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

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A new diarylmido-based pincer proto ligand (^{iPr}**PN^{H}Sb^{Ph}**) with one –PPr$^{i}_{2}$ and one –SbPh$_2$ side donor has beeen synthesized. Three complexes of its amido form were prepared using standard metalation techniques: **(^{iPr}PNSb^{Ph})PdCl**, **(^{iPr}PNSb^{Ph})RhCO**, and **(^{iPr}PNSb^{Ph})Ir(COE)**, where COE = *cis*-cyclooctene. These complexes were compared with their previously reported analogs incorporating a –PPh$_2$ side donor in place of –SbPh$_2$. The –SbPh$_2$ donor arm is less donating towards the metal and is less strongly trans-influencing, based on the structural and IR spectroscopic analysis of the Rh complexes. The redox potential of the Pd complexes is only marginally affected by the change from –PPh$_2$ to –SbPh$_2$. **(^{iPr}PNSb^{Ph})Ir(COE)** proved to be a slower a less selective catalyst in the dehydrogenative borylation of terminal alkynes (DHBTA) than its –PPh$_2$ analog.

Introduction.

Pincer ligands are widely used in the studies of stoichiometric and catalytic reactions taking place at transition metal centers.[1,2] The design in which the central pincer donor is connected to the flanking donor sites via an *ortho*-arylene linker is among the most common. A large number of various elements have been employed in the central donor position, including B,[3] C,[4] Si,[5] Ge,[6] N,[7] P,[8] Sb,[9] O,[10] S.[11] Variations of the outer donors have been explored to some extent,[12,13,14,15] but the overwhelming majority of such pincers utilize either phosphine or nitrogenous donors in the flanking sites. We became interested in examining the potential of stibines in the flanking position of a diarylamido-based pincer and report our efforts in the synthesis and characterization of representative complexes of a new ^{iPr}PNSb^{Ph} ligand (Figure 1). Stibines (SbR$_3$) have occasionally been utilized in coordination chemistry, and their use and properties have been reviewed.[16,17] However, stibines have not found widespread use as components of multidentate ligands. To the best of our knowledge, the only prior example of the use of an organostibine as a flanking donor in any pincer ligand is in a recent PhD thesis.[18] The role of Sb as a central atom in pincer and tripodal ligand designs has been extensively explored by the Gabbai group, with the focus on the non-innocence of the coordination and redox behaviour of Sb ligands.[9,19,20]

Our previous work on dissymetric PNP' and PNN pincers[7] targeted (pincer)PdCl complexes for the evaluation of the ease of oxidation of the diarylamido-based ligand and (pincer)RhCO complexes for the comparison of the overall donor ability towards the metal. Various (PNP)Ir complexes proved to be excellent catalysts for the dehydrogenative borylation of terminal alkynes (DHBTA).[21] Here, we focused on the analogous ^{iPr}PNSb^{Ph} derivatives for convenient comparison with the ^{iPr}PNP^{Ph} counterparts (Figure 1).

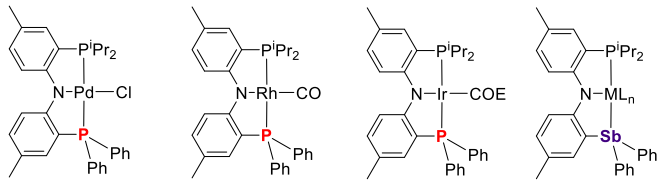

Figure 1. Comparison of ^{iPr}PNP^{Ph} and ^{iPr}PNSb^{Ph} complexes.

Results and Discussion.

Synthesis and Spectroscopic Characterization

Similar to the syntheses of ^{iPr}PNP' ligands,[7] **^{iPr}PN^{H}Br** served as a convenient precursor in the synthesis of **^{iPr}PN^{H}Sb^{Ph}** (Scheme 1). Lithiation of **^{iPr}PN^{H}Br** with 2 equiv. of ^{n}BuLi followed by

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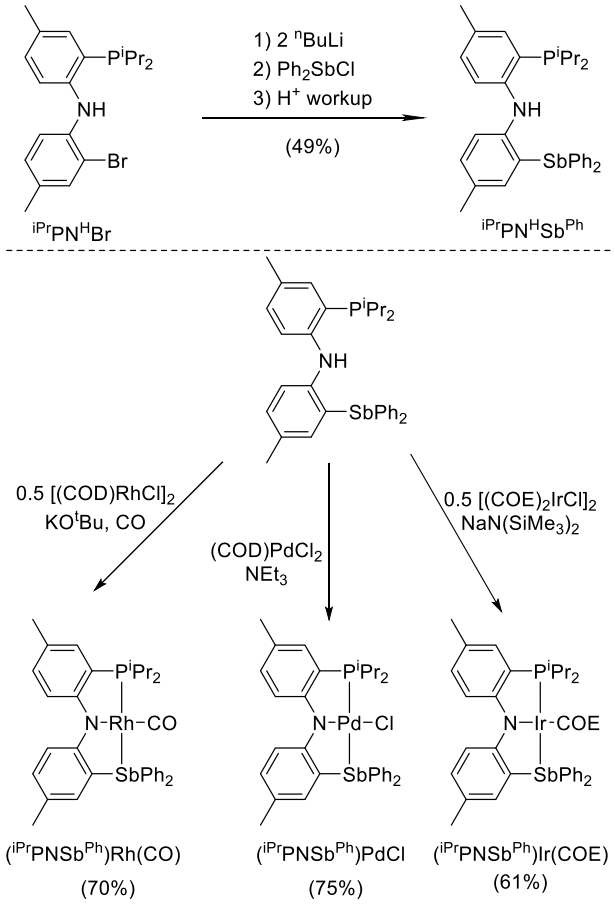
reaction with one equiv of Ph_2SbCl produced **^{iPr}PN^{H}Sb^{Ph}**, which was isolated in 49% yield upon workup. **^{iPr}PN^{H}Sb^{Ph}** presented the expected C_s symmetry in its NMR spectra. Its ^{31}P NMR resonance at -15.4 ppm, and the ^{1}H NMR N-H resonance at 7.27 ppm (d, J_{H-P} = 6 Hz) appear at chemical shifts similar to the corresponding PN^{H}P' ligands.

The synthesis of **(^{iPr}PNSb^{Ph})RhCO** was accomplished by treatment of **^{iPr}PN^{H}Sb^{Ph}** with $[(COD)RhCl]_2$, potassium *t*-butoxide, and CO, with a 70% isolated yield. Reaction of **^{iPr}PN^{H}Sb^{Ph}** with $(COD)PdCl_2$ in the presence of Et_3N permitted isolation of **(^{iPr}PNSb^{Ph})PdCl**. It was obtained in ca. 95% purity and ca. 75% yield. Recrystallization yielded analytically pure samples of (^{iPr}PNSb^{Ph})PdCl at the expense of yield (26%). Interestingly, **(^{iPr}PNSb^{Ph})PdCl** appears in two solid forms of different color (purple and bright green). Dissolution of either results in a turquoise solution of identical spectral properties.



Scheme 1. Synthesis and metalation of the ^{iPr}PN^{H}Sb^{Ph} proligand

To prepare an Ir derivative, **^{iPr}PN^{H}Sb^{Ph}** was reacted with one equiv of $NaN(SiMe_3)_2$, followed by 0.5 equiv of $[(COE)_2IrCl]_2$, providing upon workup a 61% yield of **(^{iPr}PNSb^{Ph})Ir(COE)**. C_6D_6 solutions of **(^{iPr}PNSb^{Ph})Ir(COE)** were observed to undergo decomposition to unidentified compounds upon standing for 24 h.

Similarly to **^{iPr}PN^{H}Sb^{Ph}**, the Rh and Pd complexes possess an apparent C_s symmetry in their NMR spectra at ambient temperature. The six aromatic resonances of the diarylamine backbone exhibit closely similar patterns in the three metal complexes, consistent with the structural similarity of the meridionally disposed diarylamido-PNSb ligand. Some of the Sb-C_6H_5 and the P-$CHMe_2$ resonances of **(^{iPr}PNSb^{Ph})PdCl** are significantly broadened in the ^{1}H NMR spectrum. It is possible that this reflects the slowed "flipping" motion of the two aromatic rings of the diarylamido backbone past each other. In **(^{iPr}PNSb^{Ph})Ir(COE)**, this motion is apparently even slower, resulting in the observed C_1 symmetry by NMR spectroscopy at ambient temperature. We previously analyzed this in (PNN)PdCl complexes,[7,22] coming to the conclusion that the enlarged ring size associated with the imine vs phosphine side donor pushes the two diarylamido rings closer together. Although PNSb forms the same {5,5}-pincer rings (in the Fryzuk notation)[23] as PNP, Sb is a considerably larger atom that may result in an effect similar to that caused by ring expansion. VT-NMR studies of **(^{iPr}PNSb^{Ph})PdCl** evince C_1 symmetry at -40 °C (inequivalent Ph groups and inequivalent ^{i}Pr groups) and C_s symmetry with sharp lines at +60 °C, consistent with the "flipping" proposal.

The $^{1}J_{P\text{-}Rh}$ = 167 Hz in **(^{iPr}PNSb^{Ph})RhCO** is greater than the analogous value for the $-P^{i}Pr_2$ phosphine (133 Hz) in the **(^{iPr}PNP^{Ph})RhCO** analog. Considering the IR spectra, the ν_{CO} value in **(^{iPr}PNSb^{Ph})RhCO** is higher than that in **(^{iPr}PNP^{Ph})RhCO** (1951 vs 1941 cm^{-1}). Cyclic voltammetry studies indicated that the redox potential for **(^{iPr}PNSb^{Ph})PdCl** ($E_{1/2}$ = 0.00 V vs Fc/Fc^{+}) does not differ significantly from that of **(^{iPr}PNP^{Ph})PdCl** ($E_{1/2}$ = -0.02 V vs Fc/Fc^{+}). The range of redox potential values among the various (PNP)PdCl complexes with different organic substituents on the P donors exceeded 0.02 V.[7] Our data suggest that the $-SbPh_2$ donor is less donating towards the metal and possesses weaker *trans*-influence than $-PPh_2$, but has a similar influence on the ease of oxidation of the diarylamido π-system. The conclusion concerning the donor strength and the *trans*-influence of a stibine vs phosphine agrees with the discussion by Levason and Reid in their 2006 review.[16]

Structural characterization of (^{iPr}PNSb^{Ph})RhCO

An X-ray diffraction study on a single crystal of **(^{iPr}PNSb^{Ph})RhCO** allowed the determination of the solid-state structure of this complex (Figure 2). As expected, an approximately square-planar environment was determined about the Rh center. The Rh-P distance (2.2626(14) Å) is slightly shorter than the Rh-$P^{i}Pr_2$ distance in **(^{iPr}PNP^{Ph})RhCO** (2.2861(4) Å), consistent with the notion of $-SbPh_2$ exerting weaker *trans*-influence than $-PPh_2$. The Rh-Sb distance of 2.5539(5) Å appears to be unremarkable. For comparison, Rh-Sb distances determined for the structures of $(Ph_3Sb)_3Rh(COMe)(CO)$,[24] $(Ph_3Sb)_3Rh(Cl)(CO)$, and *trans*-$(Ph_3Sb)2Rh(Cl)(CO)$ fall into the 2.55-2.63 Å range.[25]

The larger size of Sb vs P does have an influence on the exact geometry of the diarylamido backbone. As illustrated in Figure 3, the dihedral angle (C6-C1-C8-C9) between the two diarylamido rings is greater, the C1-N-C8 angle is smaller, and the distance between the two *ortho*-CH carbons (C6-C9) is smaller in **(^{iPr}PNSb^{Ph})RhCO** than in **(^{iPr}PNP^{Ph})RhCO**. These

differences, albeit modest, are consistent with the greater difficulty of the "flipping" of the two rings past each other in PNSb complexes because of the extra hindrance arising from the closer disposition of the C-H bonds from C6 and C9.

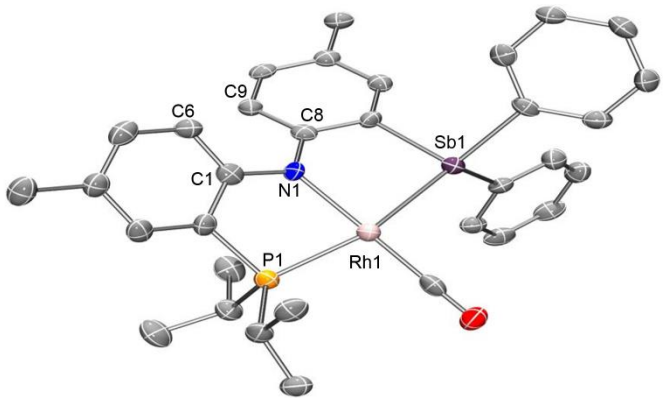
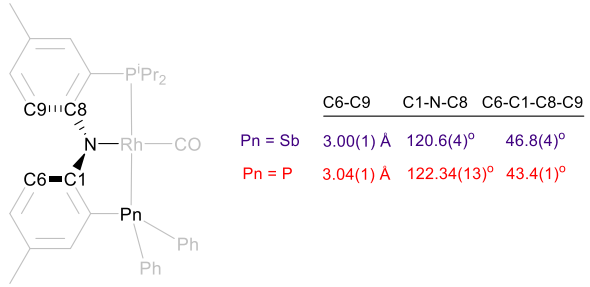


Figure 2. ORTEP drawing (50% probability ellipsoids) of **(^{iPr}PNSb^{Ph})Rh(CO)**. H atoms are omitted for clarity. Selected distance (Å) and angles (deg): Rh1-N1, 2.105(4);Rh1-P1, 2.263(1); Rh1-Sb1, 2.5539(5); P1-Rh1-Sb1, 161.30(4).

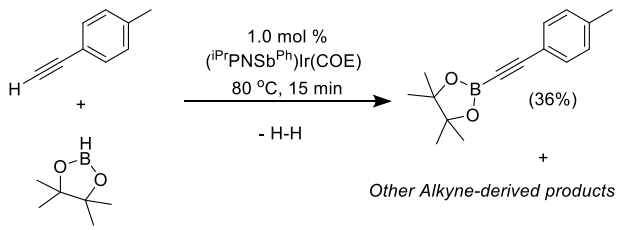


	C6-C9	C1-N-C8	C6-C1-C8-C9
Pn = Sb	3.00(1) Å	120.6(4)°	46.8(4)°
Pn = P	3.04(1) Å	122.34(13)°	43.4(1)°

Figure 3. Selected metrics from the X-ray structures of **(^{iPr}PNSb^{Ph})RhCO** and **(^{iPr}PNP^{Ph})RhCO**.

Catalytic activity of (^{iPr}PNSb^{Ph})Ir(COE) in DHBTA

Iridium complexes supported by the ^{iPr}PNP^{Ph} and other tested PNP ligands proved to be excellent catalysts for DHBTA.[21] For example, with 0.25% loading of **(^{iPr}PNP^{Ph})Ir(COE)** as the precatalyst, DHBTA of *p*-MeC$_6$H$_4$CCH was observed to be complete within 10 min at ambient temperature. In contrast, the reactivity of **(^{iPr}PNSb^{Ph})Ir(COE)** as a DHBTA catalyst turned out to be poor (Scheme 2). A negligible amount of the DHBTA product of *p*-MeC$_6$H$_4$CCH was detected after 40 min at ambient temperature with 1% of **(^{iPr}PNSb^{Ph})Ir(COE)** as the precatalyst. Heating of the mixture at 80 °C for 15 min did result in the consumption of *p*-MeC$_6$H$_4$CCH, however, only 36% of the alkyne was converted into the DHBTA product, with hydroboration products acconting for another 38% (25% trans, 13% cis). The remaining organic products in the mixture were not identified. Thus, ^{iPr}PNSb^{Ph} as the supporting ligand results in a much lower DHBTA reaction rate and much poorer chemoselectivity when compared with ^{iPr}PNP^{Ph}.



Scheme 2. Catalytic dehydrogenative borylation of p-MeC$_6$H$_4$CCH

Conclusions

In conclusion, we have synthesized –PdCl, -RhCO, and -Ir(COE) complexes of a new diarylamido-based ^{iPr}PNSb^{Ph} ligand with a flanking stibine donor site. Comparison of these complexes with the ^{iPr}PNP^{Ph} analogs indicated that a) –SbPh$_2$ acts as donor of lesser trans influence and lesser donor ability than –PPh$_2$; 2) –SbPh$_2$ vs –PPh$_2$ substitution does not significantly affect the ease of oxidation of the diarylamido ligand system; 3) ^{iPr}PNSb^{Ph} is not an effective supporting ligand for Ir in the catalysis of DHBTA, in contrast to ^{iPr}PNP^{Ph} and other PNP ligands.

Experimental.

General Considerations

Unless otherwise stated, all experiments were carried out using standard glovebox and Schlenk line techniques under a dry argon atmosphere. C$_6$D$_6$ was dried over NaK, benzophenone, and 18-crown-6, distilled, and stored over molecular sieves in an argon glovebox prior to usage. Diethyl ether, pentane and toluene were dried and deoxygenated using a PureSolv MD-5 solvent purification system and were stored over molecular sieves in an argon-filled glovebox. PNBr[26] was synthesized using previously reported procedures. Ph$_2$SbCl was synthesized by a neat 2:1 reaction of SbPh$_3$ and SbCl$_3$, used as received from commercial suppliers. NMR spectra were recorded on a Varian iNova 500 (^{31}P{^{1}H} NMR, 202.276 MHz; ^{13}C{^{1}H} NMR, 125.670 MHz; ^{1}H NMR, 499.678 MHz) spectrometer in given solvents. Chemical shifts are reported in ppm (δ). ^{31}P{^{1}H} NMR spectra were referenced externally to an 85% phosphoric acid standard at δ 0ppm. ^{13}C{^{1}H} and ^{1}H NMR spectra were internally referenced to residual solvent resonances.[27] In reporting spectral data, the following abbreviations were utilized: s = singlet; d = doublet; t = triplet; dd = doublet of doublets; dm = doublet of multiplets; sept. d. = septet of doublets; m = multiplet. NMR resonances assigned to either the "*aromatic backbone C-H*" or annotated as "*Sb-ring C-H*" or "*P-ring C-H*" refer to those arising from the general ditolylamine ligand motif, or those specific rings containing the respective stibine or phosphine donor. Infrared spectra were collected on an Agilent CARY FT-IR spectrometer. Elemental analyses were performed by CALI, Inc. (Highland Park, NJ, USA).

Electrochemical Analysis

Electrochemical studies were carried out using a GAMRY Ref600 potentiostat under argon with a three electrode setup: A glassy carbon disk (BasInc) working electrode, a non-aqueous reference electrode (Ag/Ag^+ CH_2Cl_2; BasInc) separated from solution by a fine porosity frit, and graphite counter electrode (Alfa Aesar). Solutions were 1.0 mM in analyte and 0.1 M in supporting electrolyte (NBu_4PF_6) and spectra were referenced to the ferrocene/ferrocenium redox couple.

^{iPr}PN^{H}Sb^{Ph}. To a 50 mL Schlenk flask equipped with magnetic stir bar was added **^{iPr}PN^{H}Br** (530 mg, 1.35 mmol) and 30 mL diethyl ether. To this stirring solution was added a 2.5 M solution of *n*-butyllithium in hexanes (1.08 mL, 2.7 mmol) causing the solution to become yellow and slightly cloudy. The mixture was allowed to stir for 3 h, and then Ph_2SbCl (441 mg, 1.42 mmol) was added in one portion, resulting in an immediate darkening of solution and formation of a colorless precipitate. The resultant mixture was allowed to stir for 24 h, then 1 mL degassed H_2O was added, and the solvent was removed under reduced pressure, providing a yellow, sticky solid. This residue was then dissolved in diethyl ether, filtered through Celite and silica, and dried under reduced pressure to give a yellow powder. The powder was washed with *iso*octane and dried *in vacuo* to provide the product as a white, free-flowing solid. Yield: 387 mg (49%). ^{1}H NMR (500 MHz, C_6D_6): δ 7.55 (dd, *J* = 7.5, 1.8 Hz, 4H, *-SbPh$_2$*), 7.34 (d, *J* = 12.2 Hz, 1H, *N-H*), 7.29 (s, 1H, *Sb-ring C-H*), 7.28 (d, *J* = 8.1 Hz, 1H, *P-ring C-H*), 7.10 (m, 7H, *-SbPh$_2$ and overlapping aromatic backbone C-H*), 6.95 (m, 2H, two overlapping *aromatic backbone C-H*), 6.86 (dd, *J* = 8.3, 1.6 Hz, 1H, *P-ring C-H*), 2.16 (s, 3H, *benzylic CH$_3$*), 1.97 (s, 3H, *benzylic CH$_3$*), 1.87 (sept. d., *J* = 6.9, 2.9 Hz, 2H, *iPr-methine*), 1.01 (dd, *J* = 15.6, 7.0 Hz, 6H, *iPr-CH$_3$*), 0.91 (dd, *J* = 12.1, 6.9Hz, 6H, *iPr-CH$_3$*). ^{13}C{^{1}H} NMR (126 MHz, C_6D_6): δ 150.2 (d, *J* = 19.5 Hz), 146.5 (d, *J* = 1.4 Hz), 139.1, 137.9, 137.3, 137.0, 135.0, 134.2 (m), 133.3, 131.3, 131.0, 129.3, 128.7, 124.2, 120.2 (d, *J* =14.7 Hz), 116.0 (d, *J* = 2.8 Hz), 23.7 (d, *J* = 10.5 Hz), 20.9 (d, *J* = 8.0 Hz), 20.6, 20.4, 19.3 (d, *J* = 9.3 Hz). ^{31}P{^{1}H} NMR (202 MHz, C_6D_6): δ -15.4. ATR-IR = ν_{N-H} - 3255 cm^{-1}. Elem Anal Found (calc): C: 65.16 (65.32) H: 6.41 (6.34)

(^{iPr}PNSb^{Ph})RhCO. To a 10 mL Teflon stoppered flask equipped with a magnetic stir bar was added **^{iPr}PN^{H}Sb^{Ph}** (50 mg, 0.085 mmol), $[(COD)Rh(\mu\text{-}Cl)]_2$ (21 mg, 0.042 mmol), KO^{t}Bu (14 mg, 0.13 mmol), and 4 mL PhF as solvent, forming a yellow-orange suspension. The suspension was frozen, degassed, and refilled with 1 atm CO, then placed in an oil bath set to 60 °C for 24 h. Over this time, the solution darkened in color. The resultant solution was filtered through a plug of Celite and silica, and solvent was removed *in vacuo* to give a dark residue. The residue was washed with cold pentane and dried to provide the product as a red-orange solid. Single crystals suitable for X-ray diffraction were grown over 48 h from a concentrated diethyl ether solution at -38 °C. Yield: 42 mg (70%). ^{1}H NMR (500 MHz, C_6D_6) δ 7.75 (d, *J* = 8.5 Hz, 1H, *Sb-ring C-H*), 7.69-7.63(m, 5H, *-SbPh$_2$ and overlapping P-ring C-H*), 7.29 (d, *J* = 1.9 Hz, 1H, *Sb-ring C-H*), 7.04 – 6.97 (m, 6H, *-SbPh$_2$*), 6.89 (dd, *J* = 8.3, 1.8 Hz, 1H, *aromatic backbone C-H*), 6.82 (dd, *J* = 8.5, 2.2 Hz, 1H, *aromatic backbone C-H*), 6.77 (d, *J* = 8.6 Hz, 1H, *P-ring C-H*), 2.19 (sept., *J* = 7.5 Hz, 2H, *iPr-methine*), 2.17 (s, 3H, *benzylic CH$_3$*), 1.99 (s, 3H, *benzylic CH$_3$*), 1.30 (dd, *J* = 17.2, 6.9 Hz, 6H, *iPr-CH$_3$*), 1.05 (dd, *J* = 15.5, 6.9 Hz, 6H, *iPr-CH$_3$*). ^{13}C NMR (126 MHz, C_6D_6): δ 196.1 (dd, J_{Rh-C} = 63.6, $^2J_{Pj-C}$ = 13.7 Hz, *Rh-CO*), 164.3 (dd, *J* = 21.5, 2.1 Hz), 160.6, 136.2, 132.6, 132.0, 131.5, 130.0, 129.6 (*two overlapping singlets*), 127.5 (d, *J* = 20.3 Hz), 126.7, 125.3 (d, *J* = 6.5 Hz), 121.3 (d, *J* = 40.4 Hz), 118.5 (d, *J* = 12.3 Hz), 117.7, 26.2-25.4 (m), 20.5, 20.3, 19.5, 18.4. ^{31}P{^{1}H} NMR (202 MHz, C_6D_6): δ 71.1 (d, J_{Rh-P} = 167 Hz). ATR-IR: ν_{Rh-CO} - 1951 cm^{-1} Elem Anal Found (calc): C: 55.30(55.18) H: 4.99(5.05)

(^{iPr}PNSb^{Ph})PdCl. To a J. Young tube was added **^{iPr}PN^{H}Sb^{Ph}** (48 mg, 0.082 mmol), $(COD)PdCl_2$ (23 mg, 0.081 mmol), triethylamine (14 µL, 0.10 mmol), and PhF, forming a dark yellow-green suspension. The suspension was heated in an oil bath at 60 °C for 1 h, and then placed on a rotator for 18 h over which time a dark turquoise solution had formed with a colorless precipitate (presumed to be $HNEt_3Cl$) observed. Filtration through a plug of Celite and silica, followed by solvent removal under reduced pressure providea dark turquoise solid determined to be ca. 95% pure (^{1}H and ^{31}P{^{1}H} NMR evidence). Crude yield: 44 mg (75%). This solid could be recrystallized from a concentrated Et_2O solution at -38 °C to give separate polymorphic crops of bright green and purple solids. Recrystallized yield: 15 mg (26%). Upon dissolving, both form a turquoise solution, and share identical spectroscopic characteristics. ^{1}H NMR (500 MHz, C_6D_6) δ 7.96-7.37 (v br, 4H, *-SbPh$_2$*) 7.64 (d, *J* = 8.5 Hz, 1H, *Sb-ring C-H*), 7.55 (dd, *J* = 8.6, 4.3 Hz, 1H, *P-ring C-H*), 7.26 (s, 1H, *Sb-ring C-H*), 6.97 (br, 6H, *-SbPh$_2$*), 6.80 (d, *J* = 10.0 Hz, 1H, *aromatic backbone C-H*), 6.78 (dd, *J* = 8.6, 2.2 Hz, 1H, *aromatic backbone C-H*), 6.71 (d, *J* = 8.6 Hz, 1H, *aromatic backbone C-H*), 2.31 (v br, 2H, *iPr-methine*), 2.11 (s, 3H, *benzylic CH$_3$*), 1.93 (s, 3H, *benzylic CH$_3$*), 1.46 (dd, *J* = 17.5, 6.5 Hz, 6H, *iPr-CH$_3$*), 1.12 (br, 6H, *iPr-CH$_3$*). ^{13}C{^{1}H} NMR (126 MHz, C_6D_6): δ 163.8 (d, *J* = 20 Hz), 160.4, 136.5 (br), 136.3, 133.1, 132.0, 131.4, 130.1, 129.6, 128.8, 126.7 (d, *J* = 6.7 Hz), 124.1 (d, *J* = 3.9 Hz), 120.3 (d, *J* = 14.3 Hz), 119.8 (d, *J* = 42.8 Hz), 118.8, 115.5 (d, *J* = 21.0 Hz), 28.4, 20.4, 20.3, 18.7 (br), 17.8 (br). ^{31}P NMR (202 MHz, C_6D_6) δ 69.6. Elem. Anal. Found (calc). C: 52.89 (52.71); H: 5.10 (4.98)

(^{iPr}PNSb^{Ph})Ir(COE). To a 20 mL scintillation vial was added **^{iPr}PN^{H}Sb^{Ph}** (60 mg, 0.10 mmol), $NaN(SiMe_3)_2$ (18 mg, 0.10 mmol), and 2 mL PhF, resulting in a bright yellow solution. The resultant solution was then transferred to a stirring PhF solution of $[(COE)_2IrCl]_2$ (45 mg, 0.050 mmol) causing a color change to dark red with immediate formation of colorless solids (presumed to be NaCl). The suspension was allowed to stir for 1.5 h after which time it was filtered through a plug of Celite and silica, and solvent was removed under reduced pressure to give a scarlet red residue. The residue was washed with diethyl ether (2 x 2 mL) and dried under vacuum for 24 h which removes residual diethyl ether, cyclooctene, and $HN(SiMe_3)_2$ to provide the product as a scarlet red powder of analytical purity. Yield: 55 mg (61%). In C_6D_6 solutions over 24 h at room temperature, **(^{iPr}PNSb^{Ph})Ir(COE)** can be observed (NMR evidence) to decompose to an unidentified mixture of products. ^{1}H NMR (500 MHz, C_6D_6): δ 8.01 (br s, 2H, *-SbPh$_2$*), 7.69 (d, *J* = 8.5 Hz, 1H, *aromatic backbone C-H*), 7.54 (br s, 3H, *-SbPh$_2$ and overlapping aromatic backbone C-H*), 7.24 (s, 1H, *Sb-ring C-H*), 7.03 (br s, 6H, *-SbPh$_2$*), 6.88 (d, *J* = 8.0 Hz, 1H, *aromatic backbone C-H*), 6.84 (d, *J* = 8.6 Hz, 1H, *aromatic backbone C-H*), 6.73 (d, *J* = 8.5 Hz, 1H, *P-ring C-H*), 3.26 (br s, 1H, *COE vinylic C-H*), 3.18 (br s, 1H, *COE vinylic C-H*), 2.89 (br s 1H), 2.43 – 2.28 (br m, 3H), 2.17 (s, 3H, *benzylic CH$_3$*), 2.04 (s, 3H, *benzylic CH$_3$*), 1.72 – 1.63 (m, 3H), 1.63 – 1.54 (m, 4H), 1.54 – 1.37 (m, 5H), 1.37-1.25 (m, 1H), 1.08 – 0.96 (m, 9H, *overlapping iPr-CH$_3$ and COE resonances*). ^{31}P NMR (202 MHz, C_6D_6): δ 32.5. Elem. Anal. Found (calc). C: 53.87 (53.99); H: 5.50 (5.66)

Catalytic Test for the Dehydrogenative Borylation of a Terminal Alkyne (DHBTA) with (^{iPr}PNSb^{Ph})Ir(COE). This catalytic test was

developed utilizing a previously reported procedure[21]21 and **(^{iPr}PNSb^{Ph})Ir(COE)** was recrystallized from diethyl ether at -38 °C and dried under reduced pressure prior to catalytic testing. To a J. Young tube in specific order was added a 0.162 M C_6D_6 solution of pinacolborane (0.43 mL, 0.070 mmol) followed by a 0.01 M C_6D_6 solution of **(^{iPr}PNSb^{Ph})Ir(COE)** (0.035 mL, 0.00035 mmol) to form a light yellow solution. To the resultant solution was added a 1 M solution of 4-ethynyl toluene (0.035 mL, 0.035 mmol) containing 0.35 M 1,4-dioxane as an internal standard. The J. Young tube was then closed and followed by ^{1}H NMR spectroscopy. After 40 min at room temperature the reaction was not determined to be proceeding by ^{1}H NMR spectroscopy. The tube was subsequently heated at 80 °C in an oil bath for 15 min and ^{1}H NMR spectroscopy revealed full conversion of the alkyne to a mixture of products consisting of 36% formation of the desired alkynylboronate, 25% of the *trans* hydroboration product, and 13% of the *cis* hydroboration product, with the other components not identified.

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