Catalytic Hydroamination of Alkynes and Norbornene with Neutral and Cationic Tantalum Imido Complexes

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Supporting Information

General Information. All reactions and manipulations, unless otherwise noted, were carried out in an inert atmosphere (N_2) glovebox at 10 °C or using standard Schlenk and high vacuum techniques. All glassware was dried in an oven at 150 °C for at least 12 h prior to use or was flame dried under reduced pressure. Magnetic stirring was used when necessary. Pentane, hexane, diethyl ether, benzene, toluene, and methylene chloride were dried and purified by passage through a column of activated alumina under N_2 pressure, sparging with N_2 and storage over 4Å sieves.¹ Fluorobenzene, aniline, 2,6-dimethylaniline, 1-pentyne, 2-hexyne, 3-hexyne, 1-phenylpropyne, and phenylacetylene (Aldrich) were distilled from CaH_2 prior to use and were stored over 4Å molecular sieves. Toluidine, anisidine and *p*-chloroaniline (Aldrich) were crystallized from hot hexane prior to use. Diphenylacetylene (Aldrich) was sublimed. Norbornene (Aldrich) was vacuum transferred. $PhCH_2MgCl$, $(CH_3)_3CCH_2MgCl$, deoxybenzoin, 2-pentanone, 2-hexanone, 3-hexanone, acetophenone and methylbenzylketone (Aldrich), as well as $Ta(NMe_2)_5$ (Strem) and allene (Matheson) were purchased and used without further purification. Compound **1**,² $Ph_3CB(C_6F_5)_4$,³ and cyclonona-1,2-diene⁴ were prepared according to published protocols. Deuterated

¹ Alaimo, P. J.; Peters, D. W.; Arnold, J.; Bergman, R. G. *J. Chem. Ed.* **2001**, 78, 64.

² Sundermeyer, J.; Putterlik, J.; Foth, M.; Field, J. S.; Ramesar, N. *Chem. Ber.* **1994**, 127, 1201-1212.

³ Lambert, J. B.; Zhang, S. Z.; Ciro, S. M. *Organometallics* **1994**, 13, 2430-2443.

solvents were purchased from Cambridge Isotope Laboratories. Benzene- d_6 was vacuum transferred from purple Na/benzophenone and degassed with 3 freeze-evacuation-thaw cycles. Toluene- d_8 and chlorobenzene- d_5 were vacuum transferred from CaH_2 and degassed with 3 freeze-evacuation-thaw cycles. For non-air sensitive samples benzene- d_6 and chloroform- d were used from the supplier without further purification. ^1H , ^2H , ^{13}C , spectra were recorded on Bruker AVQ-400 (400 MHz), AV-400 (400 MHz), and DRX-500 (500 MHz) spectrometers as indicated. ^1H NMR chemical shifts (δ) are reported in parts per million (ppm) relative to residual protiated solvent (CDCl_3 , 7.25; C_6D_6 , 7.15; C_7D_8 , 2.1(CH_3); $\text{C}_6\text{D}_5\text{Cl}$, 6.99 (*o*-CH)) or an external standard of CH_2Cl_2 in C_6D_6 (4.42). Data are reported as follows: (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet; coupling constant(s) in Hz; integration; assignment). Chemical shifts were assigned with the aid of DEPT 45, 90 and 135 experiments as well as HMQC, TOCSY, NOESY and HMBC where necessary. Reactions with allene were performed by condensation of a measured pressure of C_3H_4 from a bulb of known volume into an NMR tube at -196°C . The pressure was determined using a digital MKS Baratron gauge attached to a high vacuum line. Merck silica gel, 60 Å, 230-400 mesh, grade 9385 was used in chromatography unless otherwise noted. Gas Chromatograph-Mass Spectroscopy (GC-MS) data were obtained using an Agilent Technologies Instrument 6890N GC (column #HP-5MS, 30.0m x 250 μm x 0.25 μm calibrated) and 5973N MS. Elemental analyses were performed at the UC-Berkeley Microanalytical facility with a Perkin Elmer 2400 Series II CHNO/S Analyzer.

(PhCH $_2$) $_3$ Ta=NCMe $_3$ (1a): To a slurry of $(\text{py})_2\text{Cl}_3\text{Ta=NCMe}_3$ (3.51 g, 6.79 mmol, 1.0 equiv) at -78°C in Et_2O (200 mL) was added PhCH_2MgCl (1.0 M in Et_2O , 20.4 mL, 20.40 mmol, 3.0 equiv). The reaction mixture was covered with aluminum foil and allowed to warm to 25°C and stir for 8 h in the absence of light. Volatile materials were removed under reduced pressure to give a light yellow solid which was

⁴ Skattebol, L.; Solomon, S. *Org. Synth.* **1969**, 49, 35. Shea, K. J.; Kim, J. S. *J. Am. Chem. Soc.* **1992**, 114, 3044-3051.

extracted with toluene (150 mL). The toluene solution was separated from the remaining MgCl_2 by cannula filtration. Toluene was removed under reduced pressure to give **1a** as a bright yellow solid (2.68 g, 5.10 mmol, 75%). ^1H NMR (C_6D_6 , 500 MHz) δ 7.02 (m, 9H, ArH), 6.68 (m, 6H, ArH), 1.66 (s, 6H, CH_2Ph), 1.39 (s, 9H, CMe_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 125 MHz) δ 136.4, 130.1, 129.9, and 125.7 ArC, 67.9 (CMe_3), 67.6 (CH_2Ph), 33.1 (CMe_3). Anal. Calcd. C, 57.15; H, 5.76; N, 2.67. Found C, 57.46; H, 5.97; N, 2.65.

(Me_3CCCH_2) $_3\text{Ta}=\text{NCMe}_3$ (1b**):** To a 10 °C slurry of $(\text{py})_2\text{Cl}_3\text{Ta}=\text{NCMe}_3$ (426 mg, 0.825 mmol, 1.0 equiv) in Et_2O (15 mL) was added $\text{Me}_3\text{CCH}_2\text{MgCl}$ (1.0 M in Et_2O , 2.5 mL, 2.5 mmol, 3.0 equiv). The reaction mixture was covered with aluminum foil and allowed to stir for 8 h in the absence of light. Volatile materials were removed under reduced pressure to give an off-white solid which was extracted with hexane (15 mL). The hexane solution was separated from the remaining MgCl_2 by filtration through a pipet containing a glass fiber filter. Hexane was then removed under reduced pressure to give off-white **1b** (294 mg, 0.631 mmol, 76%). ^1H NMR (C_6D_6 , 500 MHz) δ 1.62 (s, 9H, CMe_3), 1.14 (s, 27H, CH_2CMe_3), 0.81 (s, 6H, CH_2CMe_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 125 MHz) δ 108.2 (CH_2CMe_3), 68.3 (CMe_3), 35.3 (CH_2CMe_3), 35.1 (CH_2CMe_3), 34.3 (CMe_3). Anal. Calcd. C, 49.03; H, 9.10; N, 3.00. Found C, 49.27; H, 9.15; N, 3.01.

(Et_2N) $_3\text{Ta}=\text{NCMe}_3$: To a 10 °C slurry of $(\text{py})_2\text{Cl}_3\text{Ta}=\text{NCMe}_3$ (1.77 g, 3.42 mmol, 1.0 equiv) in Et_2O (15 mL) was added LiNEt_2 (813 mg, 10.3 mmol, 3 equiv). The reaction mixture was covered with aluminum foil and allowed to stir for 8 h in the absence of light. Volatile materials were removed under reduced pressure to give a brown solid which was extracted with hexane (15 mL). The hexane solution was separated from the remaining MgCl_2 by filtration through a pipet containing a glass fiber filter. Hexane was then removed under reduced pressure to give a brown oil, $(\text{Et}_2\text{N})_3\text{Ta}=\text{NCMe}_3$ (1.14g, 2.43 mmol, 71 %). ^1H (C_6D_6 , 500 MHz) δ 3.47 (q, J = 7.0 Hz, 12H, CH_2), 1.43 (s, 9H, CMe_3), 1.14 (t, J = 7 Hz, 18H, CH_3). $^{13}\text{C}\{^1\text{H}\}$ (C_6D_6 , 500 MHz) δ 66.0 (CMe_3), 47.4 (CH_2), 34.3 (CMe_3), 17.0 (CH_3).

Preparation of cationic metallacycle 3: To a 10 °C solution of $(\text{PhCH}_2)_3\text{Ta}=\text{NCMe}_3$ (114 mg, 0.217 mmol, 1.0 equiv) in fluorobenzene (10 mL) were added diphenylacetylene (39 mg, 0.22 mmol, 1.0 equiv) and $\text{Ph}_3\text{CB}(\text{C}_6\text{F}_5)_4$ (201 mg, 0.217 mmol, 1.0 equiv). The dark red homogeneous reaction mixture was

allowed to stand for 20 min at which time volatile materials were removed under reduced pressure to give a dark red oil. The oil was shaken with benzene (10 mL) to form a cloudy suspension which was layered with hexane (5 mL) and allowed to sit at 10 °C for 30 min. During this time a dark red oil precipitated. The solution was decanted and the oil was triturated with 3 x 5 mL portions of pentane to give a red foam (96 mg, 0.074 mmol, 34%). ^1H NMR ($\text{C}_6\text{D}_5\text{Cl}$, 500 MHz) δ 7.22-7.19 (m, 3H, ArH), 7.06-7.00 (m, 5H, ArH), 6.85-6.76 (m, 10H, ArH), 6.70, 6.63 (t, J = 6.5 Hz, 1H, ArH), 6.54 (t, J = 6.5 Hz, 4H, ArH), 6.02 (t, J = 7.5 Hz, 1H, p -ArH of η^2 -benzyl ligand),⁵ 3.62 (d, J = 17.0 Hz, 1H, CHHPh), 3.48 (d, J = 17.0 Hz, 1H, CHHPh), 2.86 (d, J = 11.5 Hz, 1H, CHHPh), 2.17 (d, J = 11.5 Hz, 1H, CHHPh), 0.881 (s, 9H, CMe_3). $^{13}\text{C}\{^1\text{H}\}$ ($\text{C}_6\text{D}_5\text{Cl}$, 500 MHz) δ 208.0 (*ipso*-C of η^2 -benzyl), 173.1 (NC(Ph)C), 152.0 (*ipso*-C of the phenyl group attached to the C at 173.1 ppm), 143.9 (TaCPh), 140.2 (*ipso*-C of the phenyl group attached to the C at 143.9 ppm), 149.5, 147.6, 137.4, 135.5, 134.7 (b, ArC-F), 134.3, 133.8, 131.4, 129.7, 129.6, 126.5, 126.3, 121.6, 120.5 (other ArC resonances, remaining resonances are obscured by solvent), 73.2, 46.0 (CH_2Ph), 69.2 (CMe_3), 31.9 (CMe_3). Anal. Calcd. C, 52.08; H, 2.58; N, 1.08. Found C, 51.93; H, 2.78; N, 1.25.

Preparation of an authentic imine sample: N-1,2-diphenylethylidene aniline. Compound 4. A 250 mL round bottom flask was charged with deoxybenzoin (7.27 g, 37.0 mmol, 1 equiv), aniline (15.3 g, 165 mmol, 4.4 equiv), p -toluenesulfonic acid (721 mg) and 100 mL of toluene on the bench top. The flask was attached to a Dean-Stark trap and heated at reflux for 24 h under N_2 . Upon cooling, the reaction mixture was washed with sat. NaHCO_3 . The organic layer was separated, dried with MgSO_4 , and filtered. Volatile materials were removed under reduced pressure to give a bright yellow solid (7.28 g, 26.8 mmol, 72%). ^1H NMR analysis indicated that approximately 10% of the sample was unreacted aniline. The yellow solid was crystallized in small batches from Et_2O at -35 °C as needed to give clean imine. ^1H NMR ($\text{C}_6\text{D}_5\text{Cl}$, 400 MHz) δ 7.87 (m, 2H, ArH), 7.04 (m, 5H, ArH), 6.86 (m, 6H, ArH), 6.72 (d, 2H, J =

⁵ Pindalo, G. J.; Thornton-Pett, M.; Hursthouse, M. B.; Coles, S. J.; Bochmann, M. *J. Chem. Soc., Dalton Trans.*, **1999**, 1663-1668. Bochmann, M.; Lancaster, S. J. *Organometallics*, **1993**, 12, 633. Bochmann, M.; Lancaster, S. J.; Hursthouse, M. B.; Malik, K. M. A. *Organometallics*, **1994**, 13, 2235.

7.2 Hz, ArH), 3.96 (s, 2H, CH₂Ph). ¹³C{¹H} NMR (C₆D₆, 500 MHz) δ 199.1 (imine C), 165.5, 151.9, 138.6, 137.8, 130.5, 129.3, 128.9, 128.6, 128.5, 126.4, 123.6, 119.3 (ArC), 36.1 (CH₂Ph).

Conversion of N-1,2-diphenyl-ethylidene aniline to an equilibrium mixture of imine and enamine. Compound 5. An NMR tube was charged with approximately 20 mg of **4** and 0.5 mL of C₆D₅Cl. The tube was flame-sealed and placed in a 135 °C oil bath for 12 h. Analysis by ¹H NMR spectroscopy showed a 3:1 ratio of imine to enamine. ¹H NMR of imine (C₆D₅Cl, 400 MHz) δ 7.87 (m, 2H, ArH), 7.04 (m, 5H, ArH), 6.86 (m, 6H, ArH), 6.72 (d, 2H, *J* = 7.2 Hz, ArH), 3.96 (s, 2H, CH₂Ph). ¹H NMR of enamine (C₆D₅Cl, 400MHz) δ 7.37 (m, 2H, ArH), 7.24 (m, 4H, ArH), 6.54 (t, *J* = 8 Hz, 2H, ArH) 6.41 (d, *J* = 8 Hz, 2H, ArH), (all other aryl enamine resonances overlap with imine aryl resonances), 6.02 (s, 1H, HC(NHPh)), 5.46 (s, 1H, NH), 3.88 (s, 1H, CHPh). Enamine resonances were similar to those of the analogous N-2,6-dimethylphenyl enamine.⁶

Representative procedures for alkyne and allene hydroamination reactions. In the glovebox, a vial was charged with 4 mg of **1b** (0.0086 mmol, 1 equiv) and approximately 0.5 mL of C₆D₅Cl (benzene-*d*₆ and toluene-*d*₈ were also used for these reactions but C₆D₅Cl gave better resolution of product ¹H NMR resonances.) To the resulting solution was added the alkyne or allene substrate (0.172 mmol, 20 equiv) and the amine (0.172 mmol, 20 equiv). The reaction mixture was transferred into an NMR tube, which was further charged with a capillary tube containing a solution of CH₂Cl₂/C₆D₆. The NMR tube was then fitted with a Cajon™ adaptor, removed from the glovebox, and flame sealed under static vacuum. An initial ¹H NMR spectrum of the reaction mixture was measured, following which the tube was placed in a 135 °C oil bath and monitored periodically. Hydroamination reactions with **2** were performed in a similar manner: catalyst **2** was generated *in situ* by dissolving 4 mg of **1a** (0.0076 mmol, 1 equiv) in C₆D₅Cl followed by addition of (in order) the alkyne or allene substrate (0.152 mmol, 20 equiv), Ph₃CB(C₆F₅)₄ (7.0 mg, 0.0076 mmol, 1 equiv), and the amine (0.152 mmol, 20 equiv). The preliminary hydroamination reactions with isolated **2** and **3** were also carried out similarly by combining the catalyst first with the

⁶ Walsh, P. J.; Baranger, A. M.; Bergman, R. G. *J. Am. Chem. Soc.*, **1992**, *114*, 1708-1719.

substrate and then with the aniline. For larger scale reactions 20 mg of catalyst was used with 3 mL of benzene. All reagents were combined in the same order and transferred to a teflon sealed Schlenk flask.

¹H NMR data for alkyne hydroamination reactions. Yields were determined by NMR integrations versus an external CH₂Cl₂/C₆D₆ standard.

Hydroamination of diphenylacetylene with isolated 2: Yield, 26%. Imine to enamine ratio, 3:1. ¹H NMR resonances for the imine and enamine matched authentic samples, **4** and **5**.

Hydroamination of diphenylacetylene with isolated 3: Yield, 28%. Imine to enamine ratio, 3:1. ¹H NMR resonances for the imine and enamine matched authentic samples, **4** and **5**.

Table 1, entries 1-5. All yields were > 95%. All ¹H NMR resonances for the imine and enamine matched authentic samples, **4** and **5**. Imine to enamine ratios were 3:1.

Table 1, entry 6. No reaction was observed by ¹H NMR spectroscopy.

Table 2, entry 1: Yield > 95% with **1b** and **2**. Both imine isomers were observed in a 1:1 ratio. ¹H NMR (C₆D₅Cl, 400 MHz) δ 7.07 (t, *J* = 7.6 Hz, 2H, Ar*H*), 6.80 (m, 1H, Ar*H*), 6.55 (d, *J* = 7.6 Hz, 2H, Ar*H*), 2.13 (m, 4H, CH₂), 1.85 (m, 4H, CH₂), 1.56 (q, *J* = 7.6 Hz, 2H, CH₂), 1.17 (q, *J* = 7.6 Hz, 2H, CH₂), 1.05 (t, *J* = 7.2 Hz, 3H, CH₃), 0.82 (t, *J* = 7.2 Hz, 3H, CH₃), 0.69 (t, *J* = 7.2 Hz, 3H, CH₃), 0.51 (t, *J* = 7.2 Hz, 3H, CH₃).

Table 2, entry 2: Yield >95% with **1b** and 71% with **2**. The same two imine isomers as Table 2, entry 1 were observed in a 1:1 ratio with each other and a 1:1 ratio with the other possible imine regioisomer. ¹H NMR (C₆D₅Cl, 400 MHz) δ 6.92 (t, *J* = 7.6 Hz, 1H, Ar*H*), 6.82 (m, 2H, Ar*H*), 6.35 (d, *J* = 8 Hz, 2H, Ar*H*), 1.49 (m, 2H, CH₂), 1.44 (s, 3H, CH₃), 0.75 (m, 2H, CH₂), 0.75 (m, 3H, CH₃).

Table 2, entry 3: Yield, 77% with **1b** and 66% with **2**. Only the Markovnikov product was observed. ¹H NMR (C₆D₅Cl, 400MHz) δ 7.79 (m, 2H, Ar*H*), 7.12-6.82 (bm, 6H, Ar*H*), 6.61 (d, *J* = 8 Hz, 2H, Ar*H*), 1.82 (s, 3H, CH₃).

Table 2, entry 4: Yield, 70% with **1b** and 62% with **2**. Only the Markovnikov product was observed. ¹H NMR (C₆D₅Cl, 400MHz) δ 7.07 (t, *J* = 8Hz, 2H, Ar*H*), 6.81 (t, *J* = 7.6, 1H, Ar*H*), 6.54 (d, *J* = 8 MHz, 2H, Ar*H*), 2.07 (t, *J* = 7.2 Hz, 3H, CH₂), 1.50 (m, 2H, CH₂), 1.46 (s, 3H, CH₃), 0.79 (t, *J* = 7.2 Hz, 3H, CH₃).

Table 2, entry 5: Yield, 19% for **2**. No reaction with **1b**. Only the anti-Markovnikov product was observed. ^1H NMR ($\text{C}_6\text{D}_5\text{Cl}$, 400 MHz) δ 7.32-7.01 (bm, 10H, *ArH*), 3.59 (s, 2H, CH_2), 1.55 (s, 3H, CH_3).

Table 3, entry 1: Yield, 98% with **1b** and 96% with **2**. Imine to enamine ratio, 3:1. All ^1H NMR resonances for the imine and enamine matched authentic samples, **4** and **5**. Imine to enamine ratios were 3:1.

Table 3, entry 2: Yield, 79% for **1b** and 74% for **2**. Imine to enamine ratio, 4:1. ^1H NMR ($\text{C}_6\text{D}_5\text{Cl}$, 400 MHz) δ 7.51 (m, 2H, *ArH*), 7.09 (m, 1H, *ArH*), 6.99 (m, 1H, *ArH*), 6.73 (m, 3H, *ArH*), 6.53 (m, 4H, *ArH*), 6.34 (d, $J = 8.0$ Hz, 2H, *ArH*), 6.06 (d, $J = 8.0$ Hz, 1H, *ArH*), 5.70 (s, 0.2H, enamine $\text{HC}(\text{NHPh})$), 5.17 (s, 0.2H, enamine *NH*), 3.40 (s, 2H, imine CH_2Ph), 3.26 (s, 0.2H, enamine CHPh), 1.73 (s, 3H, imine CH_3), 1.56 (s, 0.6H, enamine CH_3).

Table 3, entry 3: Yield, 31% for **1b** and 72% for **2**. Imine to enamine ratio, 7:1. ^1H NMR ($\text{C}_6\text{D}_5\text{Cl}$, 400 MHz) δ 7.54 (m, 2H, *ArH*), 7.05 (m, 2H, *ArH*), 6.73 (m, 4H, *ArH*), 6.54 (m, 3H, *ArH*), 6.38 (d, $J = 8.8$ Hz, 2H, *ArH*), 6.32 (d, $J = 8.8$ Hz, 1H, *ArH*), 5.67 (s, 0.2H, enamine $\text{HC}(\text{NHPh})$), 5.20 (s, 0.2H, enamine *NH*), 3.59 (s, 2H, imine CH_2Ph), 3.40 (s, 0.2H, enamine CHPh), 3.03 (s, 3H, imine OCH_3), 2.92 (s, 0.6H, enamine OCH_3).

Table 3, entry 4: Yield, > 95% for **1b** and **2**. Imine to enamine ratio, 4:1. ^1H NMR ($\text{C}_6\text{D}_5\text{Cl}$, 400 MHz) δ 7.47 (m, 2H, *ArH*), 7.02 (m, 1H, *ArH*), 6.95 (m, 1H, *ArH*), 6.91-6.42 (m, 7H, *ArH*), 6.19 (d, $J = 8.0$ Hz, 2H, *ArH*), 5.91 (d, $J = 8.0$ Hz, 1H, *ArH*), 5.72 (s, 0.4H, enamine $\text{HC}(\text{NHPh})$), 5.07 (s, 0.4H, enamine *NH*), 3.44 (s, 2H, imine CH_2Ph), 3.44 (s, 0.8H, enamine CHPh).

Table 3, entry 5: Yield, 7% for **1b** and 69% for **2**. Only imine was observed. ^1H NMR ($\text{C}_6\text{D}_5\text{Cl}$, 400 MHz) δ 7.52 (m, 2H, *ArH*), 7.06 (m, 2H, *ArH*), 7.00-6.35 (m, 8H, *ArH*), 6.21 (t, $J = 7.6$ Hz, 1H, *ArH*), 3.39 (s, 2H, imine CH_2Ph), 1.50 (s, 6H, CH_3).

^1H NMR data for allene hydroamination reactions. Yields were determined by NMR integrations versus an external $\text{CH}_2\text{Cl}_2/\text{C}_6\text{D}_6$ standard.

Allene + 2,6-dimethylaniline: Yield, > 95%. ^1H NMR (C_6D_6 , 400 MHz) δ 7.05 (d, $J = 7.2$ Hz, 2H, ArH), 6.96 (t, $J = 7.2$ Hz, 1H, ArH), 2.02 (s, 6H, CH_3), 1.89 (s, 3H, CH_3), 1.27 (s, 3H, CH_3). These values match those in the literature.⁶

Cyclononadiene + aniline: Yield, >95%. ^1H NMR (C_6D_6 , 400 MHz) δ 7.09 (t, $J = 7.6$ Hz, 2H, ArH), 6.82 (t, $J = 7.6$ Hz, 1H, ArH), 6.60 (d, $J = 7.6$ Hz, 2H, ArH), 2.26 (m, 2H, CH_2), 2.01 (m, 2H, CH_2), 1.65 (m, 2H, CH_2), 1.48 (m, 2H, CH_2), 1.41-0.98 (m, 8H, CH_2). These values are analogous to those in the literature for cyclononylidene-(2,6-dimethylphenyl)amine: ^1H NMR (C_6D_6 , 300 MHz) δ 6.99 (d, $J = 7.6$ Hz, 2H, ArH), 6.86 (t, $J = 7.2$, 1H, ArH), 2.62 (m, 2H, CH_2), 2.11 (m, 2H, CH_2), 2.07 (s, 6H, CH_3), 1.97 (m, 2H, CH_2), 1.68 (m, 2H, CH_2), 1.68-1.48 (m, 8H, CH_2).⁷

General procedures for hydrolysis of imines. For compounds in Table 2, the solutions from NMR tube reactions were diluted with 3 mL of Et_2O , mixed with 3 mL of a 10% solution of HCl in water and allowed to stir for at least 4 h. The ethereal and aqueous layers were then separated and the aqueous layer was extracted with 3 x 2 mL of Et_2O . The combined Et_2O portions were dried over MgSO_4 and filtered. The resulting solutions were analyzed by GC-MS and compared to commercially-available authentic samples of the respective ketones by co-injection to confirm ketone identity. Trimethoxybenzene was used as an internal standard for GC-MS yields.

Table 2, entry 1: Yield, 74%. Retention time of 3-hexanone, 7.83 min. Retention time of product, 7.83min.

Table 2, entry 2: Yield, 72%. Retention time of 2-hexanone, 7.91 min. Retention time of products, 7.83 and 7.91.

Table 2, entry 3: Yield, 47%. Retention time of acetophenone, 12.78 min. Retention time of product, 12.78.

Table 2 entry 4: Yield, 40%. Retention time of 1-pentyne, 6.23 min. Retention time of product, 6.23.

⁷ Johnson, J. S.; Bergman, R. G. *J. Am. Chem. Soc.* **2001**, *123*, 2923-2924.

For compounds in Table 3, larger scale reactions were diluted with 20 mL of CH₂Cl₂, mixed with 50 mL of a 10% solution of HCl in water and allowed to stir for at least 4 h. The organic and aqueous layers were then separated. The aqueous layer was then extracted with 3 x 10 mL of CH₂Cl₂. The combined CH₂Cl₂ portions were dried over MgSO₄ and filtered. Solvent was removed under vacuum to give a yellow solid that was purified by flash chromatography (10% Et₂O in pentane). The ¹H NMR spectra of all hydrolysis products from compounds in Table 3 matched those of commercially available deoxybenzoin. ¹H NMR (C₆D₆, 400 MHz) δ 7.86 (m, 2H, ArH), 7.12-6.90 (m, 8H, ArH), 3.86 (s, 2H, CH₂). The isolated yields for entries 1, 3, and 4 are given below.

Entry 1: Diphenylacetylene (111 mg, 0.624 mmol). Aniline (58 mg, 0.624 mmol). Deoxybenzoin (92 mg, 0.47 mmol, 75%).

Entry 3: Diphenylacetylene (158 mg, 0.886 mmol). Anisidine (109 mg, 0.886 mmol). Deoxybenzoin (145 mg, 0.738 mmol, 83%).

Entry 4: Diphenylacetylene (190 mg, 1.07 mmol). p-Chloroaniline (136 mg, 1.07 mmol). Deoxybenzoin (134 mg, 0.682 mmol, 64%).

Representative procedure for the reduction of imines in Table 2. Hydroamination reaction mixtures (0.86 mmol of substrate in 3 mL of benzene) were transferred directly into a Schlenk flask containing LiAlH₄ (1.72 mmol) and THF (20 mL). The flask was fitted with a condenser and heated to 65 °C for 8 h. The flask was allowed to cool and then poured into 40 mL of water cooled with an ice water bath. This mixture was stirred while 50 mL of CH₂Cl₂ and 40 mL of 2M KOH were added. This mixture was allowed to stir for an additional 30 min. The organic layer was separated and then the aqueous layer was extracted with 3 x 20 mL of CH₂Cl₂. The combined organic portions were dried over MgSO₄ and filtered. Solvent was removed under vacuum to give a yellow oil which was purified by flash chromatography (10% Et₂O in pentane).

Table 2, entry 1: 3-Hexyne (121 mg, 1.47 mmol). Aniline (137 mg, 1.47 mmol). Amine (216 mg, 1.22 mmol, 83%). ¹H NMR (CDCl₃, 400 MHz) δ 7.28 (t, *J* = 8 Hz, 2H, ArH), 6.78 (t, *J* = 6.8 Hz, 1H, ArH), 3.5 (b, 1H, NH), 3.43 (quin, *J* = 5.6 Hz, 1H, CH), 1.77-1.48 (m, 6H, CH₂), 1.06 (t, *J* = 7.2 Hz, 6H, CH₃). These values match those in the literature.⁸

Table 2, entry 3: Phenylacetylene (92 mg, 0.90 mmol). Aniline (84 mg, 0.90 mmol). Amine (114 mg, 0.58 mmol, 64%). ^1H NMR (CDCl_3 , 400 MHz) δ 7.75-7.63 (m, 4H, ArH), 7.51 (m, 1H, ArH), 6.90 (t, J = 7.6 Hz, 1H, ArH), 6.67 (d, J = 7.6 Hz, 2H, ArH), 4.63 (q, J = 6.8 Hz, 1H, CH), 1.65 (d, J = 6.8 Hz, 3H, CH_3). These values match those in the literature.⁸

Hydroamination of norbornene with aniline. In the glovebox a vial was charged with 28 mg of **1a** (0.054 mmol, 1 equiv) and 3 mL of benzene. The resulting solution was mixed with 101 mg of norbornene (1.07 mmol, 20 equiv), 49 mg of $\text{Ph}_3\text{CB}(\text{C}_6\text{F}_5)_4$ (0.054 mmol, 1 equiv) and 199 mg of aniline (2.14 mmol, 40 equiv) in the order given. The reaction mixture was then transferred to a Schlenk flask with a Teflon stopper, taken out of the glovebox and placed in a 135 °C bath for 24 h. The reaction was allowed to cool and then transferred to a flask and diluted with 40 mL of CH_2Cl_2 at which point a flocculent precipitate was observed. The solution was filtered and then solvent was removed under vacuum. Compounds **10** and **11** were separated and purified by flash chromatography (3-20% gradient, Et_2O /pentane). Combined yield 32% (10% **10**, 22% **11**). ^1H NMR of compound **10** (CDCl_3 , 400 MHz) δ 7.17 (t, J = 7.6 Hz, 2H, H_9), 6.69 (t, J = 7.2 Hz, 1H, H_{10}), 6.59 (d, J = 7.6 Hz, 2H, H_8), 3.7 (b, 1H, NH), 3.23 (dd, J = 7.6, 2.8 Hz, 1H, H_1), 2.29 (s, 2H, H_3 , H_6), 1.82 (ddd, J = 2.4, 7.6, 12.8 Hz, 1H, H_2 endo), 1.57-1.13 (m, 7H, H_7 , H_5 , H_4 , H_2 exo). ^1H NMR C-bound (C_6D_6 , 400 MHz) δ 7.17 (d, J = 7.6 Hz, 1H, H_8), 7.09 (t, J = 7.6 Hz, 1H, H_{10}), 6.79 (t, J = 7.6 Hz, 1H, H_9), 6.71 (d, J = 7.6, 1H, H_{11}), 3.7 (b, 2H, NH_2), 2.61 (m, 2H, H_1 , H_6), 2.51 (s, 1H, H_3), 1.73-1.57 (m, 5H, H_2 exo, H_2 endo, H_4 exo, H_5 exo, H_7 syn), 1.42-1.24 (m, 2H, H_4 endo, H_5 endo), 1.05 (d, J = 9.6 Hz, 1H, H_7 anti). Both sets of NMR resonances match literature values.⁹

Compound **10** Compound **11**

⁸ Bytschkov, I.; Doye, S. *Eur. J. Org. Chem.* **2001**, 23, 4411-4418.

⁹ Brunet, J.-J.; Commenges, G.; Neibecker, D.; Philippot, K. *J. Organomet. Chem.* **1994**, 469, 221-228.

Stoichiometric addition of 2,6-dimethylaniline to compound 3. In the glovebox, a vial was charged with 42 mg (0.033 mmol, 1 equiv) of **3** and 0.5 mL of C₆D₅Cl. The resulting solution was mixed with 4 mg (0.033 mmol, 1 equiv) of 2,6-dimethylaniline and then transferred to an NMR tube. The ¹H NMR spectrum of this mixture showed that the 2,6-dimethylaniline had coordinated to the metallacycle to give complex **12**. ¹H NMR (C₆D₅Cl, 500 MHz) δ 7.24-6.65 (m, 23H, ArH), 4.17 (d, J = 15 Hz, 1H, CHHPh), 3.88 (d, J = 15 Hz, 1H, CHHPh), 3.73 (d, J = 10 Hz, 1H, CHHPh), 2.45 (s, 6H, CH₃), 1.43 (d, J = 10 Hz, 1H, CHHPh), 0.20 (s, 9H, CMe₃), -1.05 (d, J = 15 Hz, NH), -1.23 (d, J = 15 Hz, NH). The reaction mixture was allowed to sit at 25 °C for 24 h. A second NMR spectrum showed that the diastereotopic NH resonances had disappeared. The same experiment was repeated with 85% deuterated 2,6-dimethylaniline-*d*₂. The ¹H NMR spectrum of the initial reaction mixture was identical to that of **12** except for the integrations of the NH resonances which were only 0.2H. A ²H NMR spectrum of this reaction mixture (C₆F₅Cl, 500 MHz) contained a broad peak at -0.98 ppm. This reaction was also allowed to sit at 25 °C for 24 h and NMR analysis also showed disappearance of the diastereotopic ND resonances.