. The Pd–Cl and Pd–N1 bond lengths of the palladium complex **3** are slightly longer [2.3101(4) and 2.0156(12) Å] as compared to the previous published imidazole complex [2.307(1) and 2.011(2) Å].[12] The dihedral angle between the plane of imidazole ring and the square plane around the Pd is 27.57(8)°.

To avoid the formation of the bisimidazole silver complex, the silver carbene complex **4** was prepared by interaction of the imidazolium salt **1** with Ag_2O in CH_2Cl_2 at room temperature for 2 h. We have been unable to prepare the desired carbene silver complex at higher temperatures in CH_2Cl_2 as reported by Danopoulos *et al.*[11] The identity of the silver carbene complex **4** was established by a combination of analytical and spectroscopic techniques. The formation of the carbene complex was established by the presence of a peak at $\delta(^{13}C) = 180.9$ ppm, which was assigned to the 2*C*-imidazol-2-ylidene (carbene) carbon, and by the absence of the downfield peak for the 2*H*-imidazolium proton in the ^1H NMR spectra usually observed in non-protic solvents below $\delta(^1H) = 9$ ppm. The ^1H NMR spectrum of **4** shows a singlet at $\delta(^1H) = 5.32$ ppm corresponding to the CH_2 linker group. A CH_2Cl_2 solution of the corresponding

silver carbene precursor **4**, was added drop wise to a solution of $PdCl_2(CH_3CN)_2$ to yield the palladium complex **5** containing two carbene ligands. Both carbene ligands are coordinated to the Pd center and the donor groups remain dangling with the N atom uncoordinated to the metal center. The complex was obtained as a pale yellow air-stable solid and characterized by spectroscopic and analytical methods. At room temperature the ^{1}H NMR signals sharpen and two sets of peaks, corresponding to the *cis* and *trans* isomers are observed.

The silver complex **4** was stirred with the Pd precursor $Pd(COD)Cl_2$ in CH_2Cl_2 solution for 1 h to yield the palladium complex **6,** containing the donor-functionalized carbene ligand **1**. The ^{1}H NMR spectrum reported here shows very broad, merged signals at room temperature. Fluxional behavior was observed at elevated temperatures. At ambient temperature a broad singlet peak is observed for the diastereotopic methylene protons in the ^{1}H NMR spectrum, resulting from dynamic conformational flipping of the six-membered chelate ring. When cooling the solution to -30 °C, two sharp doublets at $\delta(^1H) = 5.88$ and 5.03 ppm are observed with geminal coupling constants of 14.68 Hz. No additional splitting or broadening of other signals in the spectrum is observed at this lower temperature. The thermal stabilities of the Ag(I) and Pd(II) complexes of the bidentate type ligands **4** and **5, 6** have been investigated using similar experimental conditions as for the bisimidazolium silver complex **2**. The observed spectroscopic signals correlate well with the previous ones. A simple explanation for these observations is that the presence of chelating ligands either as a spectator ligand in **4, 5** or as a chelate incorporating the carbene moiety in **6,** plays an important role for the stability of the complexes already formed.

EXPERIMENTAL

All reactions were performed under a dry argon atmosphere using standard Schlenk technique. Solvents and substrates were dried by standard procedures, distilled and kept under argon over molecular sieves. The precursors 1-cyclohexylimidazole[13] and $Pd(MeCN)_2Cl_2$[14] were prepared according to the reported literature procedures. ^{1}H and $^{13}C\{^1H\}$ NMR spectra were recorded on a JEOL-JMX-GX 400 MHz spectrometer at room temperature. ^{1}H NMR peaks are labeled as singlet (s), doublet (d) , triplet (t), multiplet (m) or broad signals (br). Infrared spectra were recorded on a Perkin-Elmer FT-IR spectrometer using KBr pellets as IR matrix. Mass spectrometric measurements were done on a Finnigan MAT 90 spectrometer using the CI or FAB technique. Elemental analyses were performed in the Microanalytical Laboratory at the TU München.

3-Cyclohexyl-1-picolylimidazolium bromide (**1**): 2-(Bromomethyl)pyridine hydrobromide (1 g, 4 mmol) was neutralized using a saturated aqueous Na_2CO_3. The liberated 2-(bromomethyl)pyridine was extracted into Et_2O (3 x 10 mL) at 0 °C, dried with Mg_2SO_4, and filtered. 1-Cyclohexylimidazole (0.60 g, 4 mmol) in MeOH was added at 0 °C to the filtrate, the Et_2O removed under reduced pressure, and the

solution stirred for 12 h at rt. The methanol was evaporated under reduced pressure, and the formed oil was purified by repetitive precipitation from CH_2Cl_2/Et_2O mixtures. Evaporation of the volatiles under reduced pressure left compound **1** as an yellow solid. The product was recrystallized from CH_2Cl_2/Et_2O, collected by filtration and dried in vacuo. Yield: 0.68 g (63 %). *Anal.* Calcd for $C_{15}H_{21}N_3Br\cdot3/2CH_2Cl_2$ (449.15): C, 44.08; H, 5.34; N, 9.35. Found: C, 44.34; H, 5.10; N, 9.69. MS (FAB): m/z 242.3, $[M-Br]^+$ (100 %); ^1H NMR (CDCl$_3$, 298 K): δ 10.72 (s, 1H, NCHN), 8.50 (d, 1H, $^3J_{HH}$ = 4.4 Hz, H$_{py}$), 7.89 (d, 1H, $^3J_{HH}$ = 8.0 Hz, H$_{py}$), 7.71 (t, 1H, H$_{py}$), 7.62 (s, 2H, H$_{im}$), 7.27-7.25 (m, 1H, H$_{py}$), 5.82 (s, 2H, CH$_2$), 4.27 (m, 1H, CH$_{Cy}$), 2.22 - 1.39 (m, 10H, CH$_{2,Cy}$). $^{13}C\{^1H\}$ NMR (CDCl$_3$, 298 K): δ 152.87 (C$_{py}$), 149.88 (C$_{py}$), 137.59 (C$_{py}$), 136.06 (NCN), 135.22 (C$_{py}$), 123.73 (C$_{py}$), 122.75 (C$_{im}$), 120.69 (C$_{im}$), 60.23 (CH$_2$), 56.84 (CH$_{Cy}$), 33.93 (CH$_{2,Cy}$), 25.18 (CH$_{2,Cy}$).

trans-[Ag(1-cyclohexylimidazole)$_2$]Br (**2**): A clear solution of **1** (1.13 g, 3.5 mmol) in CH_2Cl_2 (30 ml) and Ag$_2$O (0.4 g, 1.75 mmol) was heated to 40 ^{o}C for 2 days. The solution was filtered through Celite and the solvent removed under reduced pressure. The yellow powder obtained was washed with Et$_2$O and dried in vacuo. The product was recrystallized from CH_2Cl_2/Et_2O, collected by filtration and dried in vacuo. Yield: 0.565 g (66 %). *Anal.* Calcd for $C_{18}H_{28}N_4BrAg$ (488.21): C, 44.28; H, 5.78; N, 11.48. Found: C, 44.21; H, 6.16; N, 11.28. IR (KBr): 2930, 2859 ($v_{C-H\ aromatic}$); 1500 ($v_{C=N}$), 1444, 1271, 1233, 1107, 1081, 988 ($v_{C-H\ aliphatic}$) cm^{-1}. MS (FAB): m/z 409.1, $[M-Br]^+$ (100 %), 257.0, $[M-Br-CyIm]^+$ (90 %). ^1H NMR (CDCl$_3$, 298 K): 8.15 (s, 2x1H, NCHN), 7.04 (s, 2H, H$_{im}$), 6.95 (s, 2H, H$_{im}$), 4.02 (m, 1H, CH$_{Cy}$), 2.12 - 1.24 (m, 10H, CH$_{2,Cy}$). $^{13}C\{^1H\}$ NMR (CDCl$_3$, 298 K): δ 155.29 (NCN), 135.26 (C$_{im}$), 117.13 (C$_{im}$), 57.05 (CH$_{Cy}$), 34.45 (CH$_{2,Cy}$), 25.35 (CH$_{2,Cy}$).

trans-[Pd(1-cyclohexylimidazole)$_2$]Cl$_2$ (**3**): A mixture of **2** (0.5 g, 1.0 mmol) and Pd(MeCN)$_2$Cl$_2$ (0.13 g, 0.5 mmol) was dissolved in CH_2Cl_2 (5 mL) and stirred for 1 h. The solution was filtered through Celite, and the solvent was removed in vacuo, to give a white powder. The product was recrystallized from CH_2Cl_2/n-pentane (2 mL/10 mL), collected by filtration and dried in vacuo. Yield: 0.401 g (82 %). *Anal.* Calcd for $C_{18}H_{28}N_4Cl_2Pd$ (477.77): C, 45.25; H, 5.91; N, 11.73. Found: C, 45.09; H, 5.58; N, 11.86. IR (KBr): 2930, 2859 ($v_{C-H\ aromatic}$); 1514 ($v_{C=N}$), 1453, 1351, 1262, 1121, 1050, 997 ($v_{C-H\ aliphatic}$) cm^{-1}. ^1H NMR (CDCl$_3$, 298 K): δ 8.21 (s, 1H, NCHN), 7.35 (s, H$_{,im}$), 7.26 (s, H$_{,im}$), 4.0 (m, 1H, CH$_{Cy}$), 2.14 - 1.23 (m, 10H, CH$_{2,Cy}$). $^{13}C\{^1H\}$ NMR (CDCl$_3$, 298 K): δ 138.54 (NCN), 128.94 (C$_{im}$), 117.77 (C$_{im}$), 57.83 (CH$_{Cy}$), 33.77 (CH$_{2,Cy}$), 33.57 (CH$_{2b,Cy}$), 25.35 (CH$_{2,Cy}$).

[Ag(3-cyclohexyl-1-picolylimidazolin-2-ylidene)$_2$] [AgBr$_2$] (**4**): A mixture of **1** (0.5 g, 1.5 mmol) and Ag$_2$O (0.18 g, 0.7 mmol) was dissolved in CH_2Cl_2 (30 ml) and the mixture stirred for 2 h at rt. The solution was filtered through Celite and the solvent removed in vacuo to give an yellow solid. The product was recrystallized from CH_2Cl_2/Et_2O, collected by filtration and washed with Et$_2$O (10 ml). After drying in vacuo a pale-yellow powder was obtained.   Yield: 0.5 g, (60 %). *Anal.* Calcd for

$C_{31}H_{43}N_6Br_2Ag_2$ (871.00): C, 42.54; H, 4.95; N, 9.60. Found: C, 42.46; H, 5.01; N, 9.64. MS (FAB): m/z 606.2, [M-AgBr$_2$]$^+$ (10%), 242.3, [ylidene]$^+$ (100 %). ^{1}H NMR (CDCl$_3$, 298 K): 8.55 (dd, 1H, $H_{py,6}$), 7.69 (dt, 1H, $H_{py,4}$), 7.28 (d, 1H, $H_{py,3,5}$), 7.23 and 7.14 (d, 2x1H, H_{im}), 5.32 (s, 2H, CH$_2$), 4.26 (m, 1H, CH$_{Cy}$), 2.03 - 1.23 (m, 10H, CH$_{2,Cy}$). ^{13}C{^{1}H} NMR (CDCl$_3$, 298 K): δ 180.9 (NCN), 155.51 (C$_{py}$), 149.52 (C$_{py}$), 137.21 (C$_{py}$), 123.25 (C$_{py}$), 122.64 (C$_{im}$), 121.60 (C$_{im}$), 118.22 (C$_{py}$), 61.72 (CH$_2$), 56.68 (CH$_{Cy}$), 34.65 (CH$_{2,Cy}$), 25.41 (CH$_{2,Cy}$).

[Pd(3-cyclohexyl- 1-picolylimidazolin-2-ylidene)$_2$]Cl$_2$ (5): A mixture of Pd(MeCN)$_2$Cl$_2$ (21.9 mg, 0.77 mmol) and **4** (0.37 g, 0.42 mmol) was dissolved in CH$_2$Cl$_2$ (50 mL). The mixture was stirred for 1 h, and then filtered through Celite to remove precipitated silver bromide. The solvent was removed in vacuo until ca. 5 mL remained, and *n*-hexane (10 mL) was added to it. The product was recrystallized from CH$_2$Cl$_2$/ Et$_2$O (5 mL/10 mL) followed by two washings with *n*-hexane (10 mL) and dried in vacuo to afford an yellow powder. Yield: 0.193 g (69 %). MS (FAB): m/z 593.2, [M - 2Cl] $^+$ (20%); 441.3, [M - 2Cl - CyIm]$^+$ (40 %); 242.3, [ylidene]$^+$ (100 %). ^{1}H NMR (DMSO-d_6, two isomers in a 1:2 ratio (a:b)): δ 8.52 (m, 2H, $H_{py,6b}$), 8.34 (m, 2H, $H_{py,6a}$), 8.0-7.7 (m, 2H, $H_{py,4a+b}$), 7.5-7.1 (m, 8H, $H_{py,3a+b}$, $H_{py,5a+b}$), 6.6 (*H*CCH$_{a+b}$), 5.72 (s, 2H, NCH$_{2a}$), 5.51 (s, 2H, NCH$_{2b}$), 4.13 (m, 2H, NCH$_{Cy,a+b}$), 1.92-1.15 (m, 20H, NC*H*$_{2Cy,a+b}$). ^{13}C{^{1}H} NMR (DMSO-d_6): δ 180.2 (NCN), 161.9, 148.5, 137.9 (C$_{py}$), 129.1, 122.7, 120.9, 117.8 (C$_{py}$, NCCN), 57.5 (NCH2), 33.6(CH$_{Cy}$), 25.3 (CH$_{2,Cy}$).

[Pd(3-cyclohexyl- 1-picolylimidazolin-2-ylidene)]Cl$_2$ (6): A CH$_2$Cl$_2$ solution of the corresponding silver carbene complex **4** (0.3 g, 0.34 mmol) was added dropwise to a solution of Pd(COD)Cl$_2$ (0.19 g, 0.66 mmol) and stirred at rt for 40 min, than it was filtered through Celite to remove precipitated silver bromide. The remaining solid residue was washed with Et$_2$O and dried in vacuo. The product was recrystallized from CH$_2$Cl$_2$/ Et$_2$O (5 mL/10 mL) followed by washing twice with *n*-hexane 10 mL and dried in vacuo to afford an pale-yellow powder. Yield: 0.105 g (81 %). *Anal*. Calcd for $C_{15}H_{20}Cl_2N_3Pd$ · 1/2 CH$_2$Cl$_2$ (461.63): C, 40.29; H, 4.54; N, 9.09. Found: C, 40.20; H, 4.67; N, 9.05. ^{1}H NMR (CD$_2$Cl$_2$, -30 °C): δ 9.26 (br d, 1H$_{py}$), 7.88 (dt, 1H$_{py}$), 7.48 (d, 2H$_{py}$), 7.36 (m, 1H$_{py}$), 7.12 (d, 1H, *H*CCH), 6.88 (d, 1H, HCC*H*), 5.88 (d, 1H, NC*H*H), 5.03 (d, 1H, NCH*H*), 3.92 (m, 1H, CH$_{Cy}$), 2.54 - 1.12 (m, 10H, CH$_{2,Cy}$). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$): δ 182.8 (NCN), 156.7, 155.6, 133.8 (C$_{py}$), 124.8, 123.7, 121.9, 112.2 (C$_{py}$, NCCN), 56.7 (NCH2), 34.2(CH$_{Cy}$), 31.3(CH$_{2,Cy}$), 25.5 (CH$_{2,Cy}$).

Single crystal X-ray structure determination of compound 3. $C_{18}H_{28}Cl_2N_4Pd$, M_r = 477.76, yellow fragment (0.56 × 0.58 × 0.63 mm^3), monoclinic, $P2_1/n$ (No.: 14), a = 7.5022(2), b = 9.8085(2), c = 13.6610(3) Å, β = 97.114(2)°, V = 997.51(4) Å^3, Z = 2, d_{calc} = 1.591 gcm^{-3}, F_{000} = 488, μ = 1.207 mm^{-1}. Preliminary examination and data collection were carried out on an area diffraction system (Xcalibur™3, κ-CCD, OXFORD DIFFRACTIONS) and graphite monochromated MoK$_\alpha$ radiation (λ = 0.71073 Å). Data collections were performed at 153 K. Raw data were corrected for Lorentz, polarization, and, arising from

the scaling procedure, for latent decay and absorption effects. The structure was solved by a combination of direct methods and difference Fourier syntheses. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were found and refined with individual isotropic displacement parameters. Full-matrix least-squares refinements were carried out by minimizing $\Sigma w(F_o^2-F_c^2)^2$ with the SHELXL-97 weighting scheme and converged with $R1 = 0.0184$ [2200 intensities, $I_o>2\sigma(I_o)$], $wR2 = 0.0443$ [2362 intensities, all data], $GOF = 1.105$, and shift/error < 0.001. The final difference-Fourier map shows no striking features ($\Delta e_{min/max} = +0.59/-0.41$ eÅ^{-3}). Small extinction effects were corrected with the SHELXL-97 procedure [$\varepsilon = 0.0275(9)$].[15]

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REFERENCES AND NOTES

1. H. W. Wanzlick and H. J. Schönherr, *Angew. Chem.*, 1968, **80**, 154; K. Öfele, *J. Organomet. Chem.,* 1968, **12**, 42.

2. W. A. Herrmann, *Angew. Chem.*, 2002, **14,** 1343; *Angew. Chem. Int. Ed.,* 2002, **41**, 1290.

3. W. A. Herrmann and C. Köcher, *Angew. Chem., Int. Ed.,* 1997, **36**, 2162; *Angew. Chem.,* 1997, **109**, 2256; R. H. Crabtree, *Pure Appl. Chem.,* 2003, **75**, 435.

4. E. Peris and R. H. Crabtree, *C. R. Chim.,* 2003, **6**, 33.

5. M. C. Done, T. Rüther, K. J. Cavell, M. Kilner, E. J. Peacock, N. Braussaud, B. W. Skelton, and A. H. White, *J. Organomet. Chem.,* 2000, **607**, 78; T. Rüther, M. C. Done, K. J. Cavell, E. J. Peacock, B. W. Skelton, and A. H. White, *Organometallics,* 2001, **20**, 5522.

6. M. Ohff, A. Ohff, and D. Milstein, *Chem. Commun.*, 1999, 357; D. A. Alonso, C. Nájera, and M. C. Pacheco, *Org. Lett.,* 2000, **2,** 1823; F. Yang, Y. Zhang, R. Zheng, J. Tang, and M. He, *J. Organomet. Chem.*, 2002, **651**, 146; L. Botella and C. Nájera, *Angew. Chem. Int. Ed.*, 2002, **41**, 179; B. Tao and D. W. Boykin, *Tetrahedron Lett.*, 2002, **43**, 4955.

7. R. A. Batey, M. Shen, and A. J. Lough, *Org. Lett.*, 2002, **4**, 1411.

8. P. K. Byers and A. J. Canty, *Organometallics*, 1990, **9**, 210.

9. D. S. McGuinness and K. J. Cavell, *Organometallics*, 2000, **19,** 741.

10. E. Mas-Marzá, M. Poyatos, M. Sanau, and E. Peris, *Organometallics,* 2004, **23,** 323.

11. A. D. D. Tulloch, A. A. Danopoulos, S. Winston, S. Kleinhenz, and G. Eastham, *J. Chem. Soc.,*

Dalton Trans., 2000, 4499.

12.   M. C. Navarro- Ranninger, *Acta Cryst*., 1983, **C39**, 186.

13.   A. A. Gridnev and I. M. Mihaltseva, *Synth.Commun*., 1994, **24**, 1547.

14.   C. J. Mathews, P. J. Smith, and T. Welton, *J. Mol. Cat., A*, 2003, **206**, 77.

15.   Crystallographic data (excluding structure factors) for the structure reported in this paper has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-****** (**3**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk); CrysAlis Data Collection Software and Data Processing Software for Oxford Xcalibur diffractometer, Version 1.171, Oxford Diffraction Ltd., Oxfordshire, United Kingdom, 2005; A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M. C. Burla, G. Polidori, M. Camalli, *SIR92*, *J. Appl. Crystallogr.,* 1994, **27**, 435; G. M. Sheldrick, *SHELXL-97*, Universität Göttingen, Germany, 1998; L. J. Farrugia, *WINGX* (Version 1.70.01 January 2005), *J. Appl. Crystallogr.,* 1999, **32**, 837; A. L. Spek, *PLATON A Multipurpose Crystallographic Tool*, Utrecht University, The Netherlands, 2007.