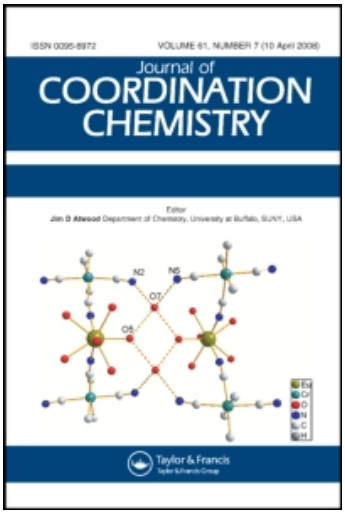

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Synthesis and characterization of cyclopalladated complexes of benzylamine by IR and NMR spectroscopy studies

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Synthesis and characterization of cyclopalladated complexes of benzylamine by IR and NMR spectroscopy studies†

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The chloro-bridged dimer $[Pd(\mu\text{-}Cl)(C_6H_4CH_2NH_2\text{-}\kappa^2\text{-}C,N)]_2$ reacts with PPh_2Et, P(p-tolyl)$_3$, $AsPh_3$, piper (piper = $C_5H_{10}N$) and Py in dichloromethane at room temperature for 24 h in a one-to-two molar ratio and undergoing bridge-splitting reactions to give $[PdCl(C_6H_4CH_2NH_2\text{–}\kappa^2\text{-}C,N)L]$ (L = PPh_2Et (**1a**), P(p-tolyl)$_3$ (**1b**), $AsPh_3$ (**1c**), piper (**1d**), $C_6H_4CH_2NH_2$ (**3e**) and Py (**1f**)). Complex **1f** in THF at room temperature reacts with a stoichiometric amount of TlTfO (thallium triflate, TfO=CF_3SO_3) and Py (molar ratio 1 : 1 : 1) to afford $[Pd(C_6H_4CH_2NH_2)(Py)_2]TfO$ (**2**). Infrared and NMR spectroscopies allow unambiguous characterization of these products.

Keywords: Cyclopalladation; Palladium complexes; Benzyl amine complexes

1. Introduction

The ortho-palladation of aliphatic and benzyl amine derivatives [1a] was initially reported by Cope and Friedrich. Preparation of cyclopalladated complexes has attracted considerable attention [1] due to their potential application in organic synthesis [2], homogenous catalysis [3] and photochemistry [4]; cyclopalladated compounds have found many applications in diverse areas of chemistry [5, 6]. In this article we report reactivity of $[Pd(\mu\text{-}Cl)(C_6H_4CH_2NH_2\text{-}\kappa^2\text{-}C,N)]_2$, giving mono palladium(II) derivatives including $[Pd(C_6H_4CH_2NH_2\text{-}\kappa^2\text{-}C,N)Cl(L)]$ (L = PPh_2Et (**1a**), P(p-tolyl)$_3$ (**1b**), $AsPh_3$ (**1c**), piper (**1d**), $C_6H_4CH_2NH_2$ (**3e**), Py (**1f**)) and $[Pd(C_6H_4CH_2NH_2)(Py)_2]TfO$ (**2**). This article also presents reactivity of $[Pd(C_6H_4CH_2NH_2\text{-}\kappa^2\text{-}C,N)Py(THF)]^+$ toward Py, which gives cationic complex **2**.

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2. Experimental

Infrared spectra were recorded on Perkin-Elmer 1430 and 16F-PC-FT spectrometers in the range 4000–20 cm^{-1} using Nujol mulls between polyethylene sheets. C, H and N analyses were carried out with a Perkin-Elmer 240C microanalyzer. Conductance measurements were carried out in ca 10^{-4} mol dm^{-3} solution with a Philips 9501 conductometer and Λ_M is given in Ω^{-1} cm^2 mol^{-1}. Melting point determinations were carried out on a Reichert apparatus and are uncorrected.

Unless otherwise stated, NMR spectra were recorded in $CDCl_3$ and CD_3COCD_3 with Varian Unity 300 and Bruker AC-400 spectrometers. Chemical shifts are referenced to TMS (^1H and ^{13}C-{^1H}) or H_3PO_4 (^{31}P-{^1H}). Reactions were carried out at room temperature without special precautions against moisture. The molar conductivities of all complexes in acetone are between 0–1 Ω^{-1} cm^2 mol^{-1}, in agreement with their nonelectrolytic nature, except for **2** whose molar conductivity is 114 Ω^{-1} cm^2 mol^{-1} in agreement with its electrolytic nature. Triphenylphosphine, tri(p-tolyl)phosphine, diphenylethylphosphine, triphenylarsine, pyridine, piperidine (Merck and Aldrich) and palladium acetate (Merck) were used as received.

2.1. *Synthesis of the mononuclear cyclopalladated complexes 1a–f*

To a suspension of $[Pd(\mu\text{-}Cl)(C_6H_4CH_2NH_2\text{-}\kappa^2\text{-}C,N)]_2$ (270.5 mg, 0.545 mmol) in dichloromethane (15 cm^3) at room temperature was added L (1.090 mmol). The resulting suspension gave a clear solution immediately. After stirring overnight at room temperature, the solvent was completely removed; CH_2Cl_2 (2 mL) and *n*-hexane (15 mL) or Et_2O (7 mL) was added giving **1a**–**f** as white precipitate, which was filtered off and air dried.

2.1.1. [Pd($C_6H_4CH_2NH_2$-κ^2-C,N)Cl(PPh_2Et)] (1a). ^1H NMR (300 MHz, $CDCl_3$, RT), δ(ppm): 7.86–7.80 (m, 4H, o, $2C_6H_5$), 7.41–7.26 (m, 6H, m: p, $2C_6H_5$), 6.95 (d, 1H, C_6H_4, $^3J_{H-H} = 7.2$ Hz), 6.82 (m, 1H, C_6H_4), 6.47 (t, 2H, C_6H_4, $^3J_{H-H} = 6.9$ Hz), 4.25 (br s, 2H, NH_2), 3.81 (br s, 2H, CH_2), 2.53 (qd, 2H, CH_2, $^2J_{P-H} = 18$ Hz, $^3J_{H-H} = 7.2$ Hz), 1.14 (td, 3H, CH_2, $^2J_{P-H} = 21.6$ Hz, $^3J_{H-H} = 7.2$ Hz); ^{31}P NMR (300 MHz, $CDCl_3$, RT): 36.85 ppm; IR (KBr, cm^{-1}): ν(N–H) = 3218–3144; ν(Pd–Cl) = 288 cm^{-1}; ν(Pd–PPh_2Et) = 1109 cm^{-1}; m.p.: 181°C; Color: white; Yield: 417 mg, 0.98 mmol, 89.9%; Λ_M: 1 Ω^{-1} cm^2 mol^{-1}. Anal. Calcd for $C_{21}H_{23}ClNPPd$ (%): C, 54.56; H, 5.02; N, 3.03. Found: C, 54.54; H, 4.98; N, 3.10.

2.1.2. [Pd($C_6H_4CH_2NH_2$-κ^2-C,N)Cl(P(p-tolyl)$_3$)] (1b). ^1H NMR (300 MHz, $CDCl_3$, and RT): δ(ppm): 7.56 (d, 6H, $3C_6H_5$, $^3J_{H-H} = 8.1$ Hz), 7.12 (d, 6H, 3 C_6H_4, $^3J_{H-H} = 6.9$ Hz), 6.96 (d, 1H, C_6H_4, $^3J_{H-H} = 7.2$ Hz), 6.83 (m, 1H, C_6H_4), 6.41 (m, 2H, C_6H_4), 4.27 (br s, 2H, NH_2), 3.91 (br, 2H, CH_2N), 2.33 (s, 9H, 3 CH_3). ^{31}P NMR (300 MHz, $CDCl_3$, RT): δ(ppm): 40.30; IR (cm^{-1}): ν(N–H) = 3252–3198, ν(Pd–P(p-tolyl)$_3$) = 1094 cm^{-1}, ν(Pd–N) = 278 cm^{-1}, ν(Pd–Cl) = 232 cm^{-1}; m.p.: 189°C; Color: white; Yield: 436 mg, 0.79 mmol, 90.2%; Λ_M: 0.75 Ω^{-1} cm^2 mol^{-1}. Anal. Calcd for $C_{28}H_{29}Cl$ NPPd (%): C, 60.68; H, 5.29; N, 2.54. Found: C, 60.56; H, 5.25; N, 2.57.

2.1.3. [Pd($C_6H_4CH_2NH_2$-κ^2-C,N)Cl($AsPh_3$)] (1c). ^{1}H NMR (300 MHz, $CDCl_3$, RT): δ(ppm): 7.6–7.3 (m, 15H, $3C_6H_5$), 6.95 (d, 1H, C_6H_4, $^3J_{H-H} = 7.2$ Hz), 6.84 (t, 1H, C_6H_4, $^3J_{H-H} = 7.2$ Hz), 6.42 (m, 2H, C_6H_4), 4.31 (t, 2H, $^3J_{H-H} = 5.7$ Hz, NH_2), 4.14 (br, 2H, CH_2N); IR (cm^{-1}): ν(N–H) = 3252–3198, ν(Pd–N) = 287 cm^{-1}, ν(Pd–Cl) = 254 cm^{-1}; m.p.: 168°C; Color: white; Yield: 121 mg, 0.220 mmol, 88.3%; Λ_M: 1 Ω^{-1} cm^2 mol^{-1}. Anal. Calcd for $C_{25}H_{23}AsClNPd$ (%): C, 54.17; H, 4.18; N, 2.53. Found: C, 53.59; H, 4.02; N, 2.60.

2.1.4. [Pd($C_6H_4CH_2NH_2$-κ^2-C,N)Cl(piper)] (1d). ^{1}H NMR (300 MHz, $CDCl_3$, and RT): δ(ppm): 7.0 (m, 3H, C_6H_4), 6.68 (d, 1H, C_6H_4, $^3J_{H-H} = 5.7$ Hz), 4.09 (br s, 4H, $CH_2N + CH_2$ (piper)), 3.05 (br, 4H, $NH_2 + CH_2$ (piper)), 2.53 (br, 1H, NH (piper)), 1.8 (m, 1H, CH_2 (piper)), 1.59 (br, 1H, CH_2 (piper)), 1.55 (br, 1H, CH_2 (piper)), 1.36 (m, 3H, CH_2 (piper)); IR (cm^{-1}): ν(N–H) = 3336–33246, 3118–3188, ν(Pd–Cl) = 274 cm^{-1}, ν(Pd–N) = 316 cm^{-1}; m.p.: 185°C (dec); Color: white; Yield: 163.5 mg, 0.400 mmol, 85.5%; Λ_M: 0 Ω^{-1} cm^2 mol^{-1}. Anal. Calcd for $C_{12}H_{19}ClN_2Pd \cdot 1/4CH_2Cl_2$ (%): C, 41.50; H, 5.54; N, 7.90. Found: C, 41.32; H, 5.12; N, 7.94.

2.1.5. [Pd($C_6H_4CH_2NH_2$-κ^2-C,N)Cl(NH_2CH_2Ph)] (1e). ^{1}H NMR (400 MHz, $CDCl_3$, and RT): δ(ppm): 7.52–7.27 (m, 5H, C_6H_5), 6.97 (m, 1H, C_6H_4), 6.96 (d, 2H, C_6H_4, $^3J_{H-H} = 5.2$ Hz), 6.80 (t, 1H, C_6H_4, $^3J_{H-H} = 4$ Hz), 4.90 (brs, 2H, NH_2(a)), 4.07 (m, 2H, CH_2(a)), 3.99 (m, 2H, NH_2(b)), 3.83 (t, 2H, CH_2(b), $^3J_{H-H} = 6$ Hz); IR (cm^{-1}): ν(N–H) = 3268–3208, 3116–3052, ν(Pd–Cl) = 236 cm^{-1}, ν(Pd–N) = 264, 288 cm^{-1}; m.p.: 178°C (dec); Color: white; Yield: 404 mg, 0.95 mmol, 77.9%; Λ_M: 0.5 Ω^{-1} cm^2 mol^{-1}. Anal. Calcd for $C_{14}H_{17}ClN_2Pd$ (%): C, 48.72; H, 4.93; N, 8.11. Found: C, 48.51; H, 4.75; N, 8.42.

2.1.6. [Pd($C_6H_4CH_2NH_2$-κ^2-C,N)Cl(Py)] (1f). ^{1}H NMR (300 MHz, $CDCl_3$, and RT): δ(ppm): 8.49 (d, 2H, py, $^3J_{H-H} = 6$ Hz), 7.63 (t, 1H, py, $^3J_{H-H} = 6$ Hz), 7.04 (m, 4H, py + C_6H_4), 6.83 (t, 1H, C_6H_4, $^3J_{H-H} = 6$ Hz), 6.08 (d, 1H, C_6H_4, $^3J_{H-H} = 9$ Hz), 4.66 (brs, 2H, NH_2), 4.20 (t, 2H, CH_2, $^3J_{H-H} = 6$ Hz); IR (cm^{-1}): ν(N–H) = 3300–3200, ν(Pd–Cl) = 239 cm^{-1}, ν(Pd–N) = 295 cm^{-1}, ν(C=N py) = 1603 cm^{-1}; m.p.: 183 (dec); Color: white; Yield: 327 mg, 1 mmol, 85%; Λ_M: 0 Ω^{-1} cm^2 mol^{-1}. Anal. Calcd for $C_{12}H_{13}ClN_2Pd$ (%): C, 44.06; H, 4.01; N, 8.58. Found: C, 43.59; H, 3.75; N, 8.50.

2.2. *Synthesis of [Pd($C_6H_4CH_2NH_2$-κ^2-C,N)Cl (Py)$_2$]TfO* (2)

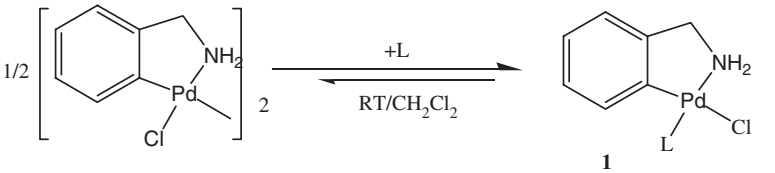
To a solution of **1f** (33.8 mg, 0.100 mmol) in THF (10 mL), TlTfO (35.5 mg, 0.100 mmol) was added. The resulting suspension was stirred for 1 h at room temperature and filtered through a plug of celite or $MgSO_4$. To the freshly obtained solution, cooled at 0°C, was added Py (8 μL, 100 mmol). After 1 h of stirring at 0°C crude complex **2** precipitated as a pale yellow solid. The solvent was completely removed and Et_2O (5 mL) was added giving a yellow powder, which was filtered off, air dried and washed with cooled Et_2O giving **2**. This complex was recrystallized from CH_2Cl_2 (2 mL) and *n*-hexane (10 mL) for elemental analysis and NMR measurements. This complex is soluble in CH_2Cl_2, $(CH_3)_2CO$, $CHCl_3$ and insoluble in Et_2O and *n*-hexane.

^{1}H NMR (300 MHz, acetone-d$_6$, RT): δ(ppm): 9.04 (d, 2H, Py, $^3J_{H-H} = 7.2$ Hz), 8.78 (q, 2H, Py, $^3J_{H-H} = 7.8$ Hz), 8.01 (tt, 1H, Py, $^3J_{H-H} = 7.8$ Hz, $^5J_{H-H} = 1.5$ Hz), 7.97 (tt, 1H, Py, $^3J_{H-H} = 7.8$ Hz, $^5J_{H-H} = 1.5$ Hz), 7.66 (dt, 2H, Py, $^3J_{H-H} = 7.2$ Hz, $^5J_{H-H} = 1.5$ Hz), 7.59 (dt, 2H, Py, $^3J_{H-H} = 7.2$ Hz, $^5J_{H-H} = 1.2$ Hz), 6.95 (q, 2H, C_6H_4, $^3J_{H-H} = 6.9$ Hz), 6.74 (t, 1H, C_6H_4, $^3J_{H-H} = 7.8$ Hz), 5.99 (dd, 1H, C_6H_4, $^3J_{H-H} = 7.8$ Hz, $^5J_{H-H} = 0.9$ Hz), 5.25 (br, 2H, NH_2), 4.28 (t, 2H, CH_2N, $^3J_{H-H} = 6$ Hz). IR (cm^{-1}): ν(N–H) = 3306–3244, ν(C=N py) = 1603, 1574 cm^{-1}, ν(Pd–N) = 279, 327 cm^{-1}; m.p.: 176°C; Color: yellow; Yield: 42 mg, 0.079 mmol, 79%; Λ_M: 114 Ω^{-1} cm^2 mol^{-1}. Anal. Calcd for $C_{18}H_{18}F_3N_3O_3PdS$ (%): C, 41.59; H, 3.49; N, 8.08; S, 6.17. Found: C, 41.20; H, 3.37; N, 8.12; S, 6.09.

3. Results and discussion

The chloro-bridged dimers undergo bridge-splitting reactions with piperidine, ethyldiphenylphosphine, tri(p-tolyl)phosphine, triphenylarsine, and benzyl amine affording the corresponding mononuclear cyclopalladated complexes **1a**–**f** (scheme 1).

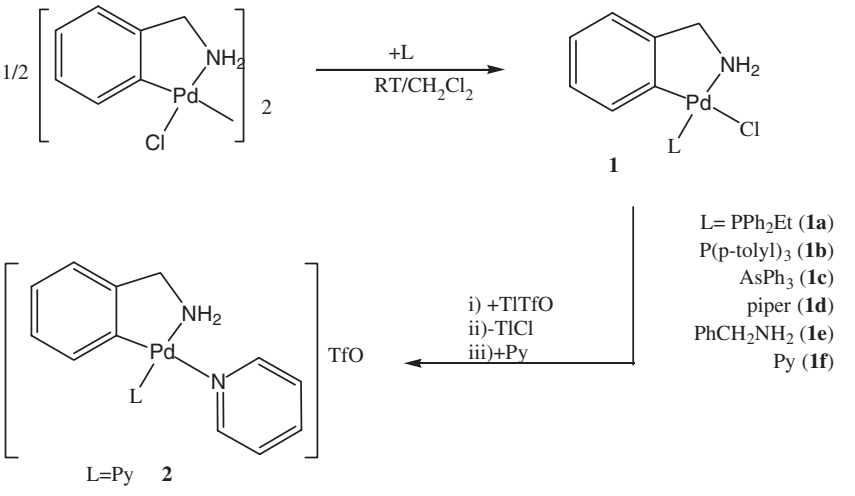
These complexes are stable in the solid state or in acetone or dichloromethane solution. Acetone solutions are conducting, but the molar conductivities of solution of **1a**–**f** are between 0–1 Ω^{-1} cm^2 mol^{-1} in agreement with nonelectrolytes. The molar conductivity of **2** is 114 Ω^{-1} cm^2 mol^{-1} corresponding to univalent electrolyte (100–135 Ω^{-1} cm^2 mol^{-1} [7]). The Pd–Cl–Pd bond is cleaved by PPh_2Et, $(p\text{-tolyl})_3P$, PPh_3, piper and Py but not so easily by $AsPh_3$ and benzylamine. $AsPh_3$ and $PhCH_2NH_2$ appear to establish an equilibrium:



1

L = $AsPh_3$
$PhCH_2NH_2$

For the tertiary phosphines, PPh_2Et is more strongly coordinated to Pd than $(p\text{-tolyl})_3P$, and this more than PPh_3. The larger $(p\text{-tolyl})_3P$ [8] compared with PPh_2Et and electron-donating Et and Me in PPh_2Et and $(p\text{-tolyl})_3P$ compared with PPh_3 are responsible for different reactivity. In ^{1}H NMR spectra of **1a**–**f** and **2**, methylene protons resonated equivalently, different from secondary benzyl amine where methylene protons are inequivalent as typical AB patterns [9, 10]. The methylene protons were usually observed as triplets due to coupling with adjacent NH_2 protons, while the NH_2 protons are one broad signal [10]. When pyridine in **2** was ligated to the palladium metal, NH_2 protons resonated as only one signal, while unsymmetric ligands such as 2-picoline and quinoline in complexes analogous to **2**, each proton of NH_2 is in a different environment [10]. In the ^{1}H NMR spectra of pyridine complexes (**1f** and **2**), one of the aromatic protons, H^6, appeared at a considerably higher field near 6 ppm from anisotropic shielding by the adjacent aromatic ring [11]. For **1a**–**f** four aromatic protons derived from the benzyl moiety were clearly detected in the region δ 6–7 ppm,



Scheme 1. Bridge-splitting reactions.

indicating that cyclopalladation remained. The *trans* (C, Cl) geometry of **1a–f** and *trans* (C, N) in **2** are evident from the high field shift of the H^6 proton in agreement with other authors [10, 12, 13]. The ^{31}P NMR spectra contain a singlet at 36.85 and 40.3 ppm for **1a** and **1b**, suggesting a single isomer.

The IR spectra show significant vibration modes: (i) N–H stretching vibration (3000–3300 cm^{-1}); (ii) ν(Pd–Cl) stretching vibrations (200–400 cm^{-1}). A decrease in ν(N–H) for mononuclear complexes indicated coordination of NH_2 with Pd. Infrared absorption near 1600 cm^{-1} is characteristic for C=N; ν(C=N) of **1f** and **2** are at 1603 and 1574 cm^{-1}, respectively. The 300–220 cm^{-1} region of the IR spectra of the chloro-complexes **1a–f** shows ν(PdCl): **1a**, 288, **1b**, 232, **1c**, 254, **1d**, 274, **1e**, 236, **1f**, 239 cm^{-1}. As ν(PdCl) *trans* to a carbon donor atom in **1a–f** is at lower frequency, it is reasonable to assume *trans* geometry in accord with the greater *trans* influence of an aryl than chloro. We suggest that in [Pd($C_6H_4CH_2NH_2$-κ^2-C,N)Cl(L)], L and aryl ligands tend not to be *trans* according to the antisymbiotic effect [14, 15].

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