Synthesis and Characterization of Rhodium, Iridium, and Palladium complexes of a Diarylamido-Based PNSb Pincer Ligand

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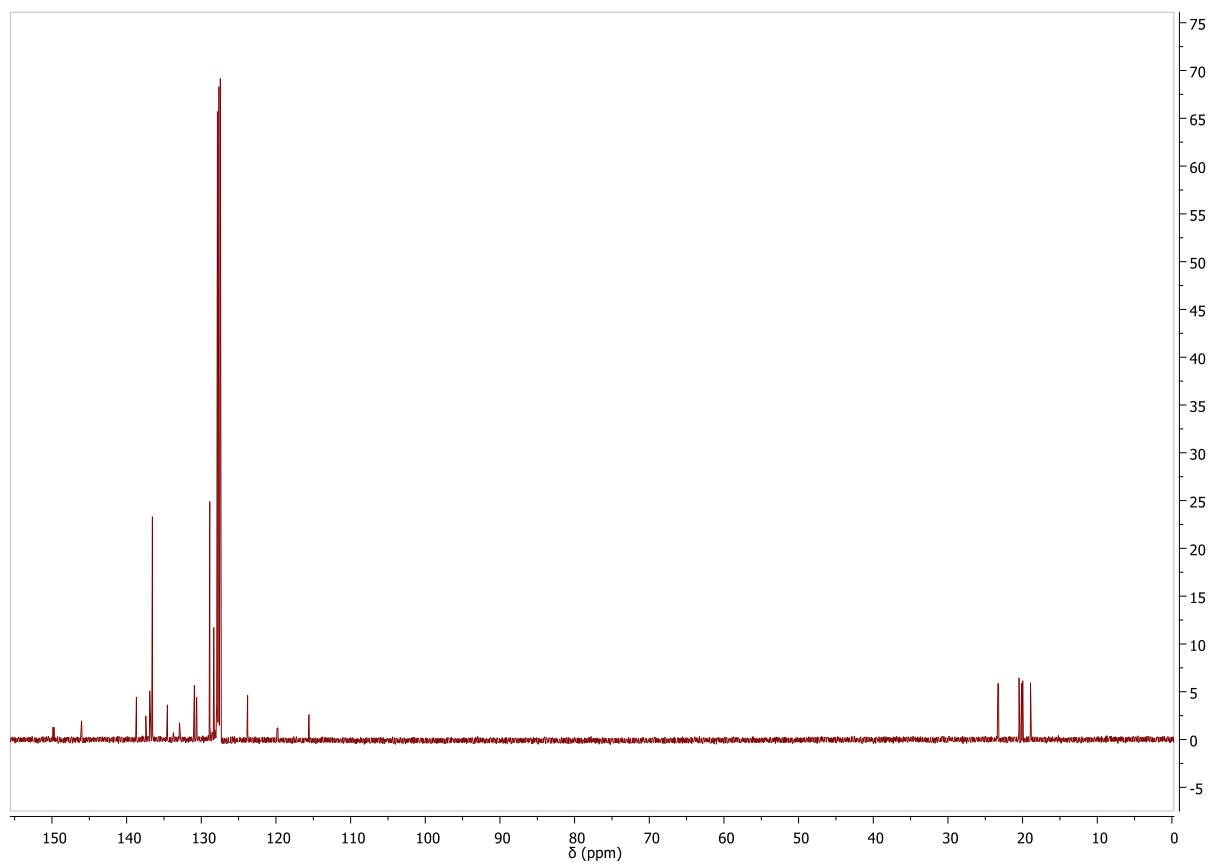
Figure S1. $^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6) spectrum of $^{iPr}PN^HSb^{Ph}$.
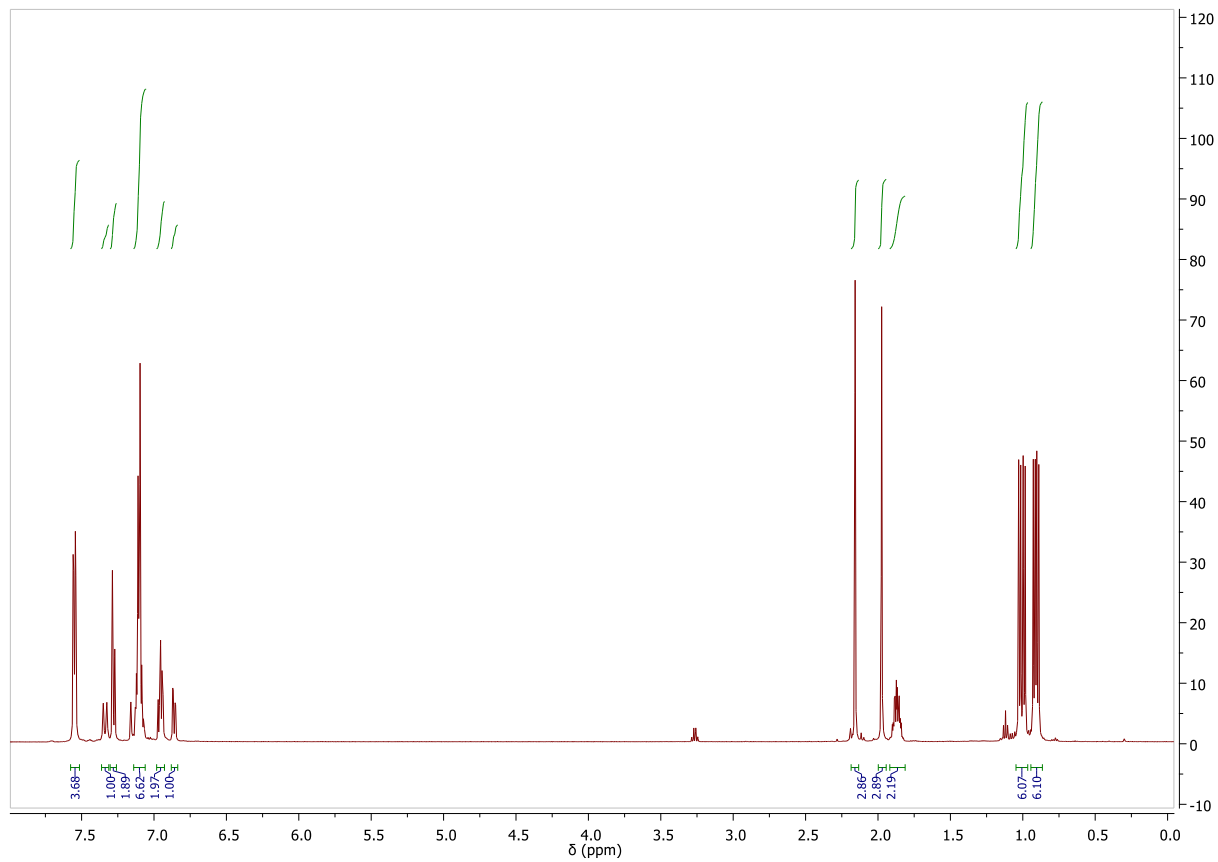
Figure S2. ^{1}H NMR (500 MHz, C$_6$D$_6$) spectrum of ^{iPr}PN^{H}Sb^{Ph}. Sample contains residual diethyl ether and grease from solvent.
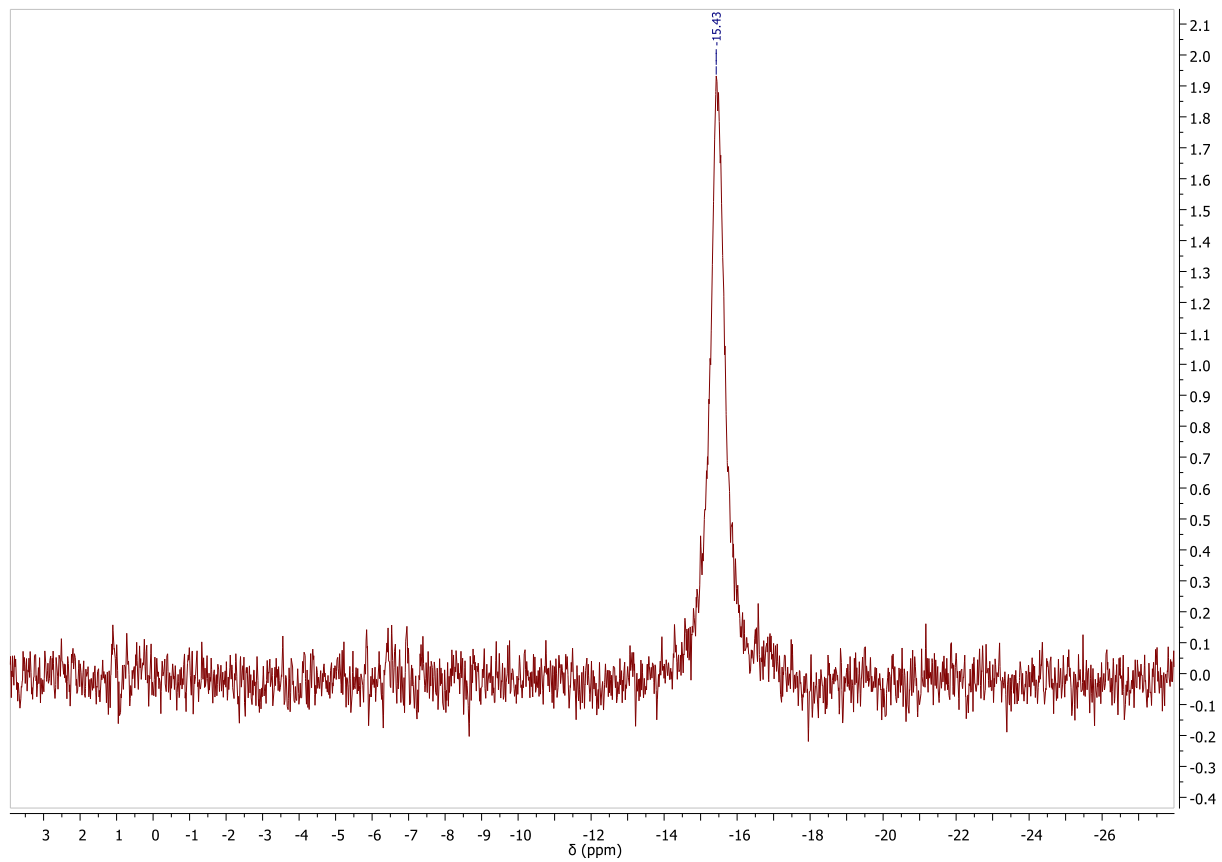
Figure S3. $^{31}P\{^1H\}$ NMR (202 MHz, C$_6$D$_6$) spectrum of **^{iPr}PN^{H}Sb^{Ph}**.
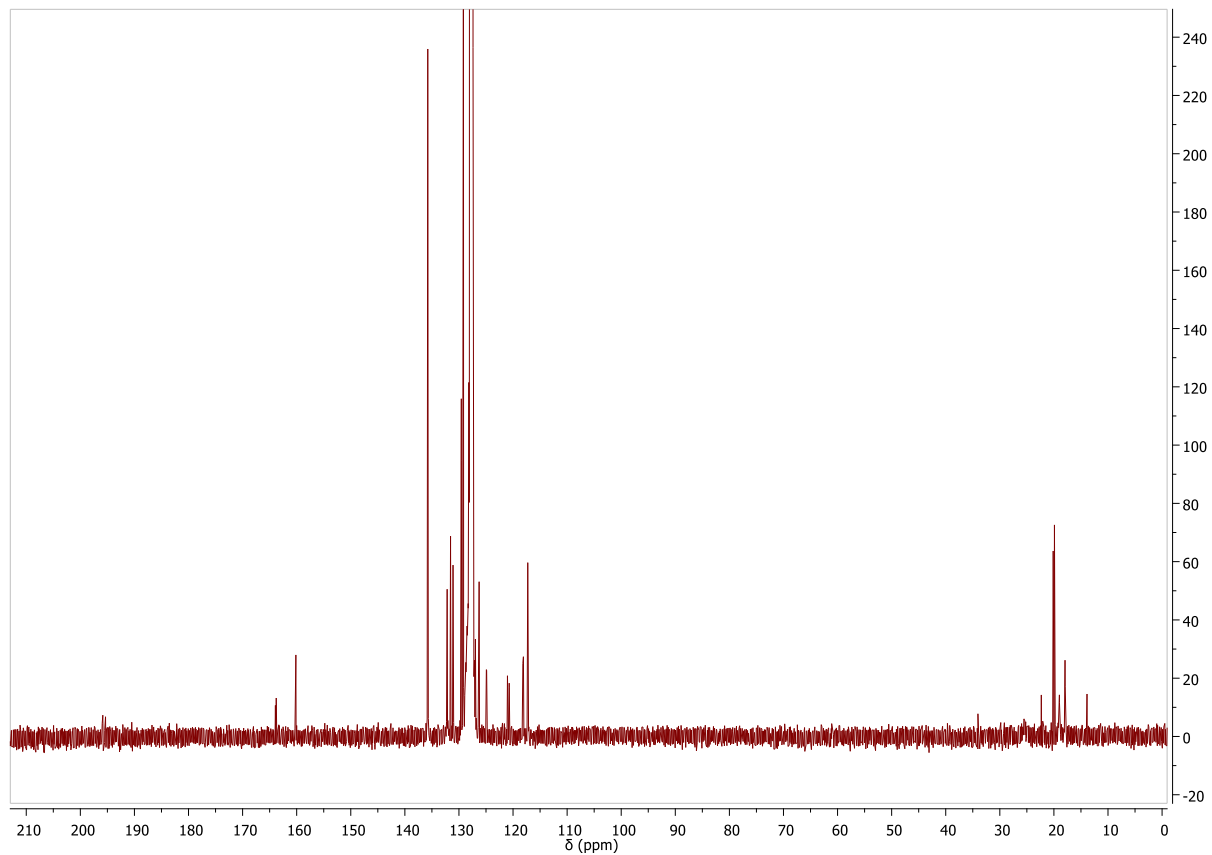
Figure S4. $^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6) spectrum of (**^{iPr}PNSb^{Ph})Rh(CO)**. Sample contains residual pentane from solvent.
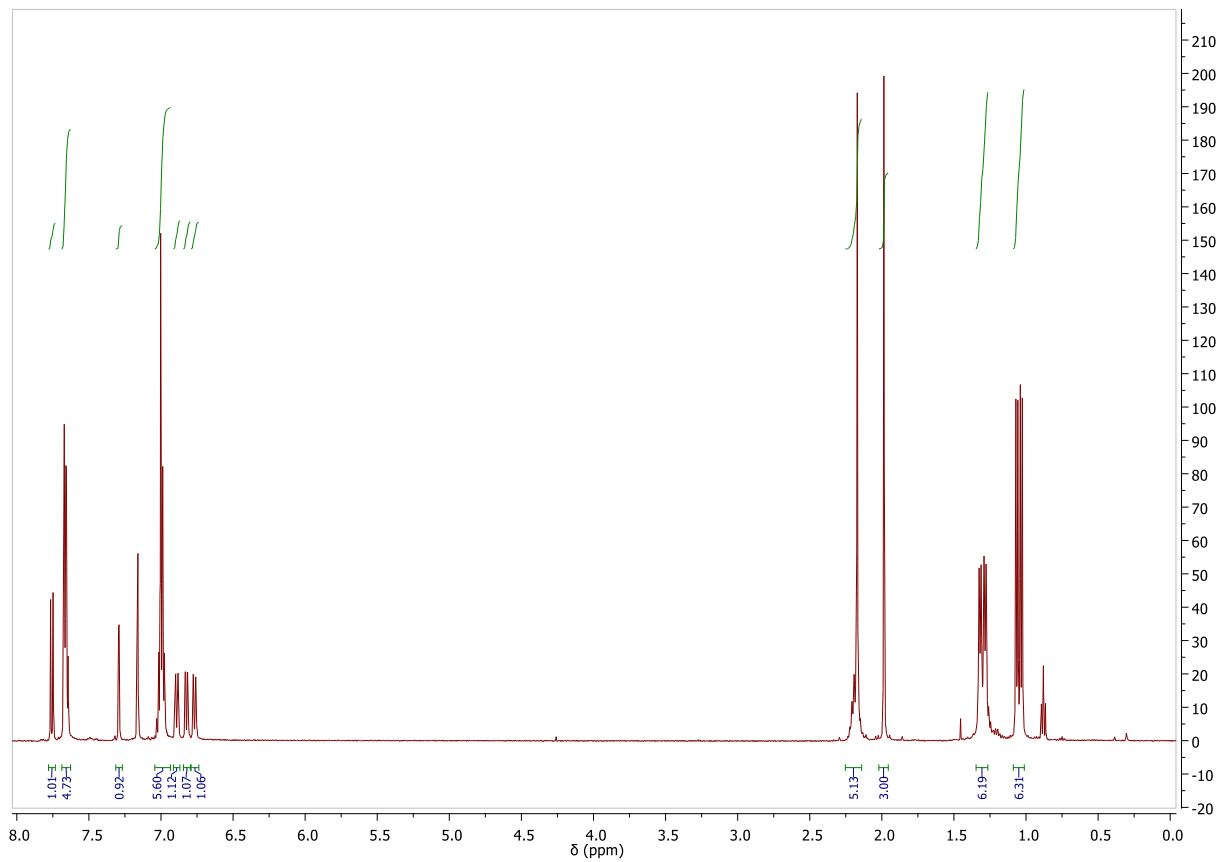
Figure S5. ^{1}H NMR (500 MHz, C$_6$D$_6$) spectrum of (**^{iPr}PNSb^{Ph})Rh(CO)**. Sample contains residual pentane and grease from solvent.
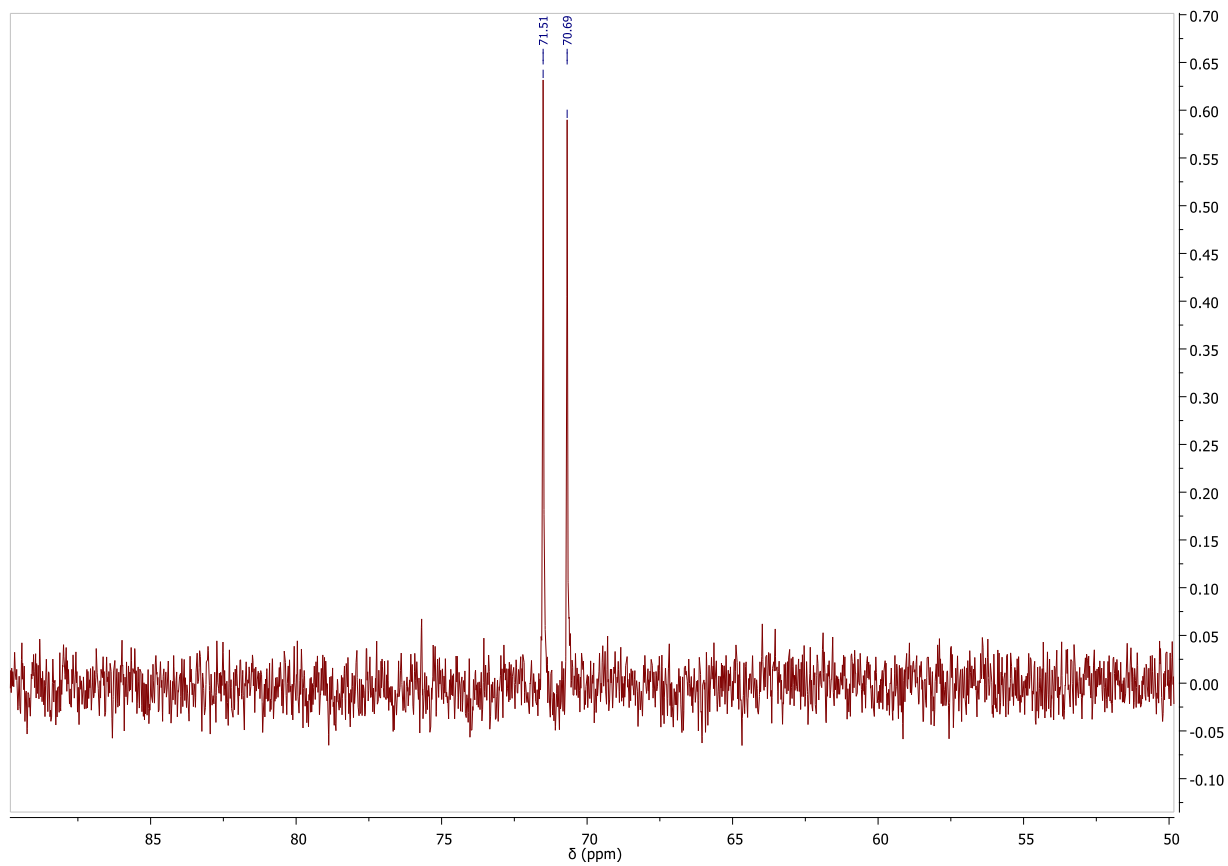
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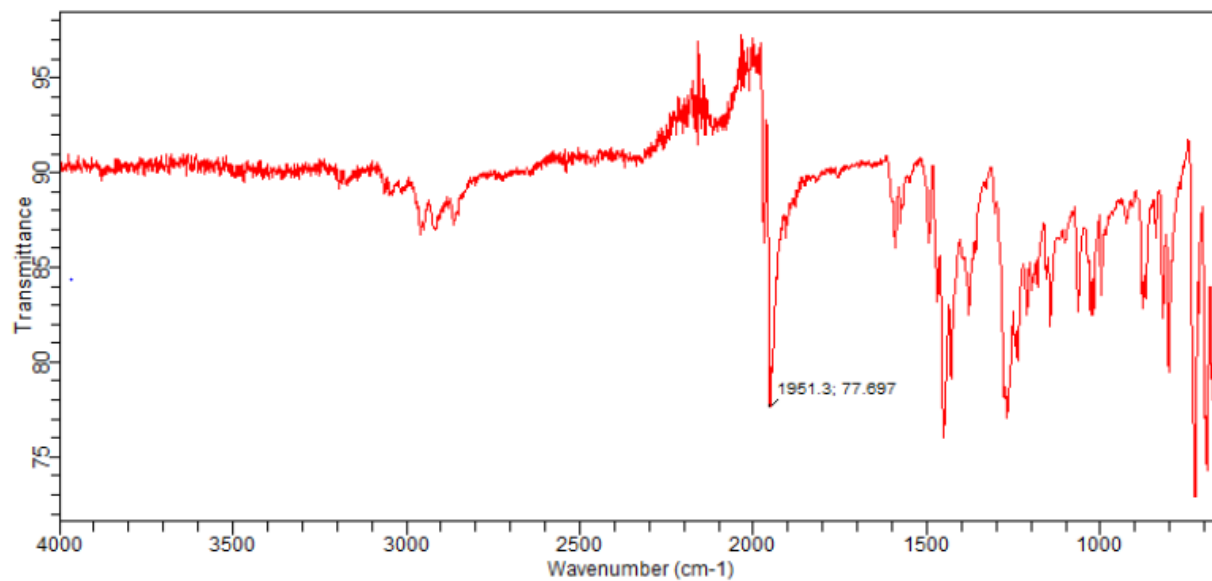
Figure S7. ATR-IR Spectrum of (**^{iPr}PNSb^{Ph})RhCO** featuring diagnostic CO stretch at 1951 cm^{-1}
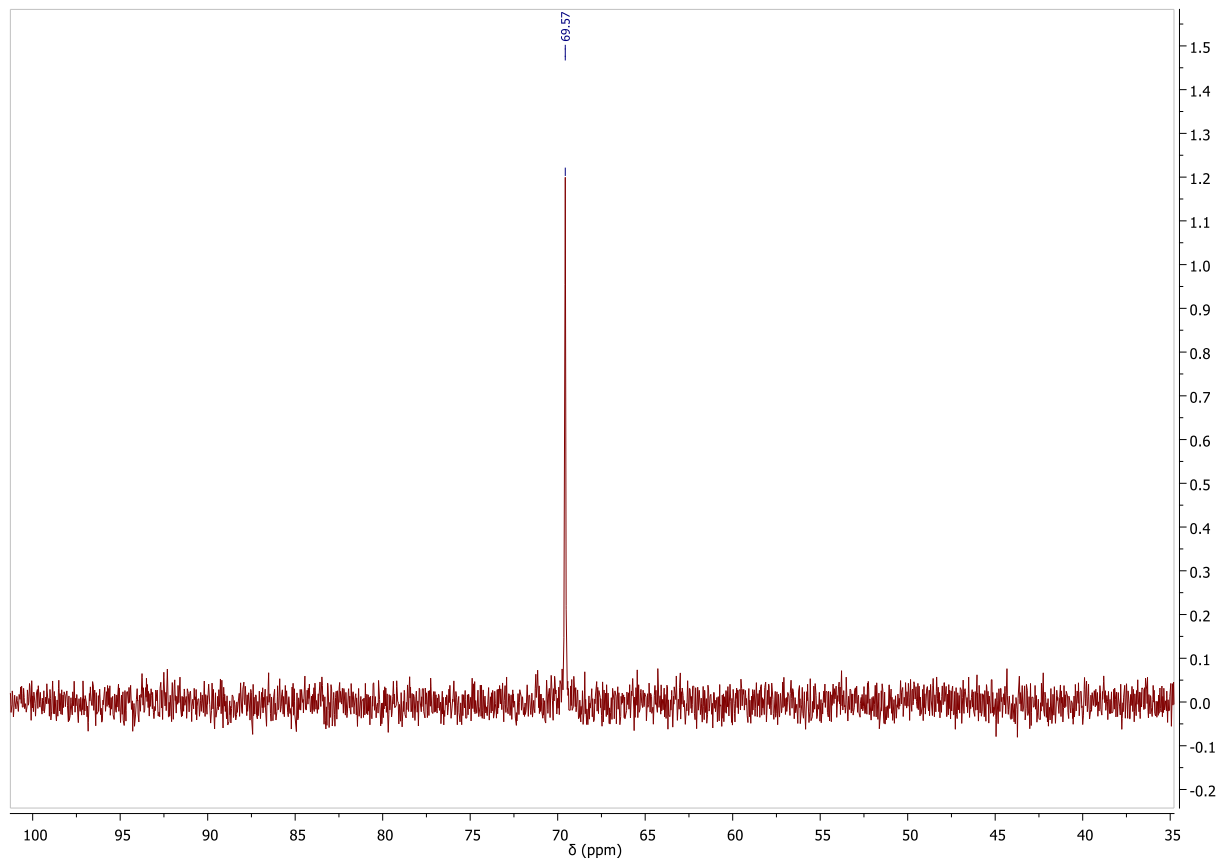
Figure S8. $^{31}P\{^1H\}$ NMR (202 MHz, C_6D_6) spectrum of **(^{iPr}PNSb^{Ph})PdCl**.
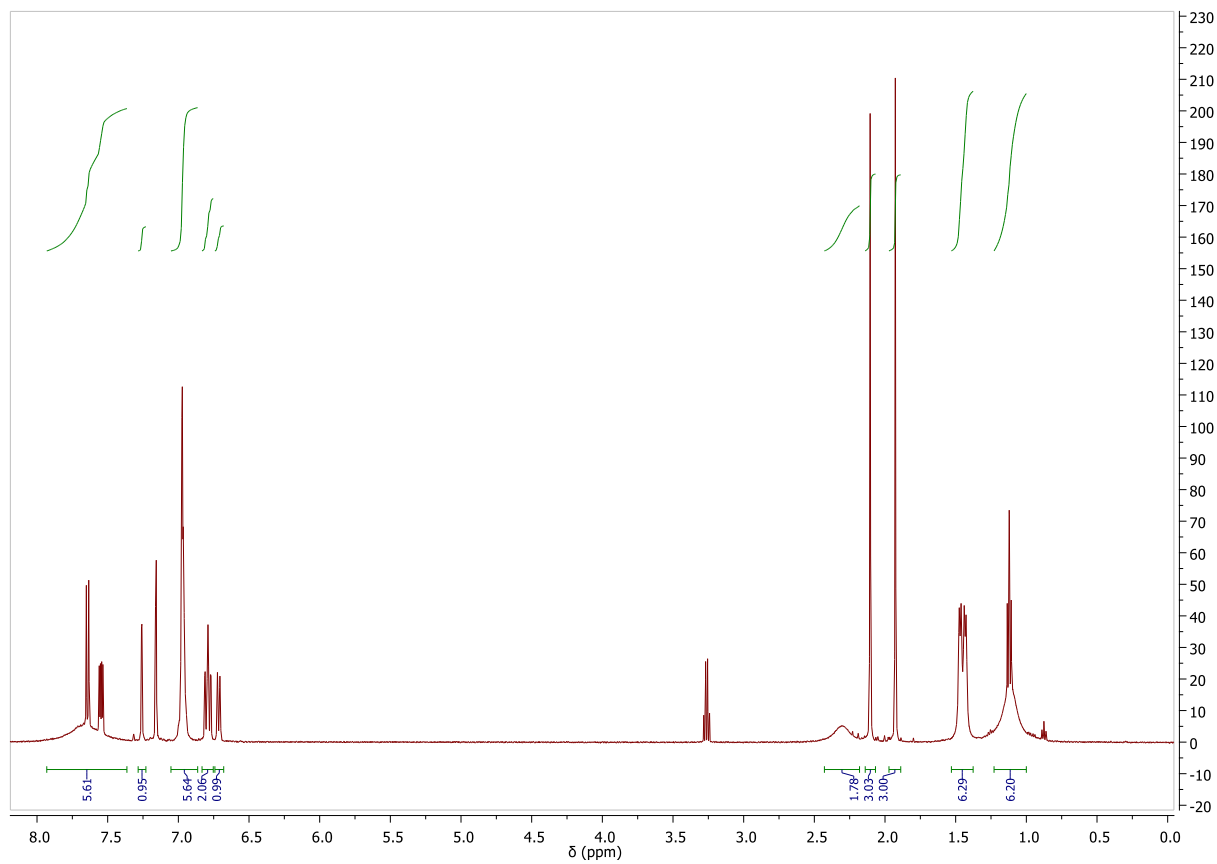
Figure S9. ^{1}H NMR (500 MHz, C$_6$D$_6$) spectrum of (**^{iPr}PNSb^{Ph})PdCl**. Sample contains residual pentane and diethyl ether from solvent.
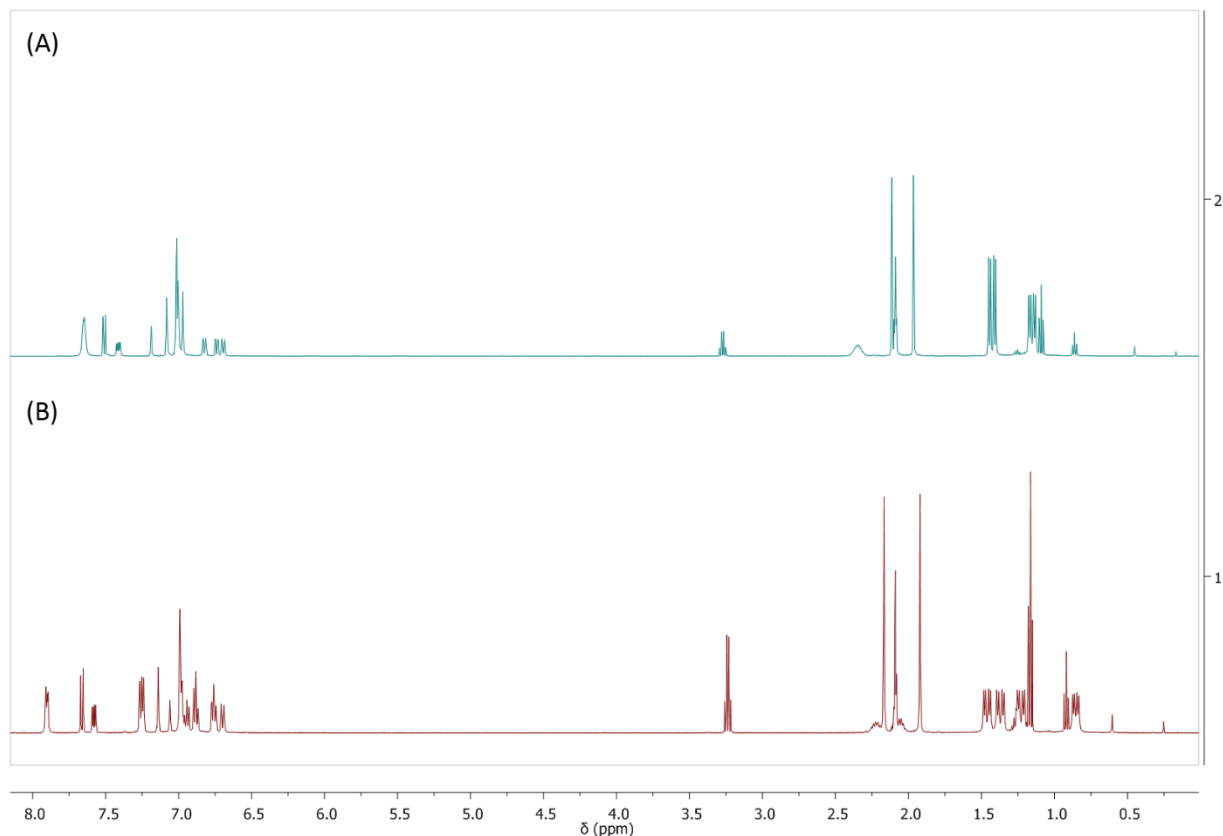
Figure S10. (A) ^{1}H NMR (500 MHz, toluene-d$_8$, 60 °C) spectrum of **(^{iPr}PNSb^{Ph})PdCl (B)** ^{1}H NMR (500 MHz, toluene-d$_8$, -40 °C) spectrum of **(^{iPr}PNSb^{Ph})PdCl**. Sample contains residual pentane and diethyl ether from solvent.

VT NMR Data for (^{iPr}PNSb^{Ph})PdCl: ^{1}H NMR (500 MHz, toluene-d$_8$, 60 °C): δ 7.65 (d, *J* = 3.6 Hz, 4H, *-SbPh$_2$*), 7.51 (d, *J* = 8.5 Hz, 1H, *Sb-ring C-H*), 7.41 (dd, *J* = 8.6, 4.2 Hz, 1H, *P-ring C-H*), 7.19 (s, 1H, *Sb-ring C-H*), 7.03 – 6.99 (m, 6H, *-SbPh$_2$*), 6.82 (d, *J* = 9.0 Hz, 1H, *aromatic backbone C-H*), 6.74 (dd, *J* = 8.4, 2.0 Hz, 1H, *aromatic backbone C-H*) 6.69 (d, *J* = 8.6 Hz, 1H, *P-ring C-H*), 2.42 – 2.30   (m, 2H, *iPr-methine*), 2.11 (s, 3H, *benzylic CH$_3$*), 1.97 (s, 3H, *benzylic CH$_3$*), 1.43 (dd, *J* = 17.6, 7.0 Hz, 6H, *iPr-CH$_3$*), 1.15 (dd, *J* = 16.1, 7.0 Hz, 6H, *iPr-CH$_3$*). ^{1}H NMR (500 MHz, toluene-d$_8$, -40 °C): δ 7.89 (dd, *J* = 6.9, 2.4 Hz, 2H, *-SbPh$_2$-ortho C-H*), 7.65 (d, *J* = 8.5 Hz, 1H, *Sb-ring C-H*), 7.57 (dd, *J* = 8.6, 4.2 Hz, 1H, *P-ring C-H*), 7.27 -7.22 (m, 3H, *overlapping* -SbPh$_2$ *and Sb-ring C-H*), 7.00 – 6.91 (m, 4H, *-SbPh$_2$*), 6.87 (t, *J* = 7.3 Hz, 2H, *-SbPh$_2$*), 6.77 – 6.72 (m, 2H, *two overlapping aromatic backbone C-H*), 6.69 (d, *J* = 8.7 Hz, 1H, *P-ring C-H*), 2.29 -2.19 (m, 1H, *iPr-methine*), 2.17 (s, 3H, *benzylic CH$_3$*), 2.07 – 2.03 (m, 1H, *iPr-methine*), 1.92 (s, 3H, *benzylic CH$_3$*), 1.46 (dd, *J* = 16.8, 6.9 Hz, 3H, *iPr-CH$_3$*), 1.37 (dd, *J* = 18.5, 7.0 Hz, 3H, *iPr-CH$_3$*), 1.23 (dd, *J* = 17.8, 7.0 Hz, 3H, *iPr-CH$_3$*), 0.85 (dd, *J* = 14.6, 6.9 Hz, 3H, *iPr-CH$_3$*).
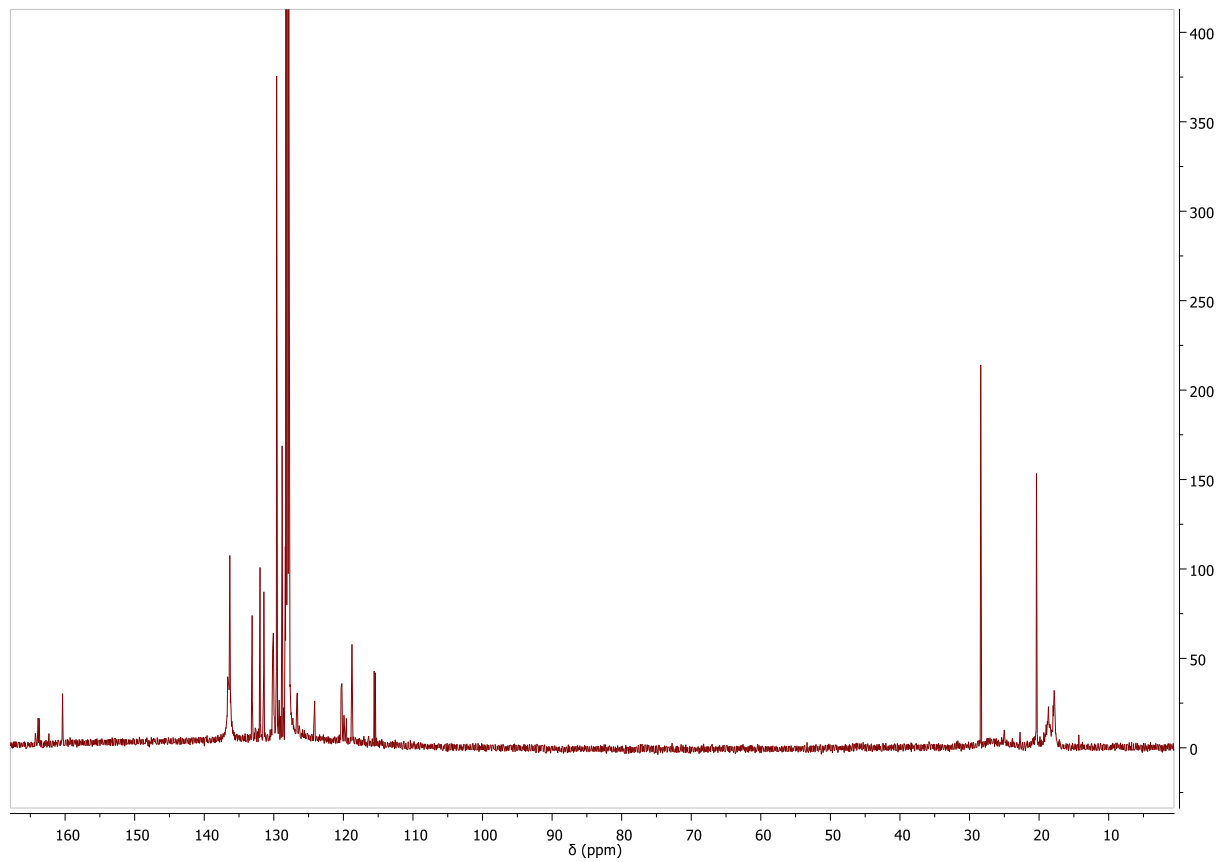
Figure S11. $^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6) spectrum of (**^{iPr}PNSb^{Ph})PdCl**.
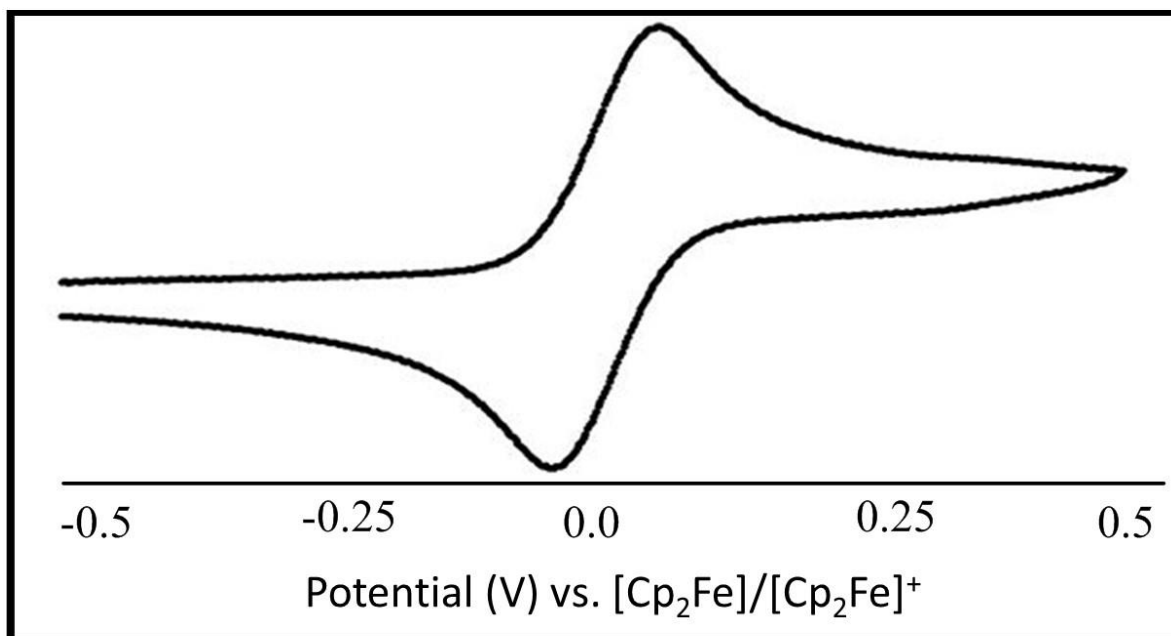
Figure S12. Cyclic voltammogram of (**^{iPr}PNSb^{Ph})PdCl** in CH_2Cl_2 at 25 °C. The scan rate was 100 mV/s in the positive direction. The cyclic voltammogram was obtained with 0.1 M [Bu$_4$N][PF$_6$] as the supporting electrolyte and resulted in a measured potential ($E_{1/2}$) equal to 0.0 V vs. [Cp$_2$Fe]/[Cp$_2$Fe]$^+$.
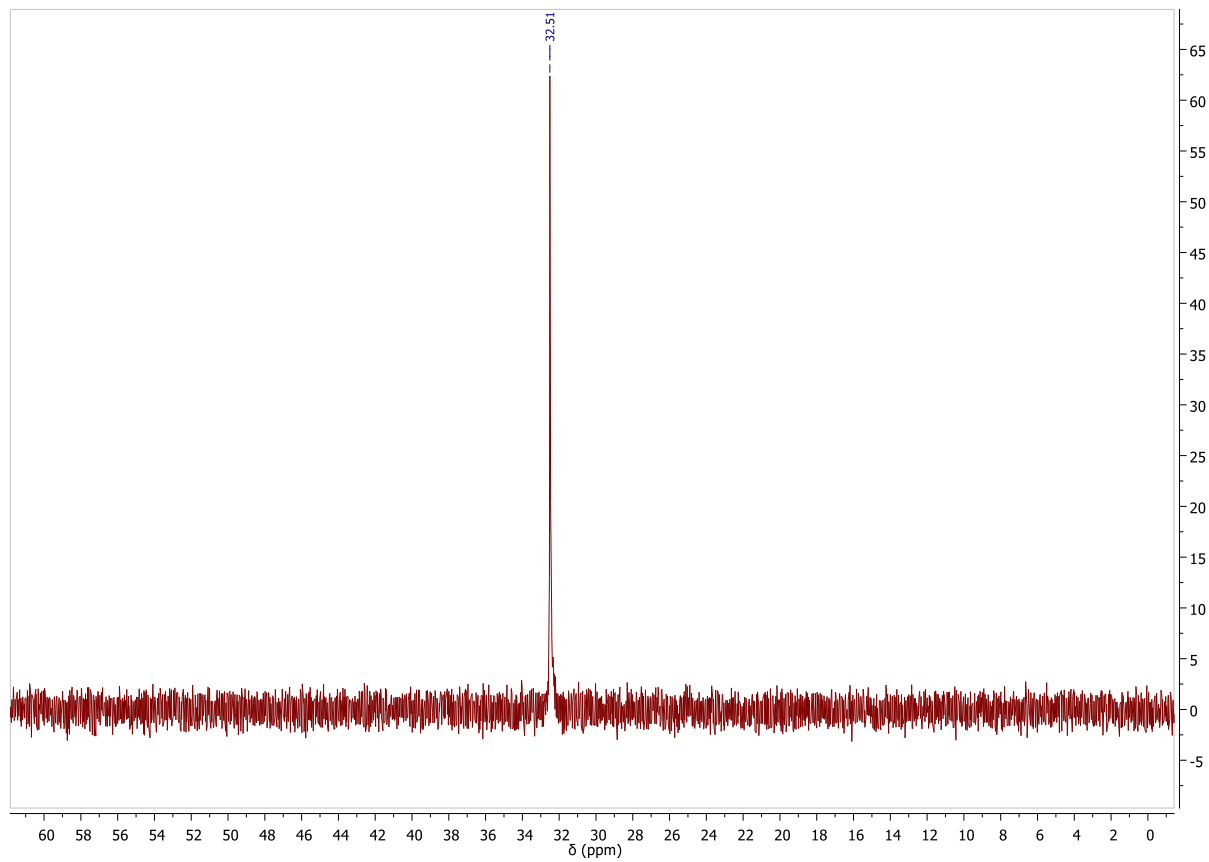
Figure S13. $^{31}P\{^1H\}$ NMR (202 MHz, C_6D_6) spectrum of **(^{iPr}PNSb^{Ph})Ir(COE)**.
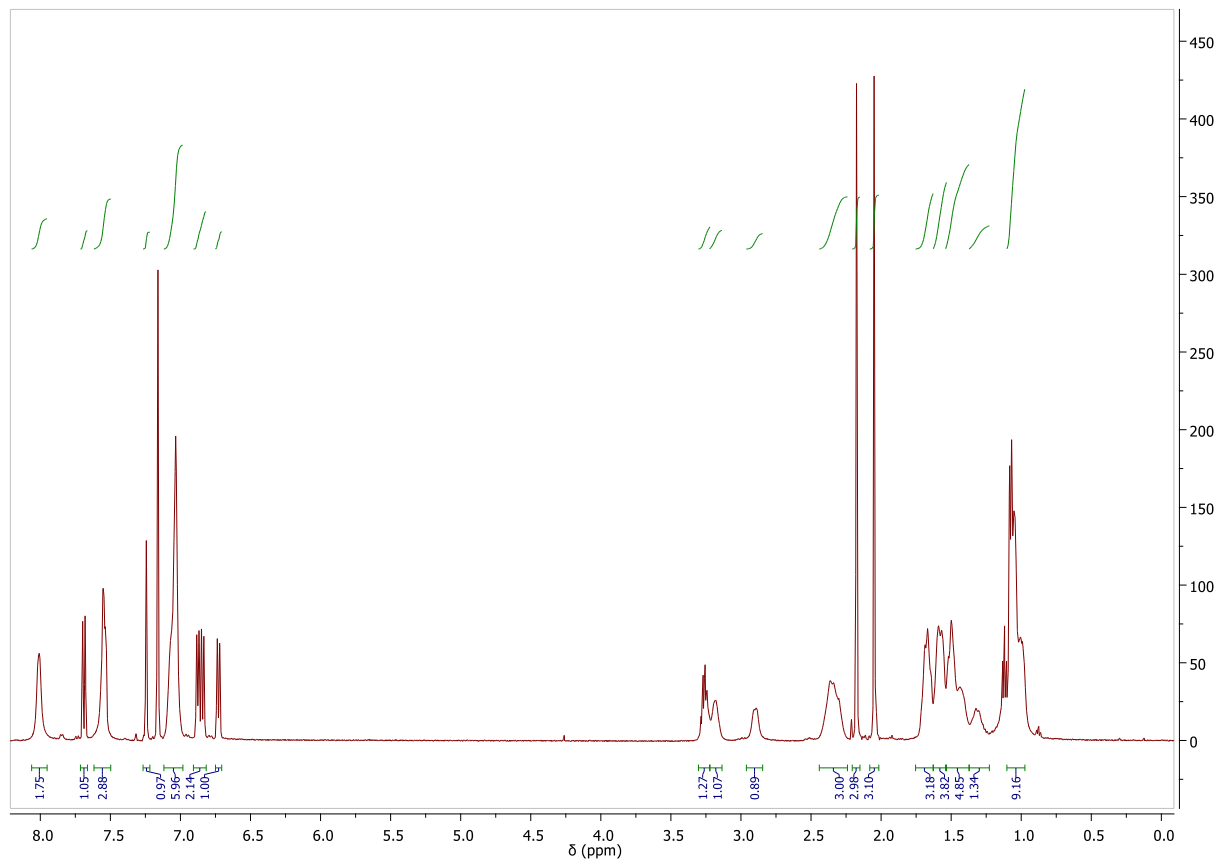
Figure S14. ^{1}H NMR (500 MHz, C$_6$D$_6$) spectrum of (**^{iPr}PNSb^{Ph})Ir(COE)**. Sample contains residual diethyl ether and pentane from solvent.

Figure S15. Test for the catalytic dehydrogenative borylation of 4-ethynyl toluene using 1 mol % (**iPrPNSbPh)Ir(COE)** with 1,4-dioxane as an internal standard, resulting in 36% formation of the desired alkynylboronate.

II. X-ray data collection, solution, and refinement for (^{iPr}PNSb^{Ph})Rh(CO) (CCDC 1843710).

Data Collection

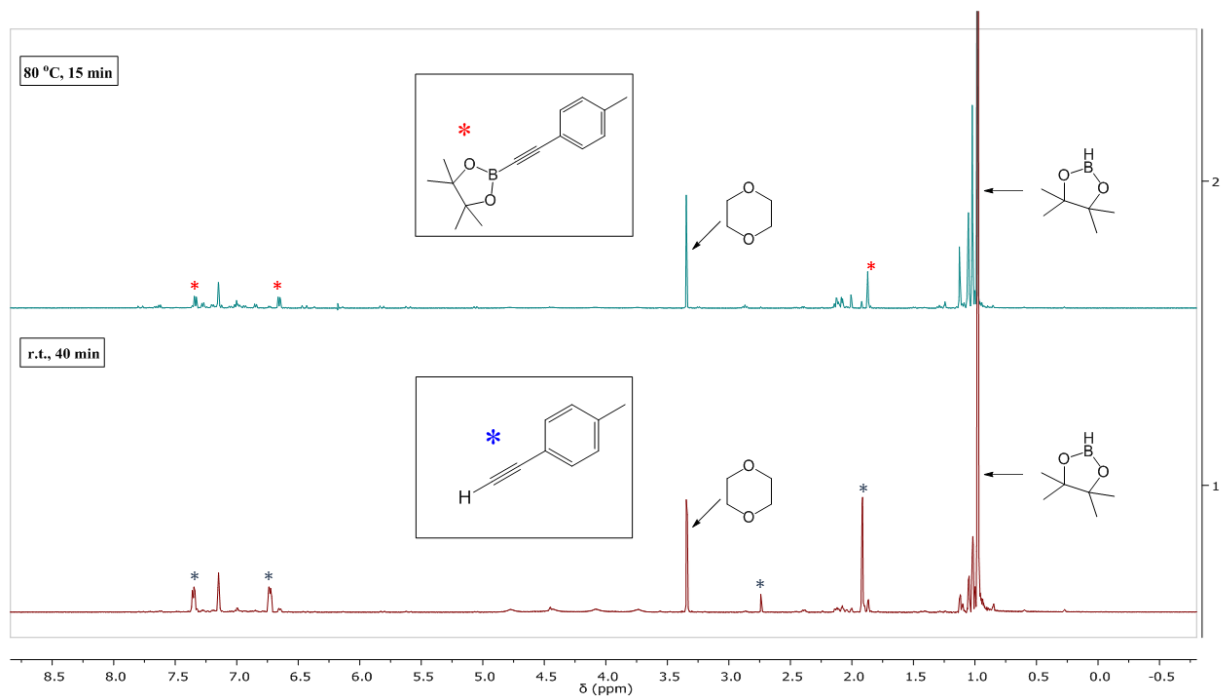A Leica MZ 75 microscope was used to identify a suitable colorless block with very well defined faces with dimensions (max, intermediate, and min) 0.021 x 0.015 x 0.013 mm^3 from a representative sample of crystals of the same habit. The crystal mounted on a nylon loop was then placed in a cold nitrogen stream (Oxford) maintained at 110 K.

A BRUKER APEX 2 Duo X-ray (three-circle) diffractometer was employed for crystal screening, unit cell determination, and data collection. The goniometer was controlled using the APEX2 software suite, v2008-6.0.[1] The sample was optically centered with the aid of a video camera such that no translations were observed as the crystal was rotated through all positions. The detector was set at 6.0 cm from the crystal sample (APEX2, 512x512 pixel). The X-ray radiation employed was generated from a IuS Cu X-ray tube (K$_\alpha$ = 1.5418 Å with a potential of 45 kV and a current of 0.65 mA).

45 data frames were taken at widths of 1.0°. These reflections were used in the auto-indexing procedure to determine the unit cell. A suitable cell was found and refined by nonlinear least squares and Bravais lattice procedures. The unit cell was verified by examination of the *h k l* overlays on several frames of data. No super-cell or erroneous reflections were observed.

After careful examination of the unit cell, an extended data collection procedure (33 sets) was initiated using omega and phi scans.

Data Reduction, Structure Solution, and Refinement

Integrated intensity information for each reflection was obtained by reduction of the data frames with the program APEX2.[3] The integration method employed a three dimensional profiling algorithm and all data were corrected for Lorentz and polarization factors, as well as for crystal decay effects. Finally, the data was merged and scaled to produce a suitable data set. The absorption correction program SADABS[2] was employed to correct the data for absorption effects.

Systematic reflection conditions and statistical tests of the data suggested the space group $P2_1/n$. A solution was obtained readily using XT/XS in APEX2.[3,3] Hydrogen atoms were placed in idealized positions and were set riding on the respective parent atoms. All non-hydrogen atoms were refined with anisotropic thermal parameters. Absence of additional symmetry and voids were confirmed using PLATON (ADDSYM).[4] The structure was refined (weighted least squares refinement on F^2) to convergence.[5,5]

Olex2 was employed for the final data presentation and structure plots.[7]

III. References

[1] APEX, Version 2 User Manual, M86-E01078, Brujer Analytical X-ray Systems, Madison, WI, June 2006.

[2] G. M. Sheldrick, SADABS (version 2008/1): Program for Absorption Correction for Data from Area Detector Frames., University of Göttingen, 2008.

[3] (a) G. M. Sheldrick, *Acta Cryst.,* 2008, **A64**, 112-122. (b) G. M. Sheldrick, *Acta Cryst.,* 2015, **A71**, 3-8. (c) G. M. Sheldrick, *Acta Cryst.,* 2015, **C71**, 3-8.

[4] (a) A. L. Spek, *J. Appl. Cryst.* 2003, **36**, 7-13. (b) A. L. Spek, PLATON, A Multipurpose Crystallographic Tool., Utrecht University, Utrecht, The Netherlands, 2008

[5] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, and H. Puschmann, *J. Appl. Cryst.,* 2009, **42**, 339-341.