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Supporting Information

Palladium complexes with 3-phenylpropylamine ligand: synthesis, structures, theoretical studies and application in the aerobic oxidation of alcohols as heterogeneous catalysts

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General information

All reactants were purchased from Merck Chemical Company and Aldrich and used as received. Solvents were used without further purification or drying.

Fourier transform infrared (FTIR) spectra were measured in KBr pellets with a Jasco FT/IR 680 plus instrument. NMR spectra were obtained on a Bruker spectrometer at 400.13 MHz (^{1}H). Elemental analysis was performed on LECO, CHNS-932 apparatus. Molar conductance of the complexes was measured in acetone at 1×10^{-3} M using an Elmetron CC-505 conductivity meter.

Synthesis of *trans*-[Pd($C_6H_5(CH_2)_3NH_2)_2(OAc)_2$] (1)

$Pd(OAc)_2$ (0.0448 g, 0.2 mmol) was added to a solution of 3-phenylprophylamine (28 μL, 0.2 mmol) in toluene (10 mL) and the resulting mixture was heated under reflux for 24 h. The solvent was then evaporated and the resulting yellow solid residue was dissolved in n-hexane (10 mL) and CH_2Cl_2 (2 mL). A pale yellow solid immediately precipitated. The mixture was stirred for 2 h at room temperature and the resulting suspension was filtered. The pale yellow solid thus obtained and air dried to give (**1**).

Complex **1**: yellow solid, Yield: (0.06533 g, 66%); m.p. 135 °C.

Anal. calcd for $C_{22}H_{32}N_2O_4Pd$: C,53.39; H, 6.52; N, 5.66. Found: C, 53.26; H, 6.65; N, 5.73.

IR: ν_{max}/cm^{-1} 1573 and 1388 (CO), 3218 and 3118 (NH_2).

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm): 1.85 (s, 3H, $MeCO_2$), 2.04 (m, 2H, H_2), 2.53 (m, 2H, H_1), 2.60 (t, $^3J_{HH}$ = 7.6 Hz, 2H, H_3), 3.77 (m, 2H, NH_2), 7.17-7.30 (m, 5H, C_6H_5). ^{13}C{^{1}H} NMR ($CDCl_3$, 25 °C, TMS): δ (ppm): 23.51 (Me), 32.50 (C_2), 32.90 (C_3), 43.23 (C_1), 126.15-140.85 ($C_{aromatic}$), 180.18 (CO).

Synthesis of *trans*-[Pd($C_6H_5(CH_2)_3NH_2)_2(Cl)_2$] (2)

To a suspension of **2** in methanol was added excess NaCl and the resulting mixture stirred for 12 h at room temperature. The solvent was then evaporated and the resulting yellow solid residue was dissolved in n-hexane (10 mL) and CH_2Cl_2 (2 mL). The mixture was stirred for 2 h at room temperature and the resulting suspension was filtered. The pale yellow solid thus obtained and air dried to give (**2**).

Complex **2**: yellow solid, Yield: (0.04656 g, 52%); m.p. 170 °C.

Anal. calcd for $C_{18}H_{26}Cl_2N_2Pd$: C, 48.29; H, 5.85; N, 6.26. Found: C, 47.79; H, 5.92; N, 6.16.

IR: ν_{max}/cm^{-1} 3223 and 3270 (NH_2).

^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm): 2.03 (m, 2H, H_2), 2.67 (m, 2H, H_1), 2.69 (m, 2H, H_3), 2.78 (m, 2H, NH_2), 7.17-7.31 (m, 5H, C_6H_5). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C, TMS): δ (ppm): 32.85 (C_2), 33.10 (C_3), 44.87 (C_1), 126.22-140.65 ($C_{aromatic}$).

Synthesis of *trans*-[Pd($C_6H_5(CH_2)_3NH_2)_2$ ($PPh_3)_2$]$2Cl^-$ (3)

To a suspension of palladium complex **2** (0.275 g, 0.5 mmol) in dichloromethane (15 mL) was added PPh_3 (0.262 g, 1 mmol). The resulting solution was stirred for 6 h and then filtered through a plug of $MgSO_4$. The filtrate was concentrated to ca. 2 mL, and n-hexane (10 mL) was added to the precipitate **3** as a pale yellow solid, which was collected and air-dried.

Complex **3**: yellow solid, Yield: (0.05047 g, 56%); m.p. 171 °C (dec.). Δ_M (Ω^{-1} cm^2 mol^{-1})/110.

IR: ν_{max}/cm^{-1} 3395 and 3451 (NH_2). ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm): 1.28 (m, 2H, H_2), 2.09 (m, 2H, H_1), 2.75 (t, $^3J_{HH}$ = 7.2 Hz, 2H, H_3), 3.06 (m, 2H, NH_2), 7.28-7.75 (m, C_6H_5). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 25 °C): δ (ppm): 23.26 (s, 1P, PPh_3 (complex 3)), 17.85 (s, 1P, PPh_3 ($Pd(PPh_3)_4$).

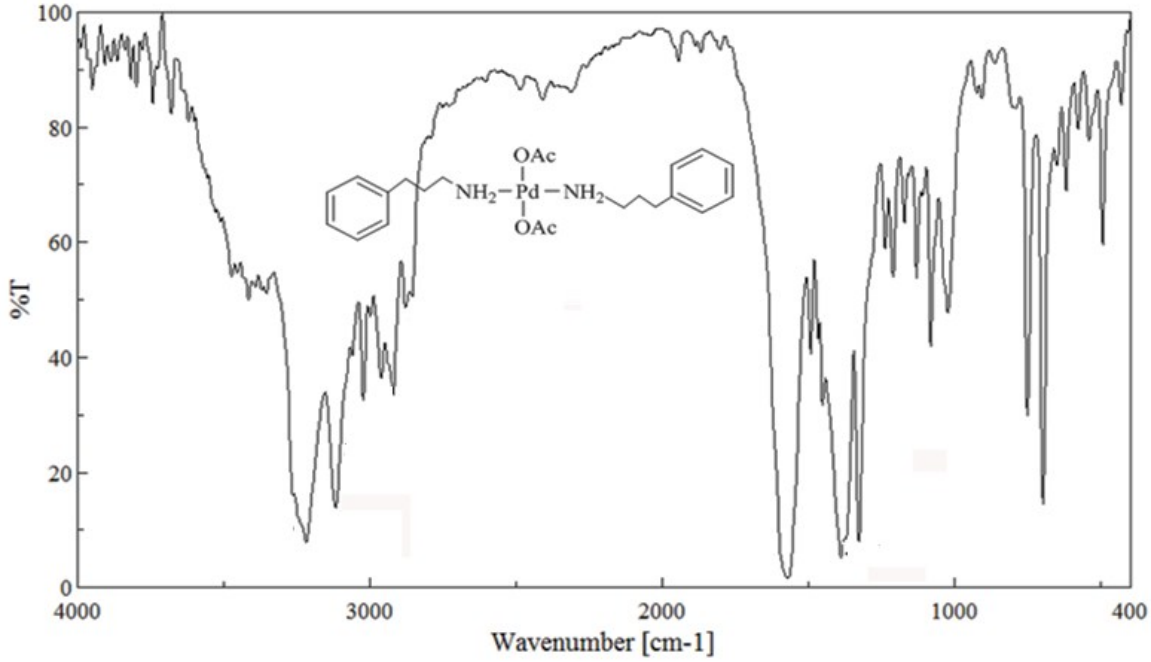

Fig. S1 FTIR spectrum of palladium complex **1** (*trans*-[Pd($C_6H_5(CH_2)_3NH_2)_2(OAc)_2$]).

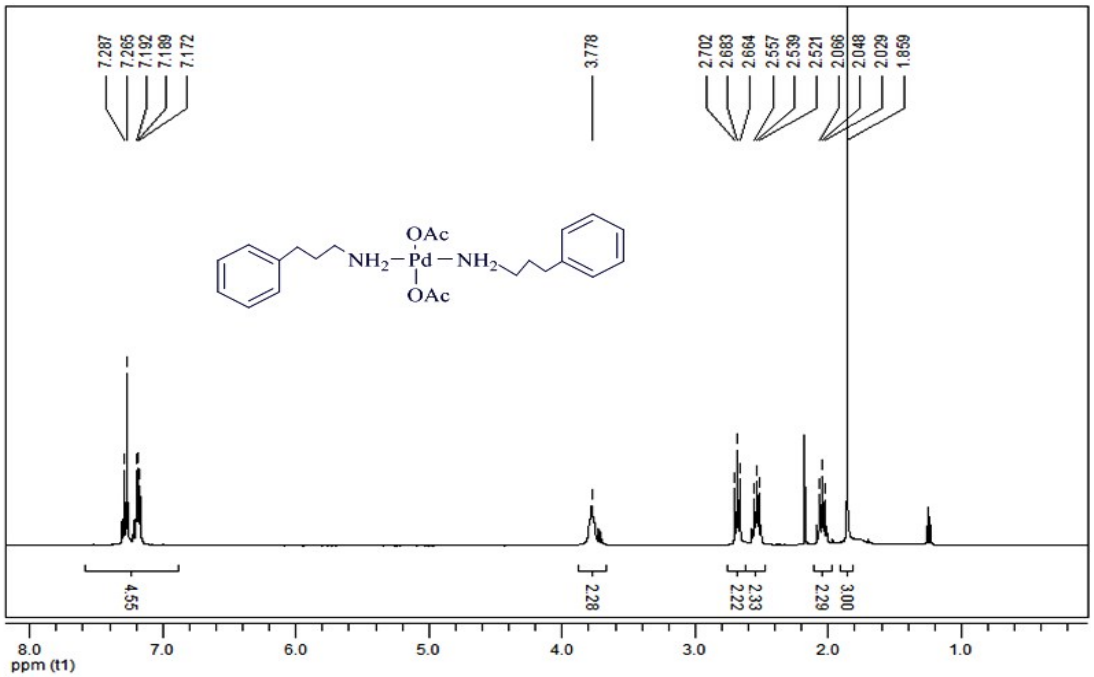

Fig. S2 ^{1}H NMR spectrum of palladium complex **1** (*trans*-[Pd($C_6H_5(CH_2)_3NH_2)_2(OAc)_2$]).

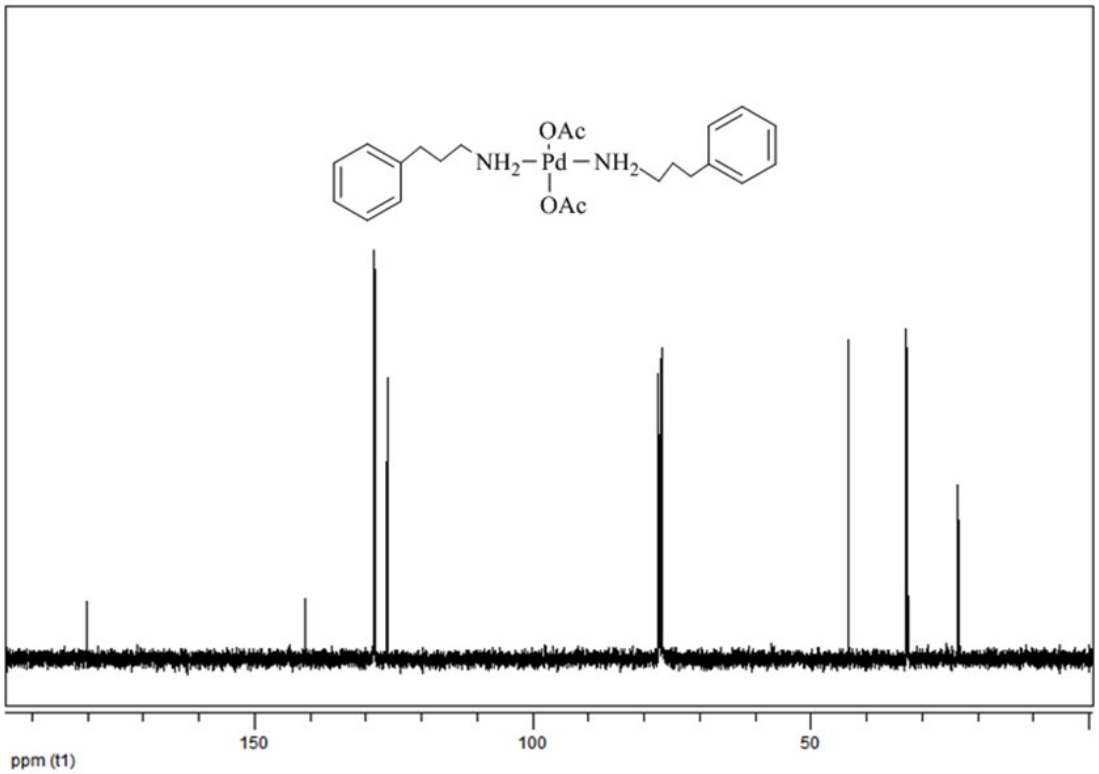

Fig. S3 $^{13}C\{^{1}H\}$ NMR spectrum of palladium complex **1** (*trans*-$[Pd(C_6H_5(CH_2)_3NH_2)_2(OAc)_2]$).

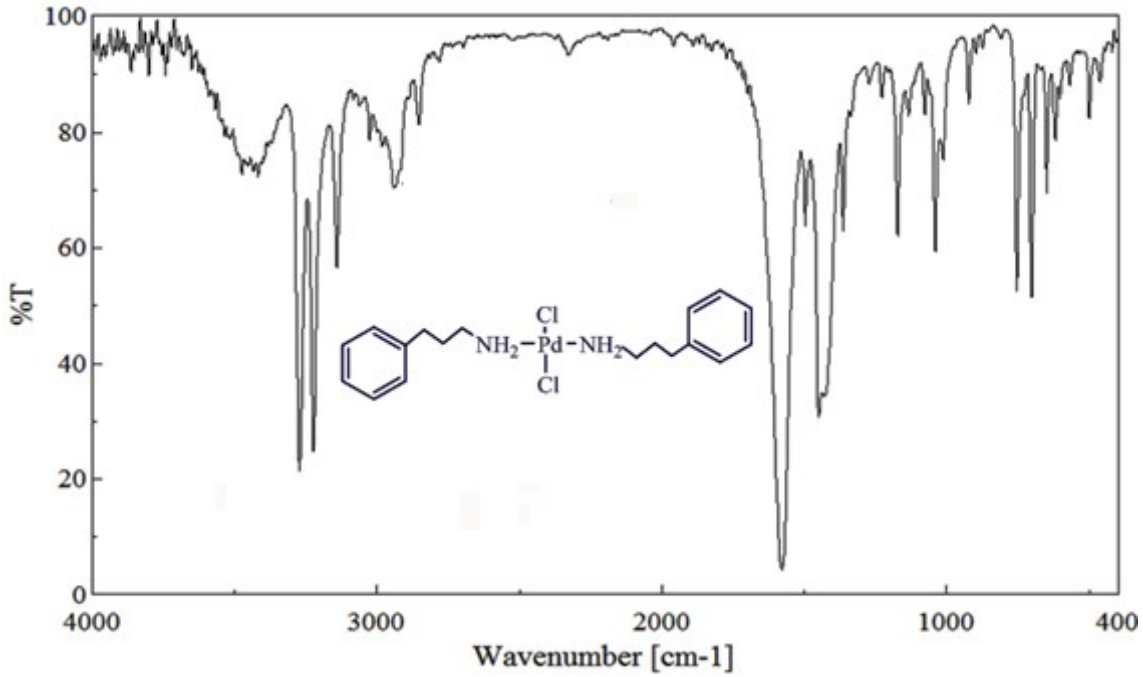

Fig. S4 FTIR spectrum of palladium complex **2** (*trans*-$[Pd(C_6H_5(CH_2)_3NH_2)_2(Cl)_2]$).

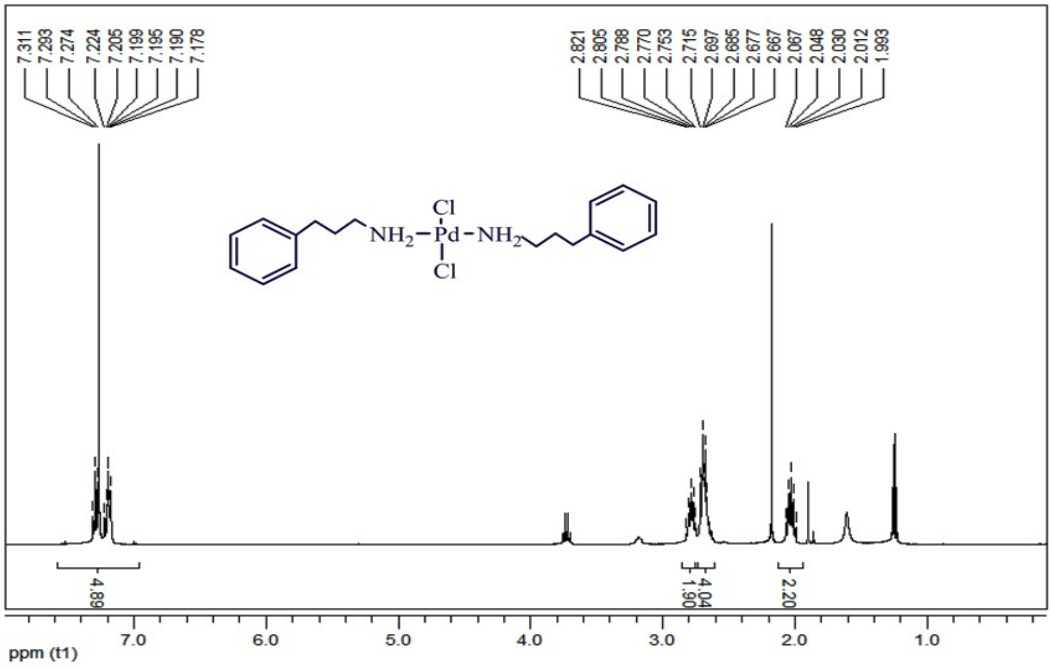

Fig. S5 ^{1}H NMR spectrum of palladium complex **2** (*trans*-[Pd($C_6H_5(CH_2)_3NH_2)_2(Cl)_2$]).

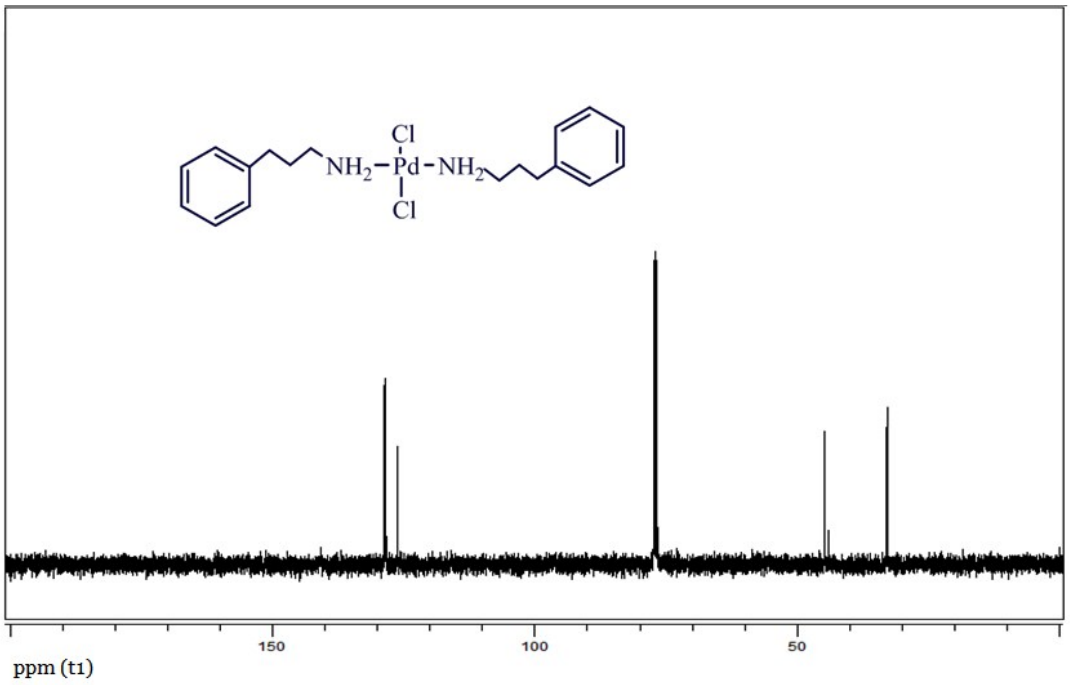

Fig. S6 $^{13}C\{^{1}H\}$ NMR spectrum of palladium complex **2** (*trans*-[Pd($C_6H_5(CH_2)_3NH_2)_2(Cl)_2$]).

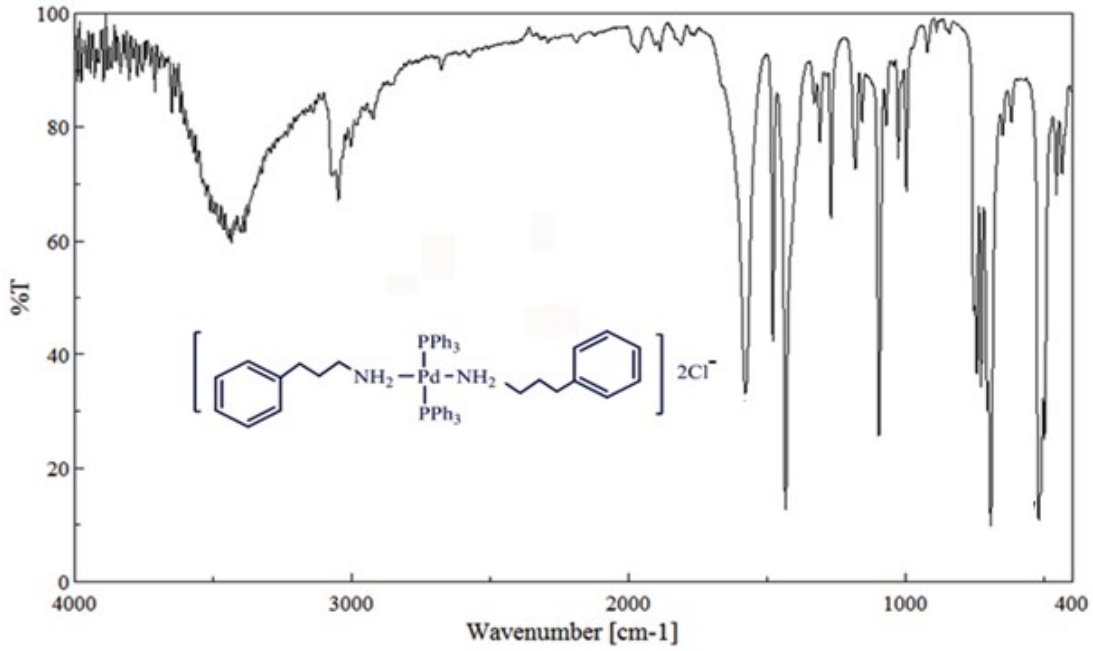

Fig. S7 FTIR spectrum of palladium complex **3** (*trans*-[Pd($C_6H_5(CH_2)_3NH_2)_2$ ($PPh_3)_2$]$2Cl^-$).

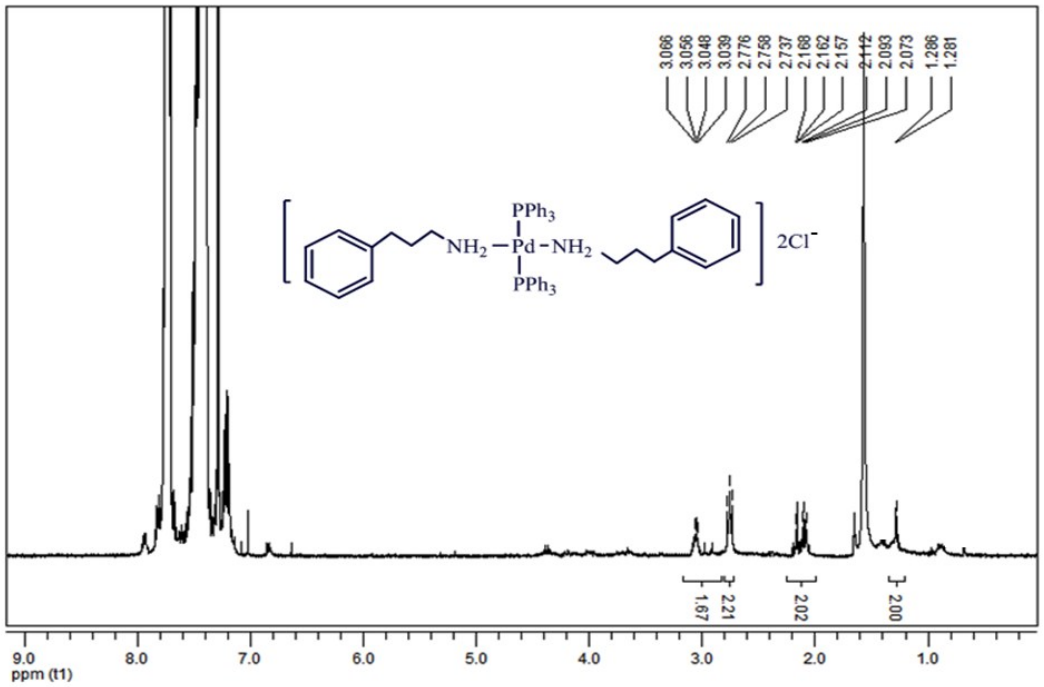

Fig. S8 ^1H NMR spectrum of palladium complex **3** (*trans*-[Pd($C_6H_5(CH_2)_3NH_2)_2$ ($PPh_3)_2$]$2Cl^-$).

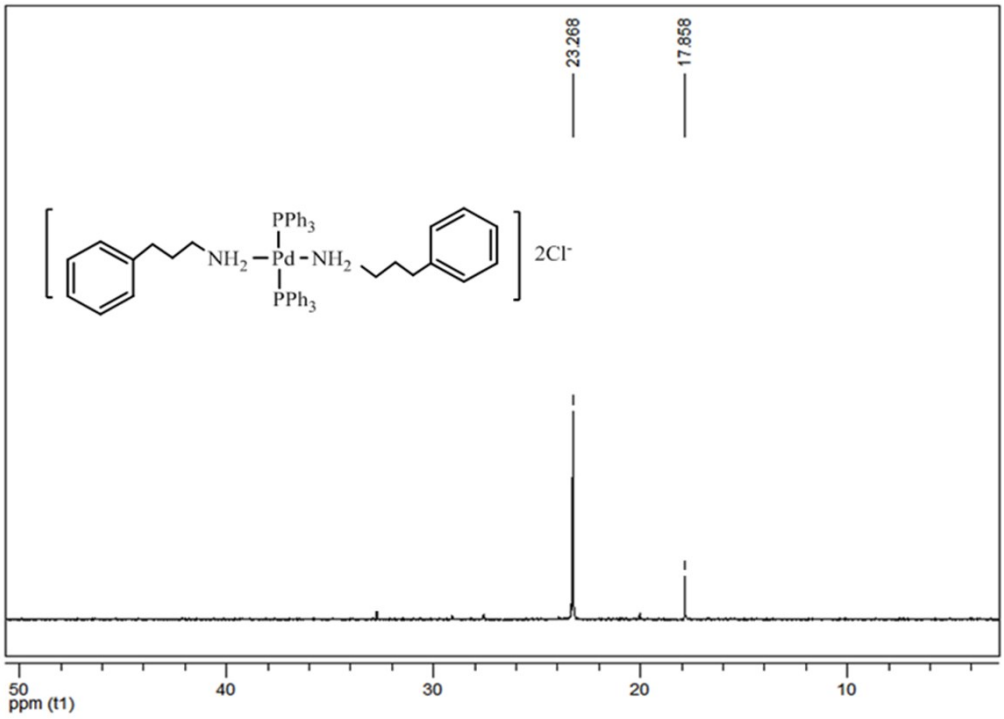

Fig. S9 $^{31}P\{^{1}H\}$ NMR spectrum of palladium complex **3** (*trans*-$[Pd(C_6H_5(CH_2)_3NH_2)_2\ (PPh_3)_2]2Cl^-$).

Table S1
Crystal data and structure refinements of complexes (**1** and **2**)

Chemical formula	$C_{22}H_{32}N_2O_4Pd$(**1**)	$C_{18}H_{26}Cl_2N_2Pd$(**2**)
Formula Mass	494.90	447.7
Crystal system	Orthorhombic	Orthorhombic
a/Å	10.6350(14)	9.0679 (3)
b/Å	6.8380(7)	8.3144 (3)
c/Å	33.586(4)	26.1253 (11)
α/°	90.00	90.00
β/°	90.00	90.00
γ/°	90.00	90.00
Unit cell volume/Å^3	2442.4(5)	1969.69 (13)
Temperature/K	100(1)	120(1)
Space group	*Pna*2$_1$	*Pbca*
No. of formula units per unit cell, *Z*	4	4
No. of reflections measured	6448	11756
No. of independent reflections	2567	1742
R_{int}	0.073	0.023
Final *R1* values ($I>2\sigma(I)$)	0.058	0.019
Final $wR(F^2)$ values ($I>2\sigma$(I))	0.107	0.029
CCDC	1060354	1060510

Table S2

Selected bond lengths (Å) and bond angles (°) for complex **1**

Bond lengths	
Pd1-N1	2.057(12)
Pd1-N2	2.059(14)
Pd1-O1	2.019(9)
Pd1-O3	2.019(10)
Bond angles	
O1-Pd1-N1	85.3(5)
O3-Pd1-N1	94.3(5)
O3-Pd1-N2	85.0(5)
O1-Pd1-N2	95.4(5)
O1-Pd1-O3	179.4(5)
N1-Pd1-N2	179.3(8)

Table S3

Selected bond lengths (Å) and bond angles (°) for complex **2**

Bond lengths	**2**
Pd1-N1	2.0361(15)
Pd1-N1^{i}	2.0361(15)
Pd1-Cl1	2.3031(5)
Pd1-Cl1^{i}	2.3031(5)
Bond angles	
N1-Pd1-Cl1	88.12(4)
N1^{i}-Pd1-Cl1	91.88(4)
N1-Pd1-Cl1^{i}	91.88(4)
N1^{i}-Pd1-Cl1^{i}	88.12(4)
Cl1-Pd1-Cl1^{i}	180.0(5)
N1-Pd1-N1^{i}	180.0(5)

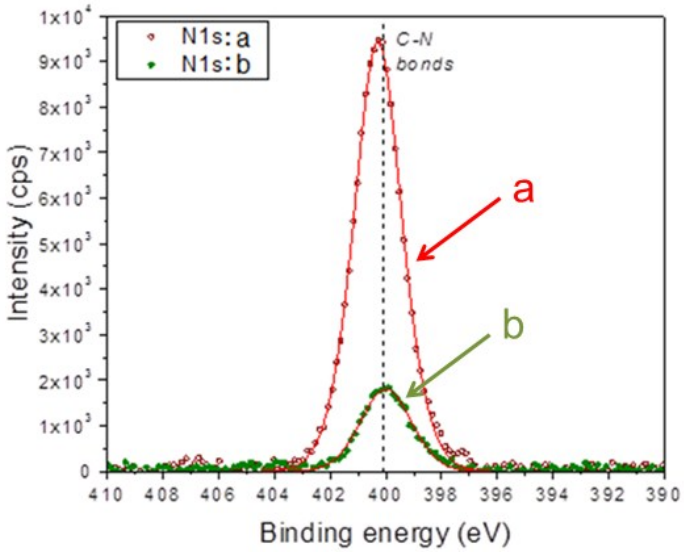

Fig. S10 HR-XPS N1s spectra of (a) fresh CB[6]-Pd NPs (**3**) and (b) CB[6]-Pd NPs (**3**) after fifth runs.