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Tandem Pinacol Coupling/Rearrangement of Aromatic Aldehydes with Hydrogen Catalyzed by a Combination of a Platinum Complex and a Polyoxometalate

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Electronic Supporting Information

Detailed Experimental Section

Instrumentation. ^{1}H and ^{13}C NMR spectra were measured on a Brucker Avance 400 instrument with TMS as standard. IR spectra were measured on a Nicolet 460 FTIR spectrophotometer. ESI-MS were measured using Micromass Platform LCZ 4000 with an aqueous sample infused at 5μl/min. Elemental analysis C, H, N was with a Thermoelectron EA112 CHNO Elemental Analyzer. Reactions were quantified by GLC-FID (HP 6890) using a 30 m 5% phenylmethyl silicone capillary column with an ID 0.32 mm and 0.25 μm coating (Restek 5MS) and products were identified by use of reference standards and by GC-MS (HP 5973) using the same column.

Synthesis of metallorganic complexes. Methyl pyrazinecarboxylate[1] was prepared by dropwise addition of thionyl chloride (13.07 ml, 0.18 mmol) to dry methanol (240 mL) over 1 h at 4-6 °C under argon. Pyrazinecarboxylic acid (20 g, 0.16 mmol) was added at 9 °C and the mixture was heated for 2 h at 60 °C. After the reaction mixture was cooled to room temperature, a solution of sodium hydrogen carbonate (29 g, 0.35 mmol) in 280 mL of water was slowly added. The methanol was distilled off on a rotary evaporator at 180 mbar and a bath temperature of 45 °C. The residue was extracted three times with dichloromethane (80 mL, 50 mL and 50 mL). Concentration of the organic phase provided 18.34 g of crude product. The residual solid was recrystallized from diisopropyl ether. The yield of methyl pyrazinecarboxylate was 14.6 g (66 %). ^{1}H NMR (250 MHz, $CDCl_3$) δ: 3.98 (s, 3H), 8.66 (d, J = 2.5 Hz, 1H), 8.72 (d, J = 2.5 Hz, 1H), 9.25 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 53.07, 143.13, 144.25, 146.14, 147.63, 164.25 ppm.

Pyrazine-2-carboxaldehyde[2] was prepared by dissolving methyl pyrazinecarboxylate (10 g, 70 mmol) in 200 mL of dry tetrahydrofuran and the mixture was cooled to -70 °C under argon. While maintaining the temperature at -68 °C to -73 °C, a 1 M solution of $LiAlH_4$ in dry tetrahydrofuran (36 mL, 36 mmol) was added with stirring over a period of 30 min. After stirring for an additional 15 min at -75 °C, the reaction was stopped by slow addition of 10 mL of glacial acetic acid. The solvent was evaporated on a rotary evaporator at 260 mbar and a bath temperature of 40 °C. The residue was dissolved in a mixture of 88 mL of 2 N hydrochloric acid and 40 mL of chloroform. The aqueous layer was extracted eight times with 20 mL portions of chloroform. The combined extracts were stirred with 20 mL of water and 10 g of sodium bicarbonate until neutral pH was obtained. The chloroform layer was filtered off, dried with anhydrous sodium sulfate and concentrated under reduced pressure. The yield of pyrazine-2-carboxaldehyde was 3.51g, (41 %), as a light yellow liquid. ^{1}H NMR (250 MHz, $CDCl_3$) δ: 8.61 (d, J = 2.5 Hz, 1H, 5-H), 8.65 (d, J = 2.5 Hz, 1H, 6-H), 8.97 (s, 1H, 3-H), 9.96 (s, 1H, H_{ald}) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 143.25, 144.74, 146.71, 148.34, 192.28 ppm.

N-(2,6-diisopropylphenyl)pyrazin-2-ylmethanimine was prepared by dissolving pyrazine-2-carboxaldehyde (0.97 g, 8 mmol) in 15 mL of trimethyl orthoformate. 2,6-Diisopropylaniline (1.41 g, 8 mmol) was added and the mixture was refluxed for 15 h. The mixture was cooled to room temperature and solvent was evaporated on a rotary evaporator at 100 mbar and a bath temperature of 40 °C. The residue was purified by flash chromatography using a methanol/chloroform (1:1) eluent mixture. The yield of *N*-(2,6-diisopropylphenyl)pyrazin-2-ylmethanimine was 0.99 g, (46 %) as pale yellow crystals. ^{1}H NMR (250 MHz, $CDCl_3$) δ: 1.18 (d, J = 5 Hz, 12H, CH_3), 2.95 (quint, J = 7.5 Hz, 2H, CH), 7.18 (m, 3H, Ar-H), 8.33 (s, 1H, HC=N), 8.69 (quad, J_1 = 2.5 Hz, J_2 = 5 Hz, 2H, $H_{pyrazine}$-5,6), 9.48 (s, 1H, $H_{pyrazine}$-3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 23.43, 27.98, 123.14, 124.88, 137.09, 143.59, 144.19, 145.80, 147.96, 149.21, 161.15 ppm.

Pt^{II}(*N*-(2,6-diisopropylphenyl)pyrazin-2-ylmethanimine)Cl_2 was prepared by dissolving $Pt(Cl)_2(DMSO)_2$ (0.42 g, 1 mmol) in 5 mL of dry methanol. *N*-(2,6-diisopropylphenyl)pyrazin-2-ylmethanimine (0.26 g, 1 mmol) separately dissolved in 5 mL of dry methanol was added to the solution. The mixture was stirred at room temperature overnight. The orange precipitation that was formed was filtered off, washed with methanol and dried under high vacuum. The yield of

the title compound was 0.41 g (80 %). Crystals of the complex for X-ray analysis were grown from a chloroform solution by slow diffusion of diethyl ether. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.13 (d, J = 8 Hz, 6H, CH_3), 1.33 (d, J = 8 Hz, 6H, CH_3), 3.15 (quint, J = 12 Hz, 2H, CH), 7.26 (d, J = 8 Hz, 2H, Ar-H), 7.39 (t, J = 8 Hz, 1H, Ar-H), 8.89 (s, 1H, HC=N), 9.11 (d, J = 4 Hz, 1H, $H_{pyrazine}$-5), 9.17 (s, 1H, $H_{pyrazine}$-3), 10.00 (d, J = 4 Hz, 1H, $H_{pyrazine}$-6) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 22.96, 24.58, 28.22, 123.59, 129.65, 141.26, 142.63, 143.32, 147.97, 150.62, 152.44, 167.06 ppm. MS (ESI) m/z 556.18 $[M + Na]^+$ 100%, 1101.41 $[2M + Na]^+$. IR (KBr) ν = 757, 800, 1058, 1184, 1363, 1411, 1463, 1521, 1600, 2869, 2964, 3064, 3093 cm^{-1}. Elemental analysis: experimental (calculated): C – 38.138 (38.28), H – 3.812 (3.97), N – 7.198 (7.88).

Pd^{II}(*N*-(2,6-diisopropylphenyl)pyrazin-2-ylmethanimine)Cl_2 was prepared by dissolving $Pd(Cl)_2(DMSO)_2$ (0.033 g, 0.1 mmol) in 15 ml of dry methanol followed by addition 2,6-bis(1-methylethyl)-N-(2-pyrazinylmethylene)phenylamine (0.026 g, 0.1 mmol) that was separately dissolved in 3 mL of dry methanol. The mixture was stirred at room temperature for 24 h. The amount of solvent was reduced under a steady stream of argon. A portion by portion addition of ether completed the precipitation, which was filtered off and dried under high vacuum. The yield of the title compound was 0.011 g (25 %). ^{1}H NMR (250 MHz, $CDCl_3$) δ: 1.15 (d, J = 5 Hz, 6H, CH_3), 1.38 (d, J = 5 Hz, 6H, CH_3), 3.22 (quint, J = 7.5 Hz, 2H, CH), 7.21 (d, J = 7.5 Hz, 2H, Ar-H), 7.37 (t, J = 7.5 Hz, 1H, Ar-H), 8.26 (s, 1H, HC=N), 9.15 (d, J = 2.5 Hz, 1H, $H_{pyrazine}$-5), 9.20 (s, 1H, $H_{pyrazine}$-3), 9.51 (d, J = 2.5Hz, 1H, $H_{pyrazine}$-6) ppm. ^{13}C NMR (100 MHz, DMSO-d6) δ: 23.23, 24.51, 26.36, 123.54, 128.88, 140.92, 143.31, 143.96, 149.43, 150.33, 152.11, 173.39 ppm. MS (ESI) m/z 468.11 $[M + Na]^+$ 100%. IR (KBr) ν = 755, 798, 1056, 1189, 1363, 1457, 1608, 2867, 2925, 2960, 3006, 3021, 3062, 3102 cm^{-1}. Elemental analysis: experimental (calculated): C - 45.91 (45.92), H- 4.33 (4.76), N - 9.27 (9.45).

Crystallographic Data Collection and Structure Determination of Pt^{II}(N-(2,6-diisopropylphenyl)pyrazin-2-ylmethanimine)Cl_2. The data was collected on orange triclinic plates, with a size of 0.1 × 0.1 × 0.05 mm^3, using a Nonius-Kappa CCD diffractometer using graphite-monochromated Mo-Kα (λ = 0.71073 Å) radiation. 49905 (11399 independent, R(int) = 0.046) reflections were collected over a range of θ = 2.74 – 27.42 ° with limiting indices of -14 ≤ h ≤ 14, -19 ≤ k ≤ 19, 0 ≤ l ≤ 19. The data were processed with Denzo-Scalepack. The structures were solved by direct methods with SHELXS-97. Full-matrix least-squares refinement was based on

F^2 with SHELX-97. Refinement of the data on 11399 unique reflections was with 524 parameters with 0 restraints. The goodness of fit on F^2 was 1.076. The final R indices for $I > 2\sigma(I)$ were $R_1 = 0.0280$ and $R_w = 0.0660$ and R indices for all data were $R_1 = 0.0366$ and $R_w = 0.0697$. The largest difference peak between peaks and hole were 1.500 and –1.218 e/Å^3. The crystallographic data are presented in the caption of the figure below and the cif file is to be found in a separate file also as supplemental information.

General procedure for the reductive coupling-rearrangement of aromatic aldehydes. Reactions were carried out in 15 mL glass pressure tubes. In a typical procedure for aromatic aldehydes 2 mmol of substrate, 0.063 g (0.03 mmol) $H_5PV_2Mo_{10}O_{40}$•34 H_2O,[3] and Pt(N-(2,6-diisopropylphenyl)pyrazin-2-ylmethanimine)Cl_2 (0.0053 g, 0.01 mmol) were placed in a glass pressure tube. The air was replaced with argon. Hydrogen, 2.5 atm, was introduced to the pressure tube by two consecutive pump-thaw cycles on Schlenk line. The tubes were placed in a thermostated oil bath at 100 °C and reactions were carried out for 18 h. The reaction mixtures were then cooled and 1 mL of dichloromethane was added; conversions and selectivity were measured by GLC with both FID and MS detectors.

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