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Synthesis of a sterically modulated pyridine–NHC palladium complex and its reactivity towards ethylene

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1. Synthetic procedures

General. 2-bromo-6-(2,6-dimethylphenyl)pyridine^{S1} and [PdCl(Me)(cod)]^{S2} were prepared according to published procedures. All other reagents were purchased from commercial sources and used without further purification. ¹H and ¹³C{¹H} NMR spectra were recorded at room temperature on 400 or 500 MHz Varian spectrometers. Chemical shifts (δ in ppm, J in Hz) were referenced to residual solvent signals relative to SiMe₄. Signal assignments are based on homo- and heteronuclear (multiple-bond) correlation spectroscopy. Microanalyses were performed with an Exeter Analytical CE-440 instrument. High-resolution mass spectrometry was carried out with a Micromass/Waters Corp. USA liquid chromatography time-of-flight spectrometer equipped with an electrospray source. HRGC analyses were run on a Carlo Erba HRGC 5300 Mega Series equipped with a SE 30 capillary column (30 m \times 0.32 mm), carrier gas He (50 KPa), split 1:60. GC/MS analyses were performed with an Agilent GC 7890 instrument using a DB-225ms column (J&W, 60m, 0.25mm ID, 0.25micron film) and He as carrier coupled with a 5975 MSD.

Compound 1. A mixture of 2-bromo-6-(2,6-dimethylphenyl)pyridine (0.39 g, 1.5 mmol) and 1-methylimidazole (0.12 g, 1.5 mmol) was kept neat at 160 °C for 24 h. After cooling, the solid formed was washed with Et₂O and dried under vacuum. Yield: 0.28 g (55%). ¹H NMR (CDCl₃, 400 MHz, 298K): δ 11.75 (s, 1H, NCHN), 8.49 (d, ³J_{HH} = 8.0 Hz, 1H, H_{py}), 8.31 (s, 1H, H_{imi}), 8.14 (t, ³J_{HH} = 8.0 Hz, 1H, H⁴_{py}), 7.70 (s, 1H, H_{imi}), 7.40 (d, ³J_{HH} = 8.0 Hz, 1H, H_{py}), 7.31–7.23 (m, 1H, H⁴_{Ar}), 7.15 (d, ³J_{HH} = 7.7 Hz, 2H, H^{3,5}_{Ar}), 4.30 (s, 3H, N–CH₃), 2.06

(s, 6H, Ar-CH₃). ¹³C{¹H} NMR (CDCl₃, 100 MHz, 298K): δ 159.8, 145.7, 140.9 (3 × C_{py}), 138.4 (C_{Ar}), 135.9 (NCN), 135.7, 128.7, 127.8 (3 × C_{Ar}), 126.1 (C_{py}), 123.9, 118.9 (2 × C_{imi}), 112.9 (C_{py}), 37.3 (N-CH₃), 20.5 (Ar-CH₃). Exact mass calcd for C₁₇H₁₈N₃ [M-Br]⁺ 264.1501; Found: 264.1496. Anal. calcd for C₁₇H₁₈BrN₃ (344.25) × H₂O: C 56.36, H 5.56, N 11.60; Found: C 56.60, H 4.91, N 11.53.

Complex 2. The imidazolium salt **1** (0.060 g, 0.17 mmol) was refluxed with Ag₂CO₃ (0.036 g, 0.13 mmol) in CH₂Cl₂ (5 ml) for 15 h and then filtered through a short pad of Celite. From this solution of the carbene silver complex, an aliquot was evaporated to dryness for spectroscopic characterization [¹H NMR (CDCl₃, 400 MHz, 298K): δ 8.15 (d, ³J_{HH} = 7.9 Hz, 1H, H_{py}), 7.98 (t, ³J_{HH} = 7.9 Hz, 1H, H⁴_{py}), 7.89 (d, ³J_{HH} = 1.9 Hz, 1H, H_{imi}), 7.30 (d, ³J_{HH} = 7.9 Hz, 1H, H_{py}), 7.25–7.17 (m, 1H, H⁴_{Ar}), 7.14–7.06 (m, 3H, H^{3,5}_{Ar} + H_{imi}), 3.96 (s, 3H, N-CH₃), 2.06 (s, 6H, Ar-CH₃).] Separately, AgBF₄ (0.039 g, 0.20 mmol) was added to a solution of [PdCl(Me)(cod)] (0.046 g, 0.17 mmol) in MeCN (2 ml). After stirring for 15 h, the mixture was filtered over Celite. The solution of carbene silver complex was added dropwise to this filtrate and the reaction mixture was stirred at room temperature for 4 h under exclusion of light. After filtration through Celite, all volatiles were removed under reduced pressure. The resulting brown oil was dissolved in CH₂Cl₂ (5 ml) and the solution was stirred over activated carbon for 30 min. and filtered again through Celite. The filtrate was concentrated in vacuo and the residue was recrystallized from MeCN/Et₂O to give an off-white solid (0.016 g, 18%). X-ray quality crystals were grown by layering a MeCN solution of **2** with Et₂O. ¹H NMR (CD₃CN, 400 MHz, 298K): δ 8.20 (t, ³J_{HH} = 8.0 Hz, 1H, H⁴_{py}), 7.86 (d, ³J_{HH} = 2.3 Hz, 1H, H_{imi}), 7.76 (dd, ³J_{HH} = 8.0 Hz, ⁴J_{HH} = 1.0 Hz, 1H, H_{py}), 7.34 (dd, ³J_{HH} = 8.0 Hz, ⁴J_{HH} = 1.0 Hz, 1H, H_{py}), 7.33–7.27 (m, 1H, H⁴_{Ar}), 7.26 (d, ³J_{HH} = 2.3 Hz, 1H, H_{imi}), 7.21 (d, ³J_{HH} = 8.0 Hz, 2H, H^{3,5}_{Ar}), 3.81 (s, 3H, N-CH₃), 2.15 (s, 6H, Ar-CH₃), 0.88 (s, 3H, Pd-CH₃). ¹³C{¹H} NMR (CDCl₃, 100 MHz, 298K): δ 166.8 (C_{carbene}-Pd), 160.5, 151.5, 143.0 (3 × C_{py}), 139.4, 137.4, 130.9, 128.6 (4 × C_{Ar}), 127.6 (C_{imi}), 126.6 (C_{py}), 117.8 (C_{imi}), 111.5 (C_{py}), 39.0 (N-CH₃), 20.6 (Ar-CH₃), -7.8 (Pd-CH₃). MS (ES): *m/z* 425 [M-BF₄]⁺. Anal. calcd for C₂₀H₂₃BF₄N₄Pd (512.65): C 46.86, H 4.52, N 10.93; Found: C 45.68, H 4.33, N 10.93.

Analytical data of compound 3. ¹H NMR (DMSO-*d*₆, 400 MHz, 298K): δ 8.30 (t, ³J_{HH} = 7.9 Hz, 1H, H⁴_{py}), 8.11 (d, ³J_{HH} = 2.2 Hz, 1H, H_{imi}), 7.86 (d, ³J_{HH} = 2.2 Hz, H_{imi}), 7.79 (dd, ³J_{HH} = 7.9 Hz, ⁴J_{HH} = 0.6 Hz, 1H, H_{py}), 7.65 (dd, ³J_{HH} = 7.9 Hz, ⁴J_{HH} = 0.6 Hz, 1H, H_{py}), 7.30–7.22 (m, 1H, H⁴_{Ar}), 7.16 (d, ³J_{HH} = 7.6 Hz, 2H, H^{3,5}_{Ar}), 3.86 (s, 3H, N-CH₃), 2.70 (s, 3H, im-CH₃),

2.02 (s, 6H, Ar-CH₃). ¹³C{¹H} NMR (DMSO-*d*₆, 100 MHz, 298K): δ 159.1, 147.2 (2 × C_{py}), 145.1 (NCN), 140.9 (C_{py}), 138.6, 135.2, 128.4, 127.5 (4 × C_{Ar}), 126.3 (C_{py}), 123.0, 118.9 (2 × C_{imi}), 117.8 (C_{py}), 35.1 (N-CH₃), 19.9 (Ar-CH₃), 11.1 (im-CH₃). Exact mass calcd for C₁₈H₂₀N₃ [M-X]⁺: 278.1657. Found: 278.1659.

2. Catalytic experiments

Time-dependent monitoring of the conversion of ethylene in the presence of complex 2.

In a typical experiment, complex 2 (3.6 mg, 7.0 μmol) was dissolved in CD₂Cl₂ (0.7 mL) and the solution was saturated with ethylene for 10 min at room temperature. A ¹H NMR spectrum was recorded every 30 min for 5 h (Fig. S1).

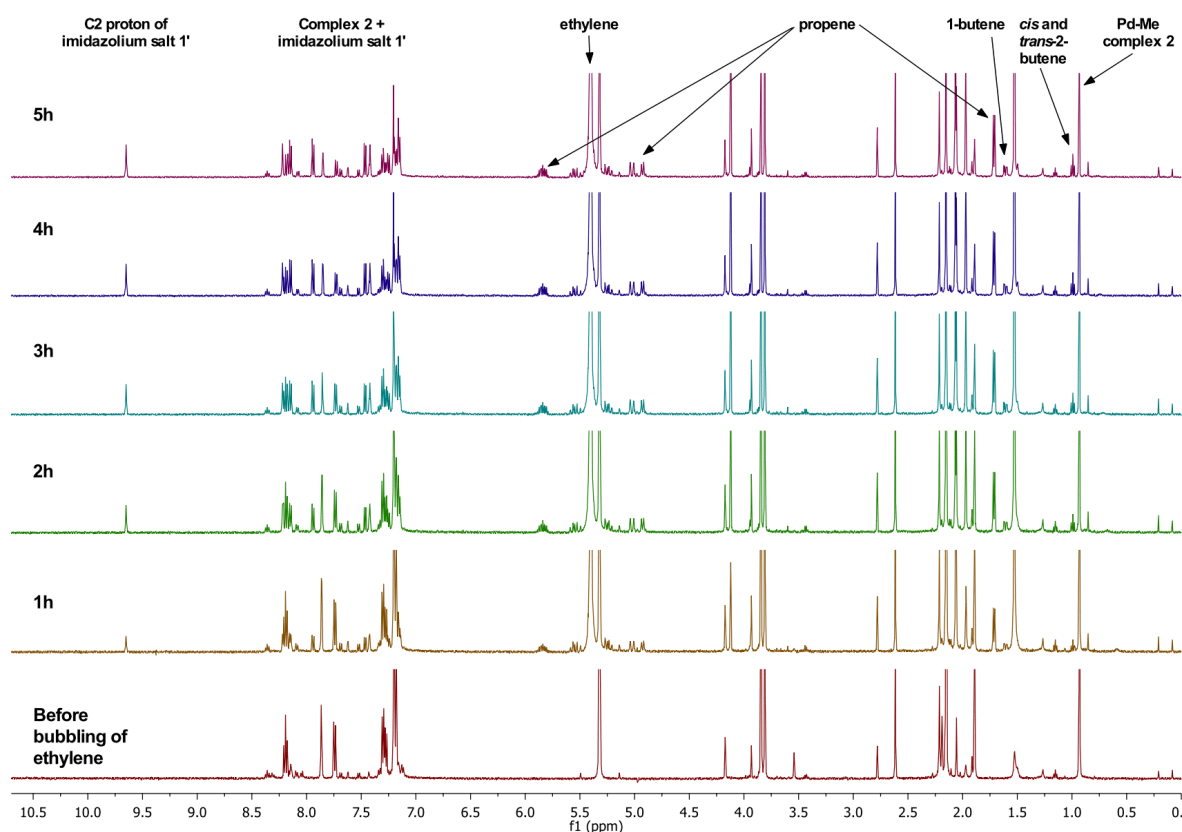


Fig. S1 Stacked ¹H NMR spectra depicting the increasing concentration of alkenes from the reaction of complex 2 with ethylene upon time. Note that the chemical shifts of the resonances attributed to the imidazolium salt are slightly different from those reported for 1 because of the different anions (Br⁻ in 1, presumably BF₄⁻ in 1' from reductive elimination) and the different solvents. The methyl group of 1-butene could not be reliably integrated due to partial overlap with the signal of residual H₂O.

High pressure polymerization reaction. The experiment was carried out in a Büchi “tinyclave steel” reactor equipped with an interchangeable 25 mL glass vessel. The reactor was loaded with complex **2** (11 mg, 21 μ mol) in CH₂Br₂ (21 mL), pressurized with ethylene (2.5 bar), and stirred at 35 °C. After 24 h, the reactor was vented and cooled to room temperature. The reaction mixture was filtered over Celite to remove palladium black and volatiles were removed under reduced pressure. The residual oil was analyzed by GC-MS and NMR spectroscopy.

3. Crystallographic details

Crystal structure determination. Crystal data for **2** were collected using an Oxford Diffraction SuperNova A diffractometer fitted with an Atlas detector (Mo–K α radiation, 0.71073 Å). A complete dataset was collected, assuming that the Friedel pairs are not equivalent. An analytical absorption correction based on the shape of the crystal was performed.^{S3} The structure was solved by direct methods using SHELXS-97 and refined by full matrix least-squares on F² for all data using SHELXL-97.^{S4} The hydrogen atoms were included in calculated positions and treated as riding atoms using SHELXL-97 default parameters. All non-hydrogen atoms were refined anisotropically. Crystal data and details of refinements are compiled in Table S1. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Centre as supplementary publication no. CCDC 872297. 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].

Table S1. Crystallographic data for complex **2**

CCDC no	872297
crystal size /mm ⁻¹	0.238 × 0.213 × 0.183
Empirical formula	C ₂₀ H ₂₃ BF ₄ N ₄ Pd
Fw	512.63
T /K	100(2)
crystal system	Monoclinic
space group	P2 ₁ /c (#14)
unit cell	
a /Å	6.98977(7)
b /Å	20.8653(2)
c /Å	14.1374(1)
α /°	90
β /°	92.862(1)
γ /°	90
Volume /Å ³	2059.28(3)
Z	4
D _{calcd} /g cm ⁻³	1.653
μ /mm ⁻¹	0.951
no. total reflcns	46383
unique reflcns	5371
R _{int}	0.0307
Absorption correction	analytical
transmission range	0.847-0.891
no. parameters, restraints	277, 0
GOF	1.074
R ₁ , ^a wR ₂ , ^b I > 2σ(I)	0.0209, 0.0484
R ₁ , ^a wR ₂ , ^b all data	0.0255, 0.0509
largest diff. hole, peak /e Å ⁻³	-0.577 0.406

$$^a R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}; \quad ^b wR_2 = \frac{[\sum w(F_o^2 - F_c^2)^2 / \sum (w(F_o^4))]}{1/2}$$

4. References

- S1 N. M. Scott, T. Schareina, O. Tok and R. Kempe, *Eur. J. Inorg. Chem.*, 2004, 3297.
- S2 R. E. Rulke, J. M. Ernsting, A. L. Spek, C. J. Elsevier, P. W. N. M. van Leeuwen and K. Vrieze, *Inorg. Chem.*, 1993, **32**, 5769.
- S3 Program CrysAlisPro Version 1.171.34.49, Agilent Technologies, 2011. Analytical numeric absorption correction using a multifaceted crystal model was based on expressions derived by Clark and Reid: R. C. Clark and J. S. Reid, *Acta Cryst.*, 1995, **A51**, 887.
- S4 G. M. Sheldrick, *Acta Cryst.*, 2008, **A64**, 112.