
Electrochemical Generation of Cationic Pd Catalysts and Pd/TEMPO Double-Mediatory Electrooxidative Wacker-type Reactions

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1. General

^1H and ^{13}C NMR spectra were recorded on Varian GEMINI 200 (^1H 200 MHz, ^{13}C 50 MHz) spectrometer in CD_3NO_2 or CDCl_3 using TMS or residual solvent as internal standard. IR spectra were recorded on a JASCO FT/IR-4100 spectrophotometer. Unless otherwise noted, all reactions were performed under air. Unless otherwise noted, all materials were obtained from commercial suppliers and used without further purification. Dried acetonitrile (CH_3CN) over CaH_2 was used in the synthesis of palladium complexes. Unless otherwise noted, all reactions were performed under air.

2. General Procedure for Electrochemical Preparation of Cationic Palladium Complex

The anodic oxidation was carried out in an H-type divided cell (glass filter) equipped with two platinum electrodes ($1.0 \times 1.5 \text{ cm}^2$). In the anodic chamber was placed a solution of $\text{Pd}(\text{OAc})_2$ (22 mg, 0.1 mmol) in 0.2 M $\text{Bu}_4\text{NBF}_4/\text{CH}_3\text{CN}$ (5.0 mL). In the cathodic chamber was placed 0.2 M $\text{Bu}_4\text{NBF}_4/\text{CH}_3\text{CN}$ (5.0 mL). Under argon, the constant current electrolysis (10 mA) was carried out at room temperature with magnetic stirring until 3.0 F/mol of electricity was passed. After the electrolysis, the anodic solution was poured into dry Et_2O (10 mL). The resulting pale yellow precipitate was washed with dry Et_2O and dried under reduced pressure to afford $[\text{Pd}(\text{CH}_3\text{CN})_4][\text{BF}_4]_2$ **1a** (26 mg, 58%).

$[\text{Pd}(\text{CH}_3\text{CN})_4][\text{BF}_4]_2$ (1a): ^1H NMR (200 MHz, CD_3NO_2) δ 2.66 (s, 12H); IR (KBr) 2359, 2342, 1084 cm^{-1} . Anal. Calcd for $\text{C}_8\text{H}_{12}\text{B}_2\text{F}_8\text{N}_4\text{Pd}$: C, 21.63; H, 2.72; N, 12.61. Found: C, 21.01; H, 2.76; N, 12.02.

$[\text{Pd}(\text{CH}_3\text{CN})_4][\text{PF}_6]_2$ (1b): ^1H NMR (200 MHz, CD_3NO_2) δ 2.66 (s, 12H). IR (KBr) 2358, 2335, 2359 cm^{-1} . Anal. Calcd for $\text{C}_8\text{H}_{12}\text{F}_{12}\text{N}_4\text{P}_2\text{Pd}$: C, 17.14; H, 2.16; N, 9.99. Found: C, 18.09; H, 2.64; N, 9.94.

$[\text{Pd}(\text{CH}_3\text{CN})_4][\text{ClO}_4]_2$ (1c): ^1H NMR (200 MHz, CD_3NO_2) δ 2.67 (s, 12H); IR (KBr) 2361, 2334, 1143, 1109, 1089 cm^{-1} .

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3. Typical Procedure for Pd/TEMPO Double-Mediatory Electrooxidative Wacker-type Reaction

The anodic oxidation was carried out in an H-type divided cell equipped with two platinum electrodes ($1.0 \times 1.5 \text{ cm}^2$). In the anodic chamber were placed 1-dodecene **2a** (85 mg, 0.5 mmol), $\text{Pd}(\text{OAc})_2$ (12 mg, 0.05 mmol), and TEMPO (22 mg, 0.14 mmol) in 0.05 M NaClO_4 solution of $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ (8.75/1.25 mL). In the cathodic chamber was placed 0.05 M NaClO_4 solution of $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ (8.75/1.25 mL). The constant current electrolysis (5 mA) was carried out at room temperature with magnetic stirring until 3.0 F/mol of electricity was passed. To the resulting mixture was added aq sat. NaCl (5 mL) and extracted with EtOAc ($3 \times 5 \text{ mL}$). The combined organic phase was washed with aq sat. NaCl (10 mL) and dried over Na_2SO_4 . Removal of solvent under reduced pressure and subsequent column chromatography on silica gel afforded dodecan-2-one **3a** (76 mg, 82%) as colorless liquid.

Dodecan-2-one (3a):³ Colorless liquid; ^1H NMR (200 MHz, CDCl_3) δ 0.88 (t, $J = 6.5 \text{ Hz}$, 3H), 1.20–1.38 (m, 14H), 1.50–1.66 (m, 2H), 2.14 (s, 3H), 2.42 (t, $J = 7.4 \text{ Hz}$, 2H); ^{13}C NMR (50 MHz, CDCl_3) δ 14.1, 22.7, 23.9, 29.2, 29.3, 29.40, 29.48, 29.55, 29.8, 31.9, 43.8, 209.2; IR (neat) 2925, 2854, 1718, 1466, 1411, 1359, 1162 cm^{-1} .

Decan-2-one (3b):⁴ Colorless liquid; ^1H NMR (200 MHz, CDCl_3) δ 0.88 (t, $J = 6.6 \text{ Hz}$, 3H), 1.20–1.36 (m, 10H), 1.50–1.64 (m, 2H), 2.14 (s, 3H), 2.42 (t, $J = 7.4 \text{ Hz}$, 2H); ^{13}C NMR (50 MHz, CDCl_3) δ 14.1, 22.6, 23.9, 29.1, 29.2, 29.4, 29.8, 31.8, 43.8, 209.2; IR (neat) 2928, 2855, 1715, 1465, 1412, 1360, 1163 cm^{-1} .

Undecan-2-one (3c):⁵ Colorless liquid; ^1H NMR (200 MHz, CDCl_3) δ 0.88 (t, $J = 6.4 \text{ Hz}$, 3H), 1.20–1.38 (m, 12H), 1.50–1.64 (m, 2H), 2.14 (s, 3H), 2.42 (t, $J = 7.3 \text{ Hz}$, 2H); ^{13}C NMR (50 MHz, CDCl_3) δ 14.0, 22.6, 23.8, 29.1, 29.2, 29.4, 29.7, 31.8, 43.7, 209.1; IR (neat) 2926, 2854, 1716, 1466, 1411, 1359, 1162 cm^{-1} .

Tetradodecan-2-one (3d): White solids; ^1H NMR (200 MHz, CDCl_3) δ 0.88 (t, $J = 6.5 \text{ Hz}$, 3H), 1.20–1.36 (m, 18H), 1.50–1.64 (m, 2H), 2.13 (s, 3H), 2.42 (t, $J = 7.4 \text{ Hz}$, 2H); ^{13}C NMR (50 MHz, CDCl_3) δ 14.1, 22.7, 23.9, 29.2, 29.3, 29.4, 29.5, 29.6, 29.8, 31.9, 43.8, 209.1; IR (KBr) 2917, 2849, 1712, 1464, 1414, 1376, 1168 cm^{-1} .

Methyl 10-oxoundecanoate (3e):⁶ Colorless liquid; ^1H NMR (200 MHz, CDCl_3) δ 1.24–1.34 (m, 8H), 1.50–1.66 (m, 4H), 2.13 (s, 3H), 2.30 (t, $J = 7.5 \text{ Hz}$, 2H), 2.42 (t, $J = 7.4 \text{ Hz}$, 2H), 3.67 (s, 3H); ^{13}C NMR (50 MHz, CDCl_3) δ 23.8, 24.9, 29.0, 29.1, 29.8, 34.0, 43.7, 51.4, 174.1, 209.1; IR (neat) 2931, 2856, 1715, 1437, 1361, 1171 cm^{-1} .

4-Phenylbutan-2-one (3f):⁵ Colorless liquid; ^1H NMR (200 MHz, CDCl_3) δ 2.15 (s, 3H), 2.72–2.94 (m, 4H), 7.16–7.32 (m, 5H); ^{13}C NMR (50 MHz, CDCl_3) δ 29.7, 30.0, 45.1, 126.0, 128.1, 128.3, 140.8,

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207.7; IR (KBr) 3062, 3028, 2925, 1717, 1603, 1496, 1453, 1409, 1358, 1162 cm^{-1} .

10-Oxoundecanal (3g):⁷ Colorless liquid; ^1H NMR (200 MHz, CDCl_3) δ 1.24–1.36 (m, 8H), 1.50–1.68 (m, 4H), 2.13 (s, 3H), 2.42 (t, $J = 7.4$ Hz, 4H), 9.76 (s, 1H); ^{13}C NMR (50 MHz, CDCl_3) δ 22.0, 23.7, 29.0, 29.1, 29.8, 43.7, 43.8, 202.7, 209.1; IR (KBr) 2930, 2856, 2720, 1717, 1464, 1411, 1361, 1166 cm^{-1} .

4-Benzyloxybutan-2-one (3h):⁸ Colorless liquid; ^1H NMR (200 MHz, CDCl_3) δ 2.18 (s, 3H), 2.72 (t, $J = 6.3$ Hz, 2H), 3.74 (t, $J = 6.3$ Hz, 2H), 4.51 (s, 2H), 7.29–7.37 (m, 5H); ^{13}C NMR (50 MHz, CDCl_3) δ 30.4, 43.7, 65.1, 73.1, 127.5, 128.2, 137.9, 207.0; IR (neat) 3063, 3031, 2867, 1715, 1496, 1421, 1364, 1233, 1171, 1105 cm^{-1} .

4. Electrooxidation of Palladium Acetate in the Presence of TEMPO

The anodic oxidation was carried out in an H-type divided cell (glass filter) equipped with two platinum electrodes ($1.5 \times 2.0 \text{ cm}^2$). In the anodic chamber was placed a solution of $\text{Pd}(\text{OAc})_2$ (225 mg, 1.0 mmol) and TEMPO (469 mg, 3.0 mmol) in 0.1 M $\text{Bu}_4\text{NBF}_4/\text{CH}_3\text{CN}$ (15 mL). In the cathodic chamber was placed 0.1 M $\text{Bu}_4\text{NBF}_4/\text{CH}_3\text{CN}$ (15 mL). Under argon, the constant current electrolysis (10 mA) was carried out at room temperature with magnetic stirring until 2.4 F/mol of electricity was passed. After the electrolysis, to the combined solution of the anodic and cathodic chambers was added dry Et_2O (30 mL). The resulting pale yellow precipitate was washed with dry Et_2O and dried under reduced pressure to afford $[\text{Pd}(\text{CH}_3\text{CN})_4(\text{tempo})][\text{BF}_4]$ (237 mg, 46%). IR (KBr) 3443, 2962, 2188, 1636, 1417 cm^{-1} . Anal. Calcd for $\text{C}_{17}\text{H}_{30}\text{BF}_4\text{N}_5\text{OPd}$: C, 39.75; H, 5.89; N, 13.63. Found: C, 39.32; H, 5.54; N, 13.66.

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