An Acyl Protection Strategy for Synthesis of a Protic NHC Complex via N-Acyl Methanolysis

*Graham E. Dobereiner, Catherine A. Chamberlin, Nathan D. Schley and Robert H. Crabtree**

Department of Chemistry, Yale University, 225 Prospect St., New Haven, CT 06520

Supporting Information

Experimental Section

$[Ir(cod)Cl]_2$ and $[Rh(cod)Cl]_2$ were prepared according to known procedures.[1] Dimethyl benzimidazole-5,6-dicarboxylate was synthesized according to a procedure described by Hamilton *et al.*[2] The syntheses of the ligand precursors and the metal complexes were conducted under argon using dry degassed solvents unless otherwise indicated. Solvents were dried on a Grubbs-type solvent purification system. All other reagents were commercially available from Sigma-Aldrich, Alfa-Aesar and Strem Chemicals and used as received unless otherwise indicated. NMR spectra were recorded at room temperature on a 400 or 500 MHz Bruker spectrometer and referenced to the residual solvent peak (δ in ppm and J in Hz). IR spectra were obtained using a Nicolet 6700 FT-IR Spectrometer equipped with an attenuated total reflectance (ATR) accessory. High resolution mass spectrometry was performed on a Bruker Qe 9.4T FT-ICR Instrument at the W.M. Keck Facility (New Haven, CT). Elemental analyses were performed by Atlantic Microlabs Inc. (Norcross, GA) and Robinson Microlit (Madison, NJ).

Dimethyl-N-benzoyl-benzimidazole-5,6-dicarboxylate (1). To a round bottomed flask was added a stir bar and dimethyl-benzimidazole-5,6-dicarboxylate (1.69g, 7.23 mmol). 35 mL of distilled water was added, forming a white suspension. K_2CO_3 (2.5 equiv, 18.1 mmol, 2.49g) was slowly added to the flask,

followed by 35 mL of tetrahydrofuran (THF), resulting in a clear solution. Benzoic anhydride was added portionwise over 10 minutes (2 equiv, 14.5 mmol, 3.27g). The reaction was allowed to stir for 2 hours, during which it became cloudy. THF was then removed via rotary evaporator; 40 mL DCM was added to the remaining material. To the reaction was added 40 mL of an aqueous saturated $NaHCO_3$ solution. The organic phase was washed twice with an aqueous saturated $NaHCO_3$ solution, twice with a 0.5M aqueous citric acid solution, and once with a brine wash. The resulting organic layer was dried with Na_2SO_4, filtered and evaporated via rotary evaporator. The resulting white solid was thoroughly washed with diethyl ester to remove benzoic acid. The product was obtained as a white solid (1.55g, 57% yield). FT-ICR MS (MeCN/aq. HCOOH): 339.0977 ($M+H^+$). 1H NMR (500 MHz, $CDCl_3$) δ8.58 (s, 1H, azole C(2)H), 8.36 (s, 1H, azole CH), 8.22 (s, 1H, azole CH), 7.82 (d, J=6.8Hz, 2H, *o*-phenyl CH), 7.74 (t, J=6.0Hz, 1H, *p*-phenyl CH), 7.62 (t, J=7.6Hz, 2H, *m*-phenyl CH), 3.96 (s, 3H, -$COOCH_3$), 3.95 (s, 3H, -$COOCH_3$). ^{13}C {^1H} NMR (125 MHz, $CDCl_3$) δ 168.10, 167.92, 166.79, 145.95, 145.48, 134.04, 133.62, 132.28, 130.17, 129.90, 129.54, 129.50, 122.06, 116.87, 53.06.

Dimethyl-N-benzoyl-N-methyl-benzimidazolium-5,6-dicarboxylate tetrafluoroborate (2). To a flame-dried round bottomed flask was added a stir bar and dimethyl-1-benzoyl-benzimidazole-5,6-dicarboxylate (253.9 mg, 0.677 mmol). 20 mL of nitromethane was added, and the solution was allowed to stir. 10 mL of a nitromethane solution containing trimethyloxonium tetrafluoroborate (130.7 mg, 0.880 mmol) was added dropwise to the reaction. After stirring for four hours at room temperature, the solvent was removed by rotary evaporation. The oily residue was triturated with dichloromethane, resulting in a white solid. The solid was filtered off and washed with dry dichloromethane to afford the product (233 mg, 76% yield). Note that the product is easily hydrolyzed in the presence of moisture. Crystals suitable for X-ray diffraction were grown by recrystallization in a solvent mixture of acetonitrile and dichloromethane. FT-ICR MS (MeCN/aq. HCOOH): 249.0868 ($C_{19}H_{17}BF_4N_2O_5 \cdot H_2O+H^+$, hydrolysis product). ^1H NMR (400 MHz, DMSO) δ 8.85 (s, 1H, azole C(2)H), 8.14 (s, 1H, azole CH), 8.07 (s, 1H, azole CH), 7.94 (dd, J = 1.3, 8.3, 2H, *o*-phenyl CH), 7.62 (t, J = 7.4, 1H, *p*-phenyl CH), 7.50 (t, J = 7.7, 2H, *m*-phenyl CH), 3.98 (s, 3H, -CH_3), 3.85 (s, 3H, -

$COOCH_3$), 3.84 (s, 3H, -$COOCH_3$). ^{13}C {^1H} NMR (125 MHz, DMSO) δ 167.68, 167.52, 167.45, 147.76, 134.93, 133.02, 130.89, 129.40, 128.72, 127.29, 126.78, 119.14, 113.11, 52.85, 52.83, 32.08.

(Benzoyl-NHC)Ir(cod)Cl (3). The benzimidazolium salt (200.0 mg, 0.443 mmol) and $[Ir(cod)Cl]_2$ (134.4mg, 0.200 mmol) were added to a 100 mL flame-dried Schlenk flask. The flask was purged and backfilled with argon three times. 50 mL of dry, degassed DCM were added via syringe and the flask was cooled to -78°C using a dry ice and acetone bath. 400 μL of a 1M solution of LiHMDS in hexanes (400 mmol) was added dropwise to the suspension, resulting in a change in color of the liquid from yellow to dark brown. The reaction was allowed to warm to room temperature and was stirred for two days, after which it became a red-orange solution. Dry, degassed diethyl ether was added to the solution until solids began to precipitate from solution. The reaction was filtered and the resulting solution was evaporated. The residue was recrystallized using DCM and hexanes to afford the product as an orange-yellow solid in (201 mg, 73% yield). ^1H NMR (500 MHz, $CDCl_3$) δ 8.27 (s, 1H, azole CH), 8.23 (d, J = 8.3Hz, 2H, *o*-phenyl CH), 7.80 (t, J = 7.5Hz, 1H, *p*-phenyl CH), 7.74 (s, 1H, azole CH), 7.55 (t, J = 7.9Hz, 2H, *m*-phenyl CH), 4.56 (m, 1H, COD CH), 4.38 (s, 3H, -CH_3), 4.31 (m, 1H, COD CH), 3.96 (s, 3H, -$COOCH_3$), 3.92 (s, 3H, -$COOCH_3$), 2.76 (m, 1H, COD CH), 2.23 (m, 1H, COD CH_2), 2.11 (m, 1H, COD CH), 2.04 – 1.93 (m, 1H, COD CH_2), 1.81 – 1.69 (m, 1H, COD CH_2), 1.64 (m, 1H, COD CH_2), 1.60 – 1.48 (m, 1H, COD CH_2), 1.43 – 1.23 (m, 2H, COD CH_2), 1.17 (m, 1H, COD CH_2). 13C {^1H} NMR (126 MHz, $CDCl_3$) δ 198.48, 170.00, 167.37, 136.88, 135.21, 134.82, 132.41, 131.89, 129.65, 129.12, 128.66, 115.64, 110.89, 89.23, 89.08, 53.61, 53.27, 53.16, 50.11, 36.42, 36.21, 30.47, 29.49, 27.31, 1.25. Anal. Calcd. for $C_{27}H_{28}ClIrN_2O_5$: C, 47.12; H, 4.10; N, 4.07. Found: C, 47.36; H, 4.17; N, 4.61.

(Benzoyl-NHC)Rh(cod)Cl (4). The benzimidazolium salt (140 mg, 0.310 mmol) and $[Rh(cod)Cl]_2$ (69.6 mg, 0.141 mmol) were added to a 100 mL flame-dried Schlenk flask. The flask was purged and backfilled with argon three times. 50 mL of dry, degassed DCM were added via syringe and the flask was cooled to -78°C using a dry ice and acetone bath. 282 μL of a 1M solution of LiHMDS in hexanes (0.282 mmol) was added dropwise to the suspension, resulting in a change in color of the liquid from

yellow to dark green. The reaction was allowed to warm to room temperature and was stirred overnight, after which it became a yellow solution. Dry, degassed diethyl ether was added to the solution until solids began to precipitate from solution. The reaction was filtered and the resulting solution was evaporated. The residue was recrystallized using DCM and hexanes to afford the product as a yellow solid (110 mg, 65% yield). 1H NMR (500 MHz, $CDCl_3$) δ 8.39 (d, J = 7.4, 2H, *o*-phenyl CH), 8.31 (s, 1H, azole CH), 7.86 (t, J = 7.5, 1H, *p*-phenyl CH), 7.75 (s, 1H, azole CH), 7.66 (t, J = 7.9, 2H, *m*-phenyl CH), 5.02 (m, 1H, COD CH), 4.60 (s, 3H, $-CH_3$), 4.58 (m, 1H, COD CH), 3.96 (s, 3H, $-COOCH_3$), 3.93 (s, 3H, $-COOCH_3$), 3.16 (m, 1H, COD CH), 2.55 (m, 2H, COD CH_2, CH), 2.07 (m, 2H, COD CH_2), 1.72 (m, 1H, COD CH_2), 1.56 (m, 2H, COD CH_2), 1.41 (m, 2H, COD CH_2). $^{13}C\{^1H\}$ NMR (125 MHz, CDCl3) δ 206.09 (d, J = 50.9), 169.98, 167.37, 167.32, 136.51, 135.15, 135.08, 132.29, 131.95, 12 9.59, 129.50, 128.75, 115.64, 110.82, 102.55 (d, J = 6.8), 100.28 (d, J = 6.5), 69.58 (d, J = 14.9), 65.84 (d, J = 14.6), 53.29, 53.18, 36.82, 35.65, 29.92, 29.61, 28.66, 26.81.Anal. Calcd for $C_{27}H_{28}ClN_2O_5Rh \cdot H_2O$: C, 52.57; H, 4.90; N, 4.54. Found: C, 52.27; H, 4.76; N, 5.34.

(Benzoyl-NHC)Ir(CO)$_2$Cl (5). Complex **3** was added to a flame-dried degassed Schlenk flask. The flask was purged and backfilled with nitrogen. Degassed dichloromethane was added and carbon monoxide gas was bubbled through the solution. The yellow-orange solution brightened over the course of a few seconds to a yellow solution. After five minutes solvent was removed in vacuo resulting in a yellow residue. The material was characterized without additional purification. 1H NMR (500 MHz, $CDCl_3$) δ 8.28 (s, 1H, azole CH), 7.94 (s, 1H, azole CH), 7.91 (d, J = 7.1, 2H, *o*-phenyl CH), 7.77 (t, J = 7.5, 1H, *p*-phenyl CH), 7.58 (t, J = 7.9, 2H, *m*-phenyl CH), 4.32 (s, 3H, $-CH_3$), 3.98 (s, 3H, $-COOCH_3$), 3.95 (s, 3H, $-COOCH_3$). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 189.95, 179.46, 168.67, 167.03, 167.01, 166.88, 135.86, 135.18, 134.44, 132.42, 131.90, 130.48, 130.36, 130.32, 129.37, 128.90, 128.68, 116.18, 112.59, 53.44, 53.36, 37.33, 28.24. IR (cm^{-1}): 2952.9, 2065.4, 1986.0, 1724.4, 1434.3, 1367.4, 1312.0, 1260.1.

[(Benzoyl-NHC)Ir(cod)(PPh$_3$)]PF$_6$ (6). To a flame-dried Schlenk flask was added complex **3** (66.9 mg, 0.0973 mmol), PPh_3 (28.0 mg, 0.107 mmol) and KPF_6 (17.9 mg, 0.0973 mmol). The flask was

evacuated and backfilled with Argon three times. Dried degassed acetone was added to the flask, resulting in a red-orange solution. The reaction was stirred for one hour. The solvent was removed *in vacuo* and dichloromethane was added the flask. The reaction was filtered through celite *in vacuo* and solvent was reduced. The resulting orange solid was purified via recrystallization (DCM/Et_2O) to afford orange crystals (57 mg, 55% yield). Efforts to identify the carbon signals of bound 1,5-cyclooctadiene by utilizing different NMR solvents and various temperatures were not successful, presumably due to rapid exchange. ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.85 (t, *J* = 7.5, 1H, *p*-phenyl CH), 7.64 (t, *J* = 7.9, 2H, *m*-phenyl CH), 7.62 (s, 1H, azole CH), 7.56 (d, *J* = 7.1, 2H, *o*-phenyl CH), 7.48 – 7.41 (m, 6H, PPh_3 CH), 7.37 (m, 3H, PPh_3 CH), 7.33 – 7.27 (m, 6H, PPh_3 CH), 6.65 (s, 1H, azole CH), 4.52 (m, 2H, COD CH), 4.00 (s, 3H, -CH_3), 3.89 (s, 3H, -$COOCH_3$), 3.75 (s, 3H, -$COOCH_3$), 2.53 (m, 4H, COD CH, CH_2), 2.18 (m, 4H, COD CH_2), 1.91 (m, 2H, COD CH_2). ^{13}C NMR (125 MHz, CD_2Cl_2) δ 200.27 (d, *J* = 8.9), 171.29, 166.92, 166.72, 137.73, 135.77, 133.92 (d, *J* = 11.1), 133.73, 131.61, 130.97, 130.83, 130.58, 130.54, 130.17, 129.85, 129.17 (d, *J* = 10.0), 128.69, 115.01, 112.01, 37.27, 29.58. ^{31}P NMR (202 MHz, CD_2Cl_2) δ 12.99 (s), -144.60 (hept, *J* = 714.2). Calcd. for $C_{45}H_{43}F_6IrN_2O_5P_2 \cdot H_2O$: C, 50.14; H, 4.21; N, 2.60. Found: C, 49.91; H, 3.84; N, 2.53.

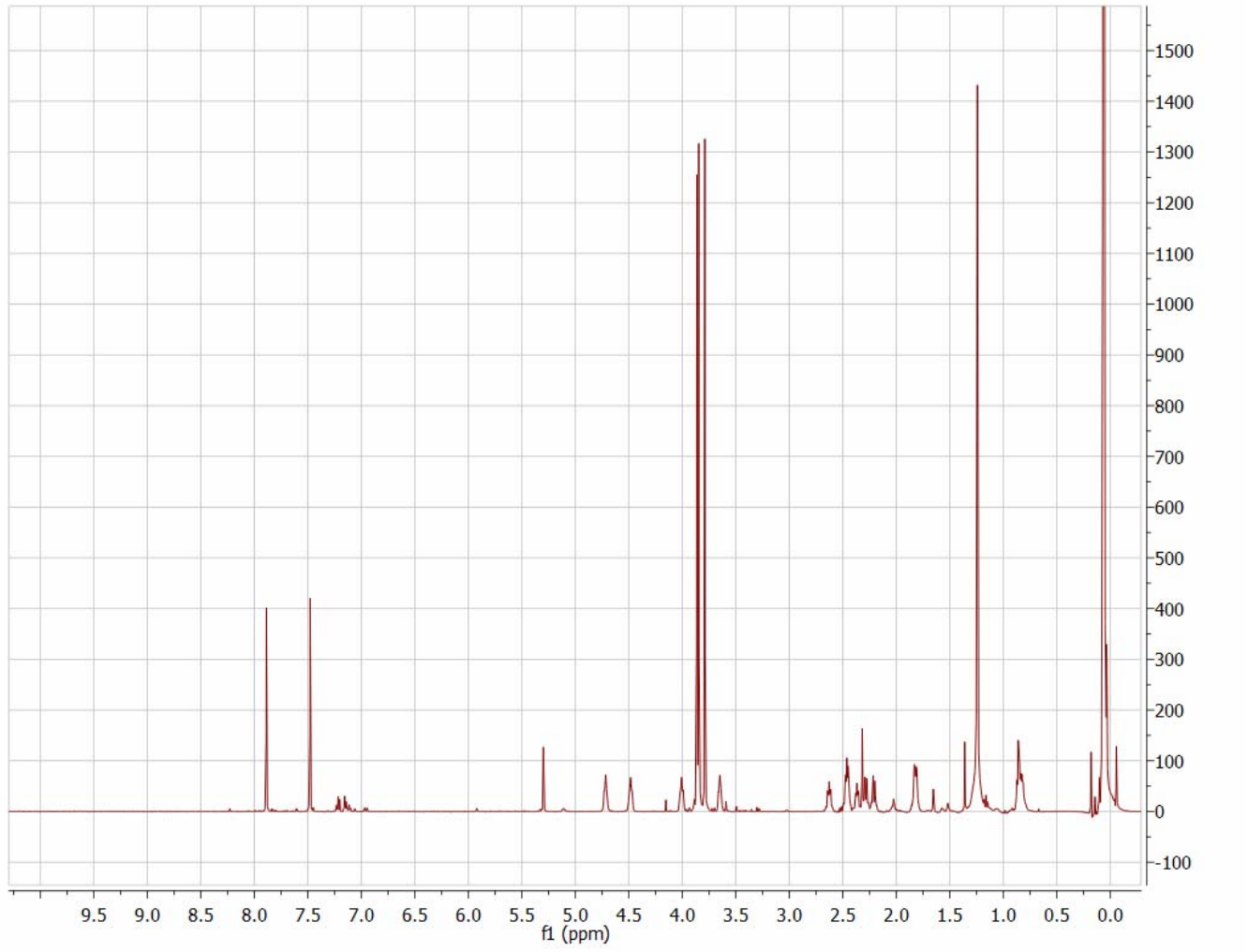
Synthesis of [(H-NHC)Ir(cod)PPh_3]PF_6 (7). To a Schlenk flask was added complex **6** (35 mg, 0.0330 mmol). The flask was evacuated and backfilled with argon three times. Degassed methanol was added and the reaction was stirred for 1 hour. The solvent was removed in vacuo. The resulting material was purified via recrystallization (DCM/Et_2O) to obtain a red-orange solid (18 mg, 57% yield). Crystals suitable for X-ray crystallographic analysis were grown by recrystallization (DCM/pentane). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.89 (s, 1H, -NH), 7.81 (s, 1H, -CH), 7.48 – 7.29 (m, 16H, -PPh_3 -CH), 4.83 (m, 1H, COD CH), 4.41 (m, 1H, COD CH), 4.13 (m, 1H, COD CH), 3.89 (s, 3H, -COOMe), 3.87 (s, 3H, -COOMe), 3.69 (m, 1H, COD CH), 3.45 (s, 3H, -NCH_3), 2.61 (m, 1H, COD CH_2), 2.42 (m, 3H, COD CH_2), 2.27 (m, 1H, COD CH_2), 2.07 (m, 1H, COD CH_2), 1.84 (m, 2H, COD CH_2). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 191.45 (d, *J* = 9.4), 167.48, 167.25, 135.49, 135.27, 133.63 (d, *J* = 11.0), 131.10, 130.21, 129.80, 128.87 (d, *J* = 10.3), 128.39, 126.65, 113.03, 110.15, 90.40 (d, *J* = 12.1), 84.92 (d, *J* =

11.4), 83.18, 82.89, 52.84, 34.23, 33.50, 32.29, 29.18, 28.67. ^{31}P NMR (202 MHz, $CDCl_3$) δ 17.19 (s), -143.93 (hept, J = 714.2). Anal. Calcd for $C_{38}H_{39}F_6IrN_2O_4P_2$: C, 47.75; H, 4.11; N, 2.93. Found: C, 48.00; H, 4.23; N, 2.91. IR (cm^{-1}): 3380.1, 2920.4, 2849.2, 1723.1, 1468.7, 1435.0, 1419.9, 1328.7, 1259.4.

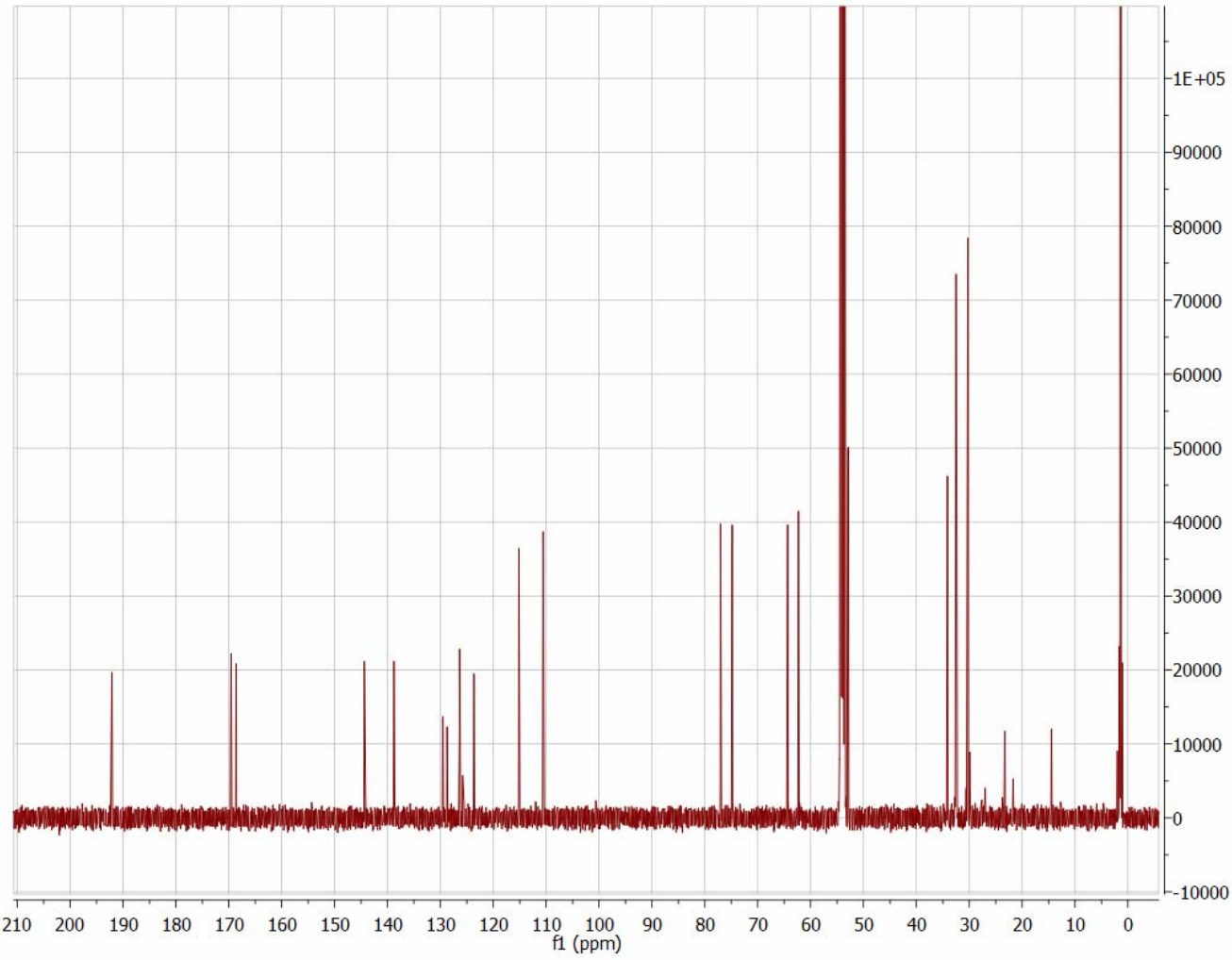
Procedure and ^{1}H and ^{13C} NMR spectra from Complex 3 Methanolysis

To a flame-dried Schlenk flask was added complex **3** (10 mg, 0.0145 mmol). The flask was evacuated and backfilled with argon three times. Degassed methanol (2 mL) was added and the suspension was allowed to stand for 7 days. A purple solid slowly precipitated from the suspension. The solvent was then removed from the flask via a filter cannula and the remaining solid was washed with toluene. The solution was filtered through celite *in vacuo* and the solution was evaporated. The resulting purple solid was subjected to NMR analysis.

^{1}H NMR, CD_2Cl_2



^{13}C NMR, CD_2Cl_2



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