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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(μ-Cl)(C₆H₄CH₂NH₂-κ²-C,N)]₂ reacts with PPh₂Et, P(p-tolyl)₃, AsPh₃, piper (piper = C₅H₁₀N) 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(C₆H₄CH₂NH₂–κ²-C,N)L] (L = PPh₂Et (1a), P(p-tolyl)₃ (1b), AsPh₃ (1c), piper (1d), C₆H₄CH₂NH₂ (3e) and Py (1f)). Complex 1f in THF at room temperature reacts with a stoichiometric amount of TlTfO (thallium triflate, TfO = CF₃SO₃) and Py (molar ratio 1:1:1) to afford [Pd(C₆H₄CH₂NH₂)(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(μ-Cl)(C₆H₄CH₂NH₂-κ²-C,N)]₂, giving mono palladium(II) derivatives including [Pd(C₆H₄CH₂NH₂-κ²-C,N)Cl(L)] (L = PPh₂Et (1a), P(p-tolyl)₃ (1b), AsPh₃ (1c), piper (1d), C₆H₄CH₂NH₂ (3e), Py (1f)) and [Pd(C₆H₄CH₂NH₂-κ²-C,N)Py(THF)]⁺ toward Py, which gives cationic complex 2.

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†Dedicated to Professor Seyyed Javad Sabounchei.
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 \(\Lambda_M\) is given in \(\Omega^{-1}\) 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\(_3\)COCD\(_3\) with Varian Unity 300 and Bruker AC-400 spectrometers. Chemical shifts are referenced to TMS (1H and 13C-\({}^1\)H) or H\(_3\)PO\(_4\) (31P-\({}^1\)H). Reactions were carried out at room temperature without special precautions against moisture. The molar conductivities of all complexes in acetone are between 0–1 \(\Omega^{-1}\) cm\(^2\) mol\(^{-1}\), in agreement with their nonelectrolytic nature, except for 2 whose molar conductivity is 114 \(\Omega^{-1}\) 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(μ-Cl)(C\(_6\)H\(_4\)CH\(_2\)NH\(_2\)-i\(^2\)-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\(_2\)Cl\(_2\) (2 mL) and n-hexane (15 mL) or Et\(_2\)O (7 mL) was added giving 1a–f as white precipitate, which was filtered off and air dried.

2.1.1. [Pd(C\(_6\)H\(_4\)CH\(_2\)NH\(_2\)-i\(^2\)-C,N)Cl(PPh\(_2\)Et)] (1a). 1H NMR (300 MHz, CDCl\(_3\), RT), δ (ppm): 7.86–7.80 (m, 4H, o, 2C\(_6\)H\(_5\)), 7.41–7.26 (m, 6H, m: p, 2C\(_6\)H\(_5\)), 6.95 (d, 1H, C\(_6\)H\(_4\), 3\(^J\) \(\text{H–H}\) = 7.2 Hz), 6.82 (m, 1H, C\(_6\)H\(_4\)), 6.47 (t, 2H, C\(_6\)H\(_4\), 3\(^J\) \(\text{H–H}\) = 6.9 Hz), 4.25 (br s, 2H, NH\(_2\)), 3.81 (br s, 2H, CH\(_2\)), 2.53 (qd, 2H, CH\(_2\), 2\(^J\) P–H = 18 Hz, 3\(^J\) \(\text{H–H}\) = 7.2 Hz), 1.14 (td, 3H, CH\(_2\), 2\(^J\) P–H = 21.6 Hz, 3\(^J\) \(\text{H–H}\) = 7.2 Hz); 31P 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\(_2\)Et) = 1109 cm\(^{-1}\); m.p.: 181\(^\circ\)C; Color: white; Yield: 417 mg, 0.98 mmol, 89.9%; \(\Lambda_M\): 1 \(\Omega^{-1}\) 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\(_6\)H\(_4\)CH\(_2\)NH\(_2\)-i\(^2\)-C,N)Cl(P(p-tolyl)\(_3\))] (1b). 1H NMR (300 MHz, CDCl\(_3\), and RT): δ (ppm): 7.56 (d, 6H, 3C \(\text{C}_6\)H\(_4\)), 7.12 (d, 6H, 3C \(\text{C}_6\)H\(_4\), 3\(^J\) \(\text{H–H}\) = 8.1 Hz), 6.96 (d, 1H, \(\text{C}_6\)H\(_4\), 3\(^J\) \(\text{H–H}\) = 7.2 Hz), 6.83 (m, 1H, \(\text{C}_6\)H\(_4\)), 6.41 (m, 2H, \(\text{C}_6\)H\(_4\)), 4.27 (br s, 2H, NH\(_2\)), 3.91 (br, 2H, CH\(_2\)N), 2.33 (s, 9H, 3 CH\(_3\)). 31P NMR (300 MHz, CDCl\(_3\), RT): δ (ppm): 40.30; IR (cm\(^{-1}\)): ν(N–H) = 3218–3144; ν(Pd–Cl) = 288 cm\(^{-1}\); ν(Pd–PPh\(_2\)Et) = 1109 cm\(^{-1}\); m.p.: 181\(^\circ\)C; Color: white; Yield: 417 mg, 0.98 mmol, 89.9%; \(\Lambda_M\): 1 \(\Omega^{-1}\) cm\(^2\) mol\(^{-1}\). Anal. Calcd for C\(_{28}\)H\(_{29}\)ClNPPd (%): C, 60.68; H, 5.29; N, 2.54. Found: C, 60.56; H, 5.25; N, 2.57.
2.1.3. \([\text{Pd}(C_6H_4CH_2NH_2-i_2-C,N)Cl(\text{AsPh}_3)] \) (1c). \(^{1}H\) NMR (300 MHz, CDCl\(_3\), RT): \(\delta\) (ppm): 7.6–7.3 (m, 15H, C\(_6\)H\(_5\)), 6.95 (d, 1H, C\(_6\)H\(_4\), \(^3J_{H-H} = 7.2\) Hz), 6.84 (t, 1H, C\(_6\)H\(_4\), \(^3J_{H-H} = 7.2\) Hz), 6.42 (m, 2H, C\(_6\)H\(_4\)), 4.31 (t, 2H, \(^3J_{H-H} = 5.7\) Hz, NH\(_2\)), 4.14 (br, 2H, CH\(_2\)N); IR (cm\(^{-1}\)): \(\nu(N-H) = 3252–3198\), \(\nu(Pd-N) = 287\) cm\(^{-1}\), \(\nu(Pd-Cl) = 254\) cm\(^{-1}\); m.p.: 168°C; Color: white; Yield: 121 mg, 0.220 mmol, 88.3%; \(M:0.5\) 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. \([\text{Pd}(C_6H_4CH_2NH_2-i_2-C,N)Cl(\text{piper})] \) (1d). \(^{1}H\) NMR (300 MHz, CDCl\(_3\), and RT): \(\delta\) (ppm): 7.0 (m, 3H, C\(_6\)H\(_4\)), 6.68 (d, 1H, C\(_6\)H\(_4\), \(^3J_{H-H} = 5.7\) Hz), 4.09 (br s, 4H, CH\(_2\)N\(^+\)CH\(_2\) (piper)), 3.05 (br, 4H, NH\(_2\)\(^+\)CH\(_2\) (piper)), 2.53 (br, 1H, NH\(_2\) (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\(^{-1}\)): \(\nu(N-H) = 3336–3324\), \(3118–3188\), \(\nu(Pd-Cl) = 274\) cm\(^{-1}\), \(\nu(Pd-N) = 316\) cm\(^{-1}\); m.p.: 185°C (dec); Color: white; Yield: 163.5 mg, 0.400 mmol, 85.5%; \(M:0.5\) cm\(^2\) mol\(^{-1}\). Anal. Calcd for C\(_{12}\)H\(_{19}\)ClN\(_2\)Pd\(_{1/4}\)CH\(_2\)Cl\(_2\) (%): C, 41.50; H, 5.54; N, 7.90. Found: C, 41.32; H, 5.12; N, 7.94.

2.1.5. \([\text{Pd}(C_6H_4CH_2NH_2-i_2-C,N)Cl(NH_2CH_2Ph)] \) (1e). \(^{1}H\) NMR (400 MHz, CDCl\(_3\), and RT): \(\delta\) (ppm): 7.52–7.27 (m, 5H, C\(_6\)H\(_5\)), 6.97 (m, 1H, C\(_6\)H\(_4\)), 6.96 (d, 2H, C\(_6\)H\(_4\), \(^3J_{H-H} = 5.2\) Hz), 6.80 (t, 1H, C\(_6\)H\(_4\), \(^3J_{H-H} = 4\) 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\(^{-1}\)): \(\nu(N-H) = 3268–3208\), \(3116–3052\), \(\nu(Pd-Cl) = 236\) cm\(^{-1}\), \(\nu(Pd-N) = 264\) cm\(^{-1}\); m.p.: 178°C (dec); Color: white; Yield: 163.5 mg, 0.400 mmol, 85.5%; \(M:0.5\) cm\(^2\) mol\(^{-1}\). Anal. Calcd for C\(_{14}\)H\(_{17}\)ClN\(_2\)Pd (%): C, 48.72; H, 4.93; N, 8.11. Found: C, 48.51; H, 4.75; N, 8.42.

2.1.6. \([\text{Pd}(C_6H_4CH_2NH_2-i_2-C,N)Cl(\text{Py})] \) (1f). \(^{1}H\) NMR (300 MHz, CDCl\(_3\), and RT): \(\delta\) (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\(_6\)H\(_4\)), 6.85 (t, 1H, C\(_6\)H\(_4\), \(^3J_{H-H} = 6\) Hz), 6.08 (d, 1H, C\(_6\)H\(_4\), \(^3J_{H-H} = 9\) Hz), 4.66 (brs, 2H, NH\(_2\)), 4.20 (t, 2H, CH\(_2\)), \(^3J_{H-H} = 6\) Hz); IR (cm\(^{-1}\)): \(\nu(N-H) = 3268–3208\), \(3116–3052\), \(\nu(Pd-Cl) = 236\) cm\(^{-1}\), \(\nu(Pd-N) = 295\) cm\(^{-1}\); m.p.: 183°C (dec); Color: white; Yield: 404 mg, 1 mmol, 85%; \(M:0.5\) cm\(^2\) mol\(^{-1}\). Anal. Calcd for C\(_{12}\)H\(_{13}\)ClN\(_2\)Pd (%): C, 48.72; H, 4.93; N, 8.11. Found: C, 48.51; H, 4.75; N, 8.42.

2.2. Synthesis of \([\text{Pd}(C_6H_4CH_2NH_2-i_2-C,N)Cl(\text{Py})_2]\text{TfO} \) (2)

To a solution of 1f (33.8 mg, 0.100 mmol) in THF (10 mL), Tf\(_2\)O (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\(_2\)O (5 mL) was added giving a yellow powder, which was filtered off, air dried and washed with cooled Et\(_2\)O giving 2. This complex was recrystallized from CH\(_2\)Cl\(_2\) (2 mL) and n-hexane (10 mL) for elemental analysis and NMR measurements. This complex is soluble in CH\(_2\)Cl\(_2\), (CH\(_3\))\(_2\)CO, CHCl\(_3\) and insoluble in Et\(_2\)O and n-hexane.
$^1$H NMR (300 MHz, acetone-$d_6$, RT): $\delta$(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$_6$H$_4$, $^3J_{H-H}$ = 6.9 Hz), 6.74 (t, 1H, C$_6$H$_4$, $^3J_{H-H}$ = 7.8 Hz), 5.99 (dd, 1H, C$_6$H$_4$, $^3J_{H-H}$ = 7.8 Hz, $^5J_{H-H}$ = 0.9 Hz), 5.25 (br, 2H, NH$_2$), 4.28 (t, 2H, CH$_2$N, $^3J_{H-H}$ = 6 Hz).

IR (cm$^{-1}$): $\nu$(N–H) = 3306–3244, $\nu$(C= N py) = 1603, 1574 cm$^{-1}$, $\nu$(Pd–N) = 279, 327 cm$^{-1}$; m.p.: 176°C; Color: yellow; Yield: 42 mg, 0.079 mmol, 79%; M: 114 g/mol, 79%; $\Lambda_M$: 114 Ω$^{-1}$cm$^2$mol$^{-1}$. Anal. Calcd for C$_{18}$H$_{18}$F$_3$N$_3$O$_3$PdS (%): 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$_2$Et, (p-tolyl)$_3$P, PPh$_3$, piper and Py but not so easily by AsPh$_3$ and benzylamine. AsPh$_3$ and PhCH$_2$NH$_2$ appear to establish an equilibrium:

For the tertiary phosphines, PPh$_2$Et is more strongly coordinated to Pd than (p-tolyl)$_3$P, and this more than PPh$_3$. The larger (p-tolyl)$_3$P [8] compared with PPh$_2$Et and electron-donating Et and Me in PPh$_2$Et and (p-tolyl)$_3$P 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,
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 H6 proton in agreement with other authors [10, 12, 13]. The 31P 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) \(\nu(Pd–Cl)\) stretching vibrations (200–400 cm\(^{-1}\)). A decrease in \(\nu(N–H)\) for mononuclear complexes indicated coordination of NH2 with Pd. Infrared absorption near 1600 cm\(^{-1}\) is characteristic for C=NH 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 \(\nu(PdCl)\): 1a, 288, 1b, 232, 1c, 254, 1d, 274, 1e, 236, 1f, 239 cm\(^{-1}\). As \(\nu(PdCl)\) 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(C6H4CH2NH2-\(\text{H}_2\)-C,N)Cl(L)], L and aryl ligands tend not to be trans according to the antisymbiotic effect [14, 15].

References


