Electronic Supplementary Material (ESI) for ChemComm.

ESI: Enhanced CO_2 Electroreduction Efficiency through Secondary Coordination Effects on a Pincer Iridium Catalyst

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Experimental Details

General Considerations. Nitrogen (N_2, 99.999%, Corp Brothers) and carbon dioxide (CO_2, 99.995%, laser grade, Praxair) with less than 2 ppm H_2O were used as received. Acetonitrile was dried and deoxygenated using literature procedures,[1] tested *via* Karl Fischer titration for trace amounts of water, and stored over 4Å molecular sieves until use. 18.2 MΩ deionized water was provided by a Milli-Q water purification system and was sparged with and stored under N_2. Tetrabutylammonium hexafluorophosphate ($^n\mathrm{Bu}_4\mathrm{NPF}_6$, electrochemical grade, Sigma-Aldrich) was dried at 60 °C under vacuum for 24 hr and stored in a glovebox. Compounds **1**,[2] **2**,[3] and $\mathrm{H[B(Ar^F)_4]{\bullet}(Et_2O)_2}$[4] ($\mathrm{B(Ar^F)_4}$ = tetrakis[3,5-bis(trifluoromethyl)phenyl]borate) were prepared as previously described. All other reagents were purchased from Aldrich, Acros, Alpha Aesar or Strem chemicals and used as received. Manipulations of air-sensitive materials were conducted using standard vacuum, Schlenk, or glovebox techniques. ^{1}H and ^{31}P NMR spectra were recorded on Bruker Avance DRX-400 (400 MHz) and Avance 600 (600 MHz) spectrometers. ^{1}H chemical shifts are referenced to residual solvent signals, and ^{31}P chemical shifts are referenced to a H_3PO_4 external standard. Gaseous products were analyzed on a Buck Scientific 910 gas chromatograph (GC) in the Multiple Gas #3 configuration with automated sample loop.

Observation of $\mathbf{[(PN^HP)IrH_2(MeCN)]^+}$ (**3**). A J. Young NMR tube was charged with $\mathrm{(PN^HP)IrH_3}$ (**1**) (10 mg, 0.020 mmol) in CD_3CN and treated with $\mathrm{H[B(Ar^F)_4]{\bullet}(Et_2O)_2}$ (26 mg, 0.030 mmol). The formation of **3** was monitored by NMR spectroscopy and complete conversion occurred within 30 min at ambient temperature. ^{1}H NMR (CD_3CN):

δ 7.71 (br s, 8H, *o*-Ar), 7.67 (br s, 4H, *p*-Ar), 3.32 (m, 2H, CH_2), 2.52 (m, 2H, CH_2), 2.19 (m, 2H, CH), 2.12 (m, 2H, CH_2), 2.06 (m, 2H, CH), 1.78 (m, 2H, CH_2), 1.24-1.29 (m, 12H, CH_3), 1.03 (dd, 6H, CH_3), 0.96 (dd, 6H, CH_3), -20.14 (t, 1H, Ir-H, J = 13 Hz), -22.27 (t, 1H, Ir-H, J = 16 Hz) (N-H resonance not located). $^{13}C\{^1H\}$ NMR taken from HSQC (CD_3CN): δ 16.5 (CH_3), 17.9 (CH_3), 19.8 (CH_3), 20.6 (CH_3), 22.5 (CH), 26.5 (CH), 32.4 (CH_2), 55.2 (CH_2), 117.6 (*p*-Ar), 134.5 (*o*-Ar). $^{31}P\{^1H\}$ NMR (CD_3CN): 51.37 (s, 2P).

General Procedures for Electrochemistry Experiments

Cyclic voltammetry and bulk electrolysis experiments were performed on a Pine Research AFCBP1 bipotentiostat. The three-electrode system included either a smaller glassy carbon (GC) working electrode (7.1 mm^2, BASi) or larger GC electrode (19.6 mm^2, Bio-Logic) and platinum (Pt) mesh counter electrode (99.9%, Alfa Aesar). The reference electrode was $Ag/AgNO_3$ (*i.e.*, Ag/Ag^+) non-aqueous electrode filled with 0.01 M $AgNO_3$ and 0.1 M $^nBu_4NPF_6$ in CH_3CN (-0.08 V *vs* Fc/Fc^+, BASi). Prior to each experiment, the GC electrode was polished in succession with a 1-µm, 0.3-µm, and 0.05-µm alumina slurry to obtain a mirror finish, sonicated in 50:50 acetone and Milli-Q water, rinsed in Milli-Q water and dried *in vacuo*. Cyclic voltammograms (CVs) were conducted in a gas-tight one-compartment cell to minimize internal resistance impacting measured potentials. For electrolysis, the counter electrode was separated from the working electrode in a gas-tight two-compartment cell with vigorous stirring in the cathode compartment. Electrolyses of 1 mM **1** were conducted under 1 atm CO_2 in 5-6 mL 12% v/v H_2O/CH_3CN (0.1 M $^nBu_4NPF_6$, RT, no *iR* compensation). For control experiments, **1** was omitted and/or N_2 replaced CO_2. Ferrocene was added at the end of each experiment and the potential was converted relative to the midpoint potential of the Fc/Fc$^+$ CV. Electrolysis experiments lasting longer than 24 hrs required enhancements to maintain system stability and to increase turnover frequency. Of note, a salt bridge separated the Ag/Ag$^+$ reference electrode from the cathode compartment to avoid contamination from Ag$^+$. A Luggin capillary was also used to reduce possible Ohmic drop between the working and reference electrodes.

Product Analysis

The liquid products of electroreduction were analyzed by ^{1}H NMR spectrometry. The liquid phase was acidified with an aqueous solution of HCl (18%), spiked with a benzene internal standard and then diluted with CD_3CN. Gaseous products of electroreduction were analyzed by gas chromatography using both a FID and a TCD. The headspace of the electrochemical cell was connected to the GC sample loop. A bubbler was then connected to the back end of the loop to confirm a gas-tight system. Gaseous products were analyzed at random points during electrolysis, at least thrice in a 24-hr period and after at least 1 hr from the start of experiment to ensure adequate degassing of connections.

Selected Spectra of Product Analysis

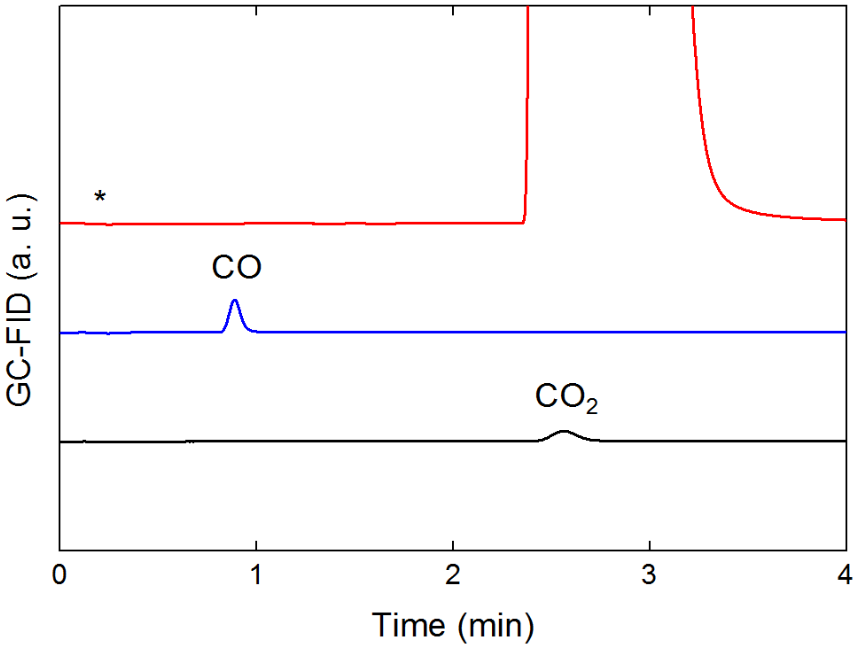

Fig. S1 GC traces from FID channel *in situ* during bulk electrolysis with potential held at -1.73 V *vs* Fc/Fc$^+$ (red) juxtaposed with calibration standards (blue and black). All traces were taken at least 1 hr after the start of electrolysis. Asterisk (*) indicates valve switching.

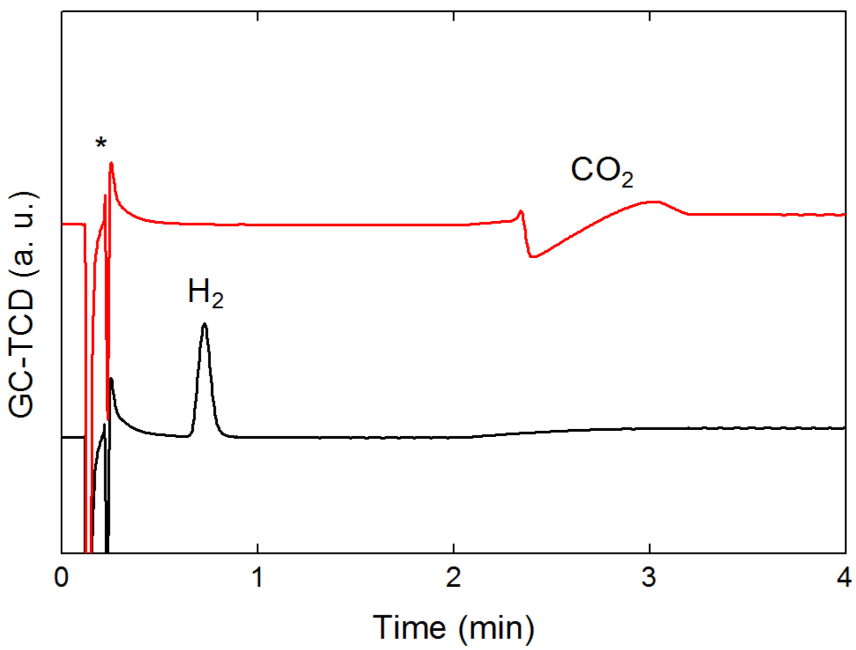

Fig. S2 GC trace from TCD channel *in situ* during bulk electrolysis with potential held at -1.73 V *vs* Fc/Fc$^+$ (red) juxtaposed with calibration standard (black). All traces were taken at least 1 hr after the start of electrolysis. Asterisk (*) indicates valve switching.

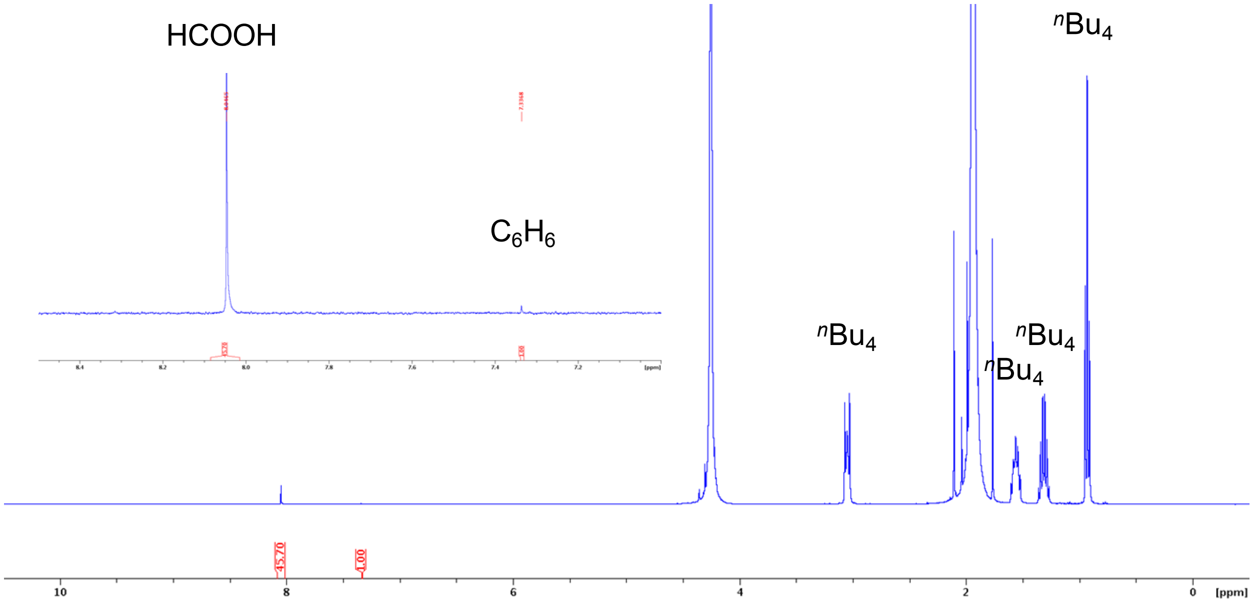

Fig. S3 ^{1}H NMR spectrum of formate electrolysis product following acidification (*vide supra*) and addition of a benzene internal standard in acetonitrile-d_3. Spectrum taken post-electrolysis with potential held at -1.73 V *vs* Fc/Fc$^+$. Insert corresponds to a spectral region between 7.0 and 8.4 ppm.

Selected Electrochemical Data

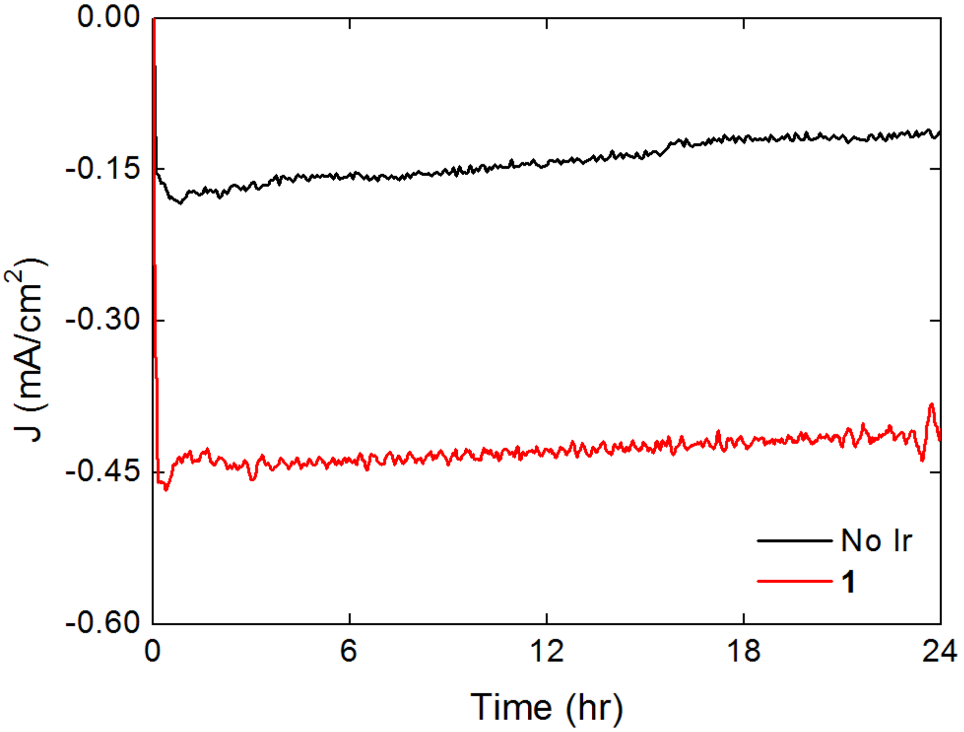

Fig. S4 Electrolysis current in the absence of catalyst (black) and in the presence of 1 mM **1** (red) under CO_2 in 12% H_2O/CH_3CN with potential held at -1.73 V *vs* Fc/Fc^+ and vigorous stirring. Additional conditions: glassy carbon electrode, 0.1 M $^n Bu_4NPF_6$ electrolyte, 1 atm CO_2, RT, no *iR* compensation.

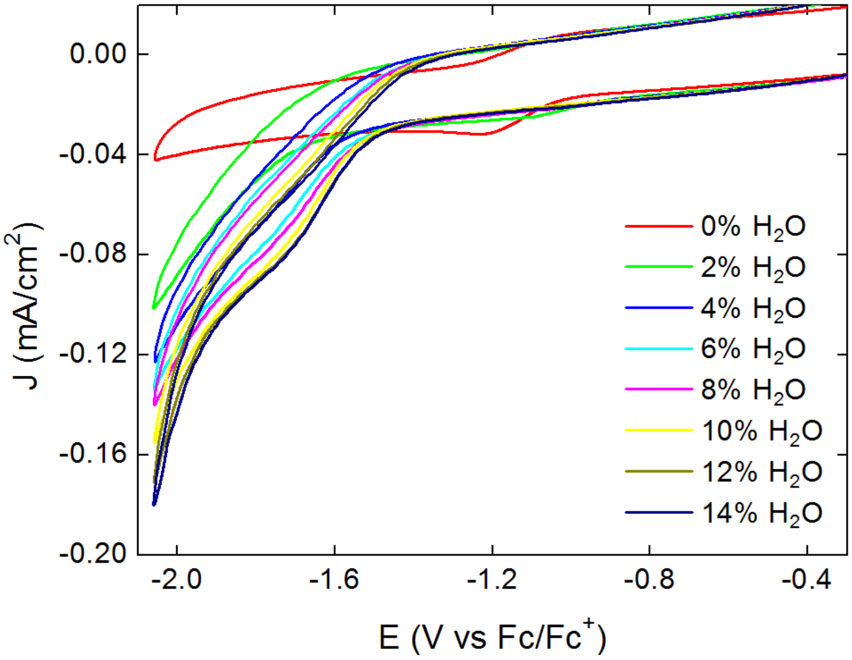

Fig. S5 CVs of 1 mM **1** in CH_3CN under CO_2 with 0-14% added H_2O from +0.2 V to -1.4 V vs Fc/Fc^+.

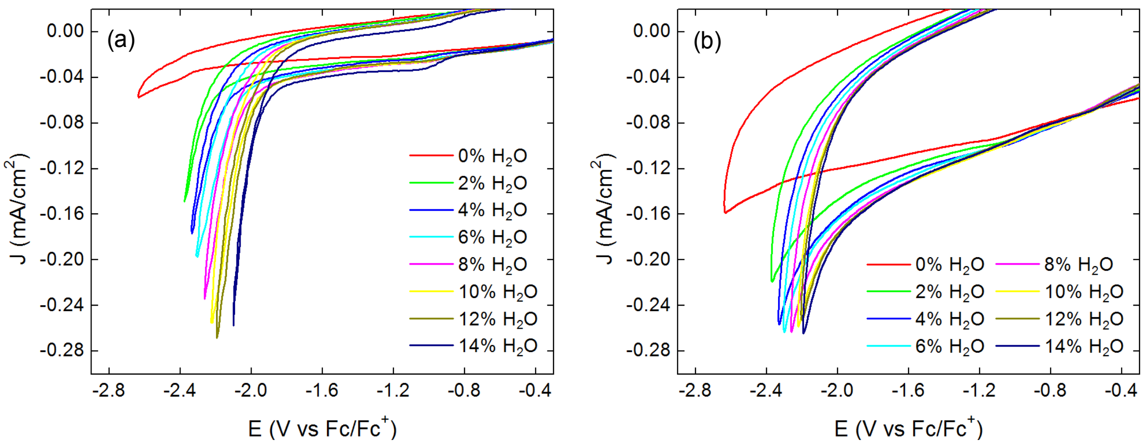

Fig. S6 CVs of electrolyte solution (0.1 M ^{n}Bu$_4$NPF$_6$) with 0-14% added H_2O under N_2 at (a) 10 mV/s and (b) 100 mV/s scan rates.

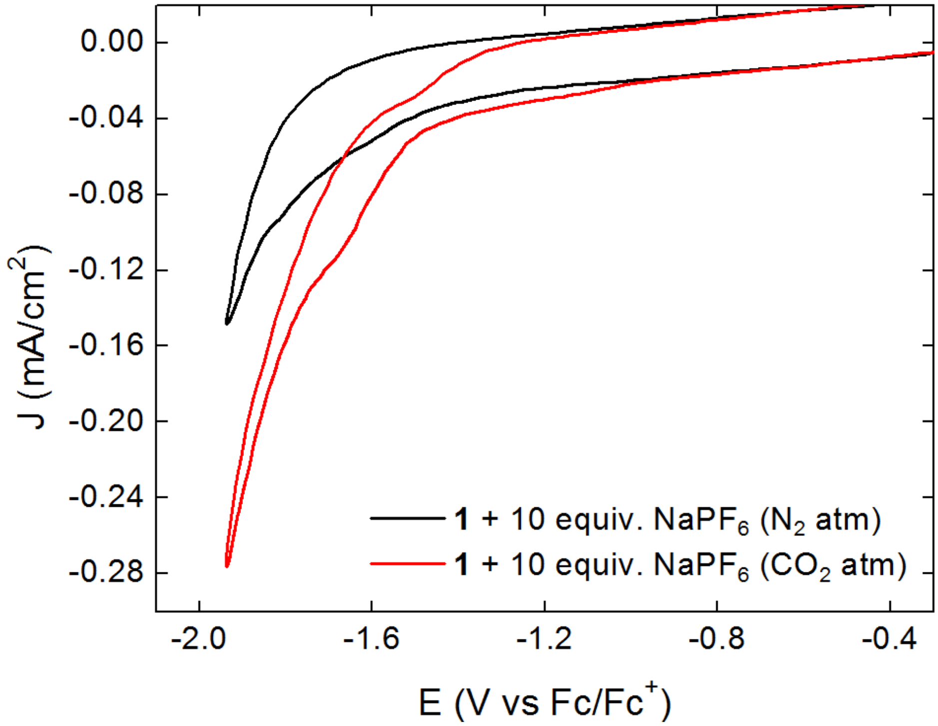

Fig. S7. CVs of 1 mM **1** and 10 mM (*i.e.*, 10 equiv.) $NaPF_6$ under N_2 (black) and 1 atm CO_2 (red). Additional conditions: glassy carbon electrode (7.1 mm^2), 12% H_2O/CH_3CN solvent, 0.1 M ^{n}Bu$_4$NPF$_6$ electrolyte, 10 mV/s scan rate.

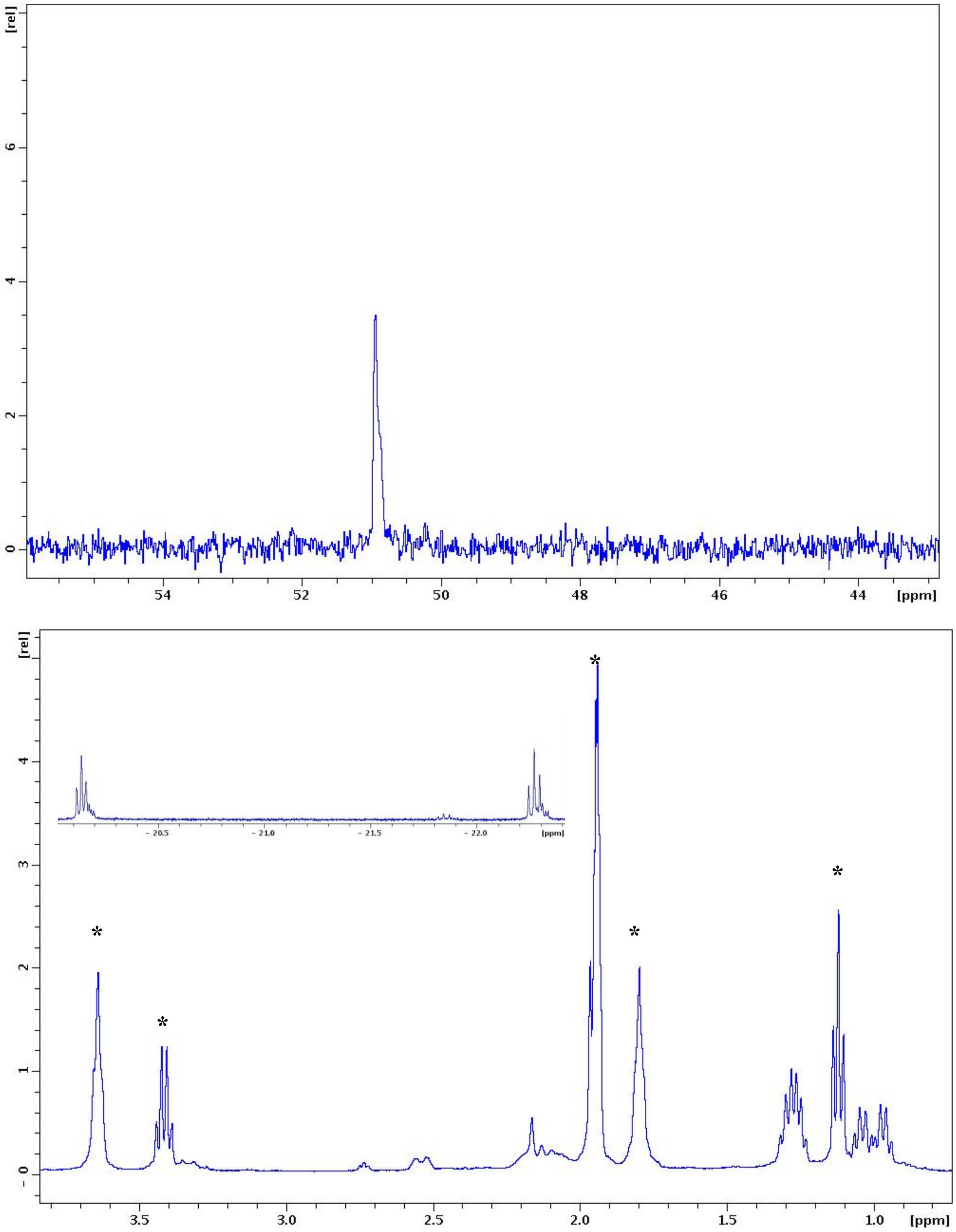

Fig. S8 $^{31}P\{^{1}H\}$ NMR (top) and ^{1}H NMR (bottom) spectra of **3** generated from $H[B(Ar^{F})_4]\bullet(Et_2O)_2$ addition to **1** in acetonitrile-*d_3*. An insert for the upfield region of the ^{1}H NMR spectrum is provided. The * denotes residual THF, diethyl ether, and acetonitrile solvents.

References

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[2] Z. E. Clarke, P. T. Maragh, T. P. Dasgupta, D. G. Gusev, A. J. Lough and K. Abdur-Rashid, *Organometallics*, 2006, **25**, 4113-4117
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