A Synthetic and Mechanistic Investigation into the Cobalt(I) Catalyzed Amination of Aryl Halides

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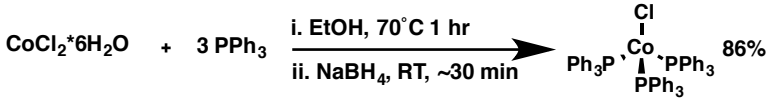
Supporting Information Table of Contents:

General Considerations. All manipulations of metal complexes were carried out in the absence of water and dioxygen using standard Schlenk techniques, or in an MBraun inert atmosphere drybox under a dinitrogen atmosphere except where specified otherwise. All glassware was oven dried for a minimum of 8 h and cooled in an evacuated antechamber prior to use in the drybox. "Schlenck tube" refers to ChemGlass© part number CG-1880-01 or CG-1880-02. Diethyl ether, tetrahydrofuran, toluene and benzene were dried and deoxygenated on a Glass Contour System (SG Water USA, Nashua, NH) and stored over 4 Å molecular sieves (Strem) prior to use. Chloroform-*d* and Benzene-d_6 were purchased from Cambridge Isotope Labs and were degassed and stored over 4 Å molecular sieves prior to use. Lithium hexamethyldisilazane was purchased from Sigma-Aldrich and recrystallized from toluene under an inert atmosphere prior to use. Cobaltous chloride hexahydrate (Puratrem, 99.99%) and DPEPhos (>99%) were purchased from Strem and used as received. Aryl halides were purchased from Sigma-Aldrich; liquids were degassed before use, and solids were used as received. $(PPh_3)_3CoCl$[1] and *tert*-butyl(4-iodophenoxy)dimethylsilane[2] were prepared according to literature procedures. All additives in Table S1 were obtained from commercial sources and used as received, except where noted; nucleophiles in entries 36-40 were obtained from commercial sources as the parent amine and lithiated with *n*-butyllithium in hexanes immediately before use. $(DPEPhos)CoCl_2$[8] and $[Co(N(SiMe_3)_2)_2]_2$[9] were prepared by literature procedures. Celite® 545 (J. T. Baker) was dried in a Schlenk flask for 24 hr under dynamic vacuum while heating to at least 150˚C prior to use in a drybox. NMR Spectra were recorded at room temperature on a Varian spectrometer operating at 500 MHz (^{1}H NMR) and 126 MHz (^{13}C NMR) and referenced to the residual $CHCl_3$ or C_6H_6 resonance (δ in parts per million, and *J* in Hz); ^{31}P Spectra were collected at 200 MHz and referenced to an external standard of H_3PO_4. Elemental analysis was performed on solid products by the University of Illinois Microanalysis Laboratory. Mass spectrometry (MS) was performed on liquids by the University of Illinois Mass Spectrometry Laboratory. Electron Impact (EI) spectra were performed at 70 eV using methane as the carrier gas on a Finnegan-MAT C5 spectrometer. Data are reported in the form of m/z (intensity relative to the base peak = 100).

Modified Synthesis of $(PPh_3)_3CoCl$ (1). *Additional characterization of the complex is presented here to complement previously published data*[3]*. Samples purchased from Strem have shown diminished reactivity with respect to freshly prepared **1**; as such the procedure is also reproduced here.*

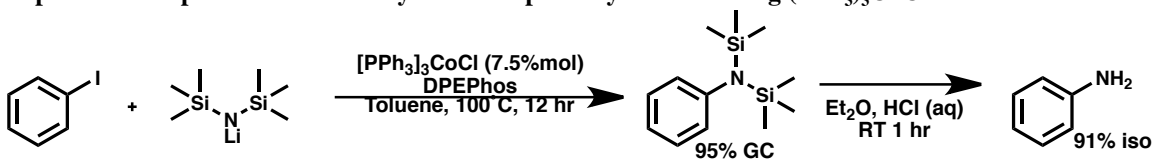


Cobaltous chloride hexahydrate (0.600 g, 2.52 mmol) is added to a round bottom flask under an N_2 atmosphere. EtOH (40 mL) is added, followed by solid triphenylphosphine (2 g, 7.63 mmol). The purple solution rapidly turns blue, and the mixture is heated to 70˚C to form a sky blue suspension. $NaBH_4$ (0.080 g, 2.11 mmol) is added against a flow of N_2 and the reaction is cooled to room temperature. The mixture exotherms slightly and begins to turn green, then darkens as a precipitate forms. Stirring is continued until the observed effervescence ceases. Once the reaction mixture has returned to room temperature, the precipitate is collected on a Büchner funnel under air and washed with ethanol until no blue color comes through the filtrate. The solid is then washed with a minimum amount of cold deionized water (~5 mL) ethanol (~10 mL) once more and then liberally with hexanes (30 mL). The solid is dried *in vacuo* to yield chlorotris(triphenylphosphine)cobalt(I) as a greenish-brown solid (1.60 g, 1.82 mmol, 86%). The compound is reasonably stable to air and moisture in the solid state, but oxidizes rapidly in solution as evidenced by the evolution of a blue color. ^{1}H NMR (500 MHz, Benzene-d_6) δ 9.93 (br, 2H), 7.44 (br, 2H), 7.09 (br, 1H); No resonances were observed in the ^{31}P NMR spectrum. Anal. Calcd for $(PPh_3)_3CoCl$ ($C_{54}H_{45}ClCoP_3$): C, 73.6; H, 5.2. Found: C, 73.2; H, 5.2. ICP-MS (Pd): 0.000088%

Synthesis of $(PPh_3)_2CoN(SiMe_3)_2$ (2). In the glovebox, chlorotris(triphenylphosphine)cobalt (440 mg, 0.5 mmol) is added to a tared 20 mL vial followed by 20 mL toluene. The mixture is stirred at room temperature for ~5-10 min to ensure homogeneity before cooling the solution to –35˚C. To this solid lithium hexamethyldisilazide (85 mg, 0.5 mmol) is added. The mixture is stirred at room temperature for

two hours then concentrated to dryness *in vacuo*. The residue is triturated with hexanes (3 x 2 mL) and the residual solids are then taken up into a minimal amount of diethyl ether (~ 2 mL). The solution is then filtered through a pad of Celite, concentrated slightly (~ 1.5 mL) and cooled to −35˚C overnight, yielding crystals suitable for X-ray diffraction. The mother liquor is concentrated further and again cooled to −35˚C, yielding pure **2** (340 mg, 0.46 mmol, 91%). ^{1}H NMR (500 MHz, Benzene-*d6*) δ 13.99, 9.61, 2.87, 1.64; No resonances were observed in the ^{31}P NMR spectrum. Anal. Calcd for $C_{42}H_{48}CoNP_2Si_2$: C, 67.81; H, 6.50; N, 1.88. Found: C, 67.95; H, 6.51; N, 1.76.

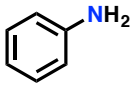
Representative procedure for the synthesis of primary anilines using $(PPh_3)_3CoCl$.



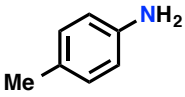
To a tared 20 mL vial in the glovebox is added solid DPEPhos (71 mg, 0.132 mmol) and chlorotris(triphenylphosphine)cobalt (58 mg, 0.066 mmol), followed by 3 mL of toluene. The mixture is heated on a hot plate set to 85˚C and stirred for twenty minutes until a translucent ruddy brown solution forms. Meanwhile, aryl halide (1 mmol) is added to a 35 mL tall Schlenck tube followed by lithium hexamethyldisilazide (437 mg, 2.62 mmol). The mixture is taken up in 2 mL toluene followed by the addition of the DPEPhos/$(PPh_3)_3CoCl$ solution. Minimal toluene is used to rinse the vial and walls of the tube; the vessel is then sealed and removed from the glovebox. The reaction is then heated for 12 hours at 100˚C in a stirred oil bath.

Work-up A (Most substrates): The reaction is then cooled before mesitylene (15 µL, 0.1 mmol) is added for GC-MS analysis. The crude mixture is then diluted with methanol (20 mL) and 1 N HCl (aq) is added (2 mL). After stirring for one hour at room temperature (completeness monitored by TLC in 10% Ethyl Acetate/Hexanes), the phases are separated and washed with 1 M KOH, then brine. The organics are dried over Na_2SO_4 before being concentrated to a colorless oil and separated by silica gel chromatography (conditions for each product specified below).

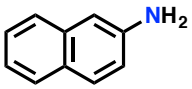
Work-up B (Acid-sensitive substrates): *Note: This method was most effective for electron-rich substrates*. The reaction is then cooled before mesitylene (15 µL, 0.1 mmol) is added for GC-MS analysis. The crude mixture is then diluted with diethyl ether (20 mL) and filtered over silica gel, using diethyl ether to wash remaining residue from the silica. The mixture is then adsorbed on silica (~1.5 g) and dried thoroughly. This was then let sit open to air for eight hours, during which time the silica begins to turn yellow. This is then loaded onto a column and the desired aniline isolated by chromatography (conditions for each product specified below).



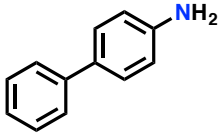
Aniline (Table 1, Entries 1a & 1b; 1a: 85 mg, 0.91 mmol, 91%, 1b: 56 mg, 0.60 mmol, 60%*)*. Colorless oil, volatile. Purified by Method A using a mobile phase of 4:1 Hexanes/Ethyl Acetate. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.20 (ddd, *J*=7.4, 6.4, 0.8 Hz, 2H), 6.80 (tt, *J*=7.4, 1 Hz, 1H), 6.71 (ddd, *J*=6.4, 1, 0.8 Hz, 2H), 3.65 (s, 2H); ^{13}C NMR (CDCl3) δ 146.3, 129.2, 118.4, 115.0. HRMS (ESI) calcd for C_6H_7N $[M+H]^+$: 94.0657, found: 94.0659.



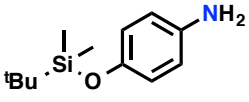
4-Toluidine (Table 1, Entries 2a & 2b; 2a: 104 mg, 0.96 mmol, 96%, 2b: 66 mg, 0.61 mmol, 61%*)*. Brown solid. Purified by Method A using a mobile phase of 9:1 Hexanes/Ethyl Acetate. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 6.97 (d, *J* = 8.3 Hz, 2H), 6.62 (d, *J* = 8.3 Hz, 2H), 3.53 (s, 2H), 2.25 (s, 3H); ^{13}C NMR (126 MHz, Chloroform-*d*) δ 143.77, 129.71, 127.74, 115.21, 20.41. Anal. Calcd for C_7H_9N: C, 78.46; H, 8.47; N, 13.07. Found: C, 77.63; H, 8.44; N, 12.99.



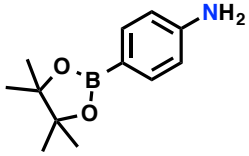
2-Aminonapthalene (Table 1, Entries 3a & 3b; 3a: 134 mg, 0.94 mmol, 94%, 3b: 91 mg, 0.63 mmol, 63%*)*. Brown solid. Purified by Method A using a mobile phase of 9:1 Hexanes/Ethyl Acetate. ^{1}H NMR (500 MHz, Benzene-d_6) δ 7.68-7.60 (m, 2H), 7.47 (d, J = 8.8 Hz, 1H), 7.34 (ddd, J = 8.2, 6.8, 1.3 Hz, 1H), 7.18 (ddd, J = 8.2, 6.8, 1.3 Hz, 1H), 6.82 (d, J = 2.3 Hz, 1H), 6.54 (dd, J = 8.8, 2.3 Hz, 1H), 2.77 (s, 2H); ^{13}C NMR (126 MHz, Benzene-d_6) δ 149.56, 145.66, 135.67, 129.07, 128.19, 126.72, 126.66, 122.83, 116.46, 104.95.



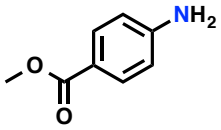
4-Aminobiphenyl (Table 1, Entries 4a & 4b; 4a: 125 mg, 0.74 mmol, 74%, 4b: 66 mg, 0.39 mmol, 39%*)*. Brown solid. Purified by Method A using a mobile phase of 9:1 Hexanes/Ethyl Acetate. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.53 (d, J=7.52 Hz, 2H), 7.41 (m, 4H), 7.27 (t, J=7.56 Hz, 1H), 6.76 (d, 8.18 Hz, 2H), 3.72 (s, 2H); ^{13}C NMR (CDCl3) δ 145.8, 141.1, 131.6, 128.61, 128.0, 126.4, 126.2, 115.3. Anal. Calcd for $C_{12}H_{11}N$: C, 85.17; H, 6.55; N, 8.28. Found: C, 85.08; H, 6.52; N, 8.29.



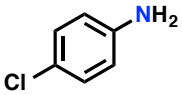
4-((tert-butyldimethylsilyl)oxy)aniline (Table 1, Entry 5; 201 mg, 0.90 mmol, 90%*)*. Yellow oil. Purified by Method B using a gradient mobile phase from pure hexanes to pure ethyl acetate in 10% increments. Slightly volatile. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 6.66 (d, J = 7.9 Hz, 2H), 5.58 (d, J = 7.9 Hz, 2H), 3.39 (s, 2H), 0.99 (s, 9H), 0.17 (s, 6H); ^{13}C NMR (126 MHz, Chloroform-*d*) δ 148.04, 140.23, 120.54, 116.18, 25.67, 18.09, -4.57. HRMS (ESI) calcd for $C_{12}H_{22}NOSi$ $[M+H]^{+}$: 224.1471, found: 224.1468.



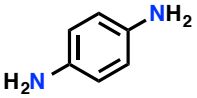
4-Aminophenylboronic Acid Pinacol Ester (Table 1, Entry 6; 199 mg, 0.91 mmol, 91%*)*. Waxy white solid. Purified by Method A using a mobile phase of 9:1 Hexanes/Ethyl Acetate; alternatively, crystallizes from methylene chloride. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.62 (d, J=8.4 Hz, 2H), 6.66 (d, J=8.4 Hz, 2H), 3.83 (s, 2H), 1.32 (s, 12H); ^{13}C NMR (CDCl3) δ 136.3, 132.0, 114.0, 109.8, 83.26, 24.82. Anal. Calcd for $C_{12}H_{18}BNO_2$: C, 65.79; H, 8.28; N, 6.39. Found: C, 66.1; H, 8.27; N, 6.49.



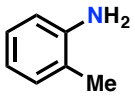
Methyl 4-Aminobenzoate (Table 1, Entry 7; 88 mg, 0.58 mmol, 58%*)*. White solid. Purified by Method A using a mobile phase of 9:1 Hexanes/Ethyl Acetate. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.84 (d, J = 8.6 Hz, 2H), 6.63 (d, J = 8.6 Hz, 2H), 4.08 (s, 2H), 3.85 (s, 3H); ^{13}C NMR (126 MHz, Chloroform-*d*) δ 167.11, 150.79, 131.53, 119.63, 113.73, 51.54. Anal. Calcd for $C_8H_9NO_2$: C, 63.56; H, 6; N, 9.27. Found: C, 63.58; H, 6.04; N, 9.32.



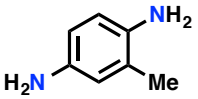
4-Chloroaniline (Table 1, Entry 8; 90 mg, 0.70 mmol, 70%*)*. White solid. Purified by Method A using a mobile phase of 9:1 Hexanes/Ethyl Acetate. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.10 (d, J = 8.32 Hz, 2H), 6.60 (d, J = 8.32 Hz, 2H), 3.65 (s, 1H); ^{13}C NMR (126 MHz, Chloroform-*d*) δ 144.90, 129.06, 123.08, 116.17. Anal. Calcd for C_6H_6ClN: C, 56.49; H, 4.74; N, 10.98. Found: C, 56.4; H, 4.7; N, 10.87.



p-Phenylenediamine (Table 1, Entry 9; 98 mg, 0.94 mmol, 94%*)*. Brown solid. Purified by Method A using a mobile phase of 1:1 Ethyl Acetate/Hexanes. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 6.57 (s, 4H), 3.33 (s, 4H); ^{13}C NMR (126 MHz, Chloroform-*d*) δ 138.56, 116.68. Anal. Calcd for C_6H_8N2: C, 66.64; H, 7.46; N, 25.9. Found: C, 67.21; H, 7.45; N, 25.51.



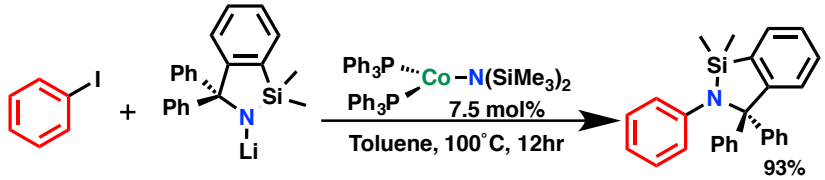
2-Toluidine (Table 1, Entry 10; 32 mg, 0.30 mmol, 30%*)*. Brown oil. Purified by Method A using a mobile phase of 9:1 Hexanes/Ethyl Acetate. Slightly volatile. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.13-6.98 (m, 2H), 6.81-6.61 (m, 2H), 3.60 (s, 2H), 2.18 (s, 3H); ^{13}C NMR (126 MHz, Chloroform-*d*) δ 144.48, 130.37, 126.89, 122.23, 118.55, 114.85, 17.28. HRMS (ESI) calcd for C_7H_9N $[M+H]^+$: 108.0813, found: 108.0812.



4-amino-2-Toluidine (Table 1, Entry 11; 83 mg, 0.69 mmol, 69%*)*. Pink solid. Purified by Method A using a mobile phase of 3:1 Hexanes/Ethyl Acetate. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 6.39 (dt, *J* = 2.1, 0.9 Hz, 1H), 6.33 (d, *J* = 7.5 Hz, 1H), 5.93 (dd, *J* = 7.5, 2.0 Hz, 1H), 4.03 (s, 2H), 3.54 (s, 2H), 2.09 (s, 3H); ^{13}C NMR (126 MHz, Chloroform-*d*) δ 143.63 , 138.23 , 127.42 , 121.33 , 119.53 , 116.78 , 17.64. HRMS (EI) calcd for $C_7H_{10}N_2$ $[M]^+$: 122.0844, found: 122.0844.

Procedure for the cross-coupling of other nucleophiles using $(PPh_3)_2CoN(SiMe_3)_2$ (2).

Note on nucleophile preparation: Due to varying stability of the lithium amides used, the compounds are stored as the parent amine and lithiated immediately before use.

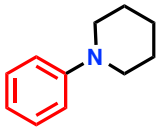


Synthesis of Lithium 1,1-dimethyl-3,3-diphenyl-1,3-dihydrobenzo[*c*][1,2]azasilol-2-ide.
Lithium 1,1-dimethyl-3,3-diphenyl-1,3-dihydrobenzo[*c*][1,2]azasilol-2-ide (above), was prepared in a manner similar to that used by Schulz et al.[7] *N*-trimethylsilyltriphenylmethylamine (497 mg, 1.5 mmol) is weighed into a tared vial in the glovebox. Diethyl ether (5 mL) is added, and the mixture is stirred at room temperature until fully dissolved, after which *n*-butyllithium (0.93 mL of 1.6 M in hexanes, 1.5 mmol) is added dropwise. Vigorous effervescence is observed, followed by the formation of a white precipitate; this precipitate briefly redissolves, yielding a pale yellow solution, before crashing out as a white powder once more, accompanied by increased effervescence. This is left stirring at room temperature for a further 45 minutes, before being concentrated to a white powder. This powder is then washed with cold hexanes (~2 mL) and dried under vacuum to remove residual ether. For catalytic reactions, this powder is used as-is; for characterization of the salt, the compound is taken up into THF, concentrated to incipient crystallization, and cooled to -40˚C overnight, yielding crystals suitable for X-ray diffraction (472 mg, 1.47 mmol 98%). HRMS (ESI) calcd for $C_{21}H_{21}LiNSi$ $[M+H]^+$: 322.1603, found: 322.1599.

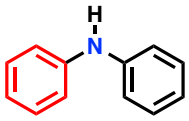
Synthesis of Lithium tert-butyltritylcarbamate.
Triphenylmethylamine (259 mg, 1.0 mmol) is weighed into a tared vial in the glovebox. Diethyl ether (10 mL) is added, and the mixture is stirred at room temperature until fully dissolved, after which *n*-butyllithium (0.65 mL of 1.6 M in hexanes, 1.0 mmol) is added dropwise. Vigorous effervescence is observed, followed by the generation of a pale yellow color. This is left stirring at room temperature for a further 45 minutes, following which di-*tert*-butyl dicarbonate (218 mg, 1.0 mmol) is added in portions as a solid. CAUTION: Great care must be taken to ensure that the reagent is added slowly, as the reaction exotherms strongly with the vigorous liberation of CO_2. The mixture is stirred for 20 minutes before being concentrated to a white powder. This powder is then washed with cold hexanes (~2 mL) and dried under vacuum to remove residual ether. For catalytic reactions, this powder is used as-is.

General cross-coupling procedure: Iodobenzene (204 mg, 1 mmol) is added to a 35 mL tall Schlenck tube, followed by nucleophile (2.62 mmol). The mixture is taken up in 3 mL toluene followed by the addition of

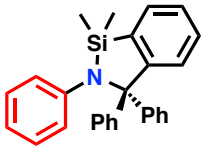
the $(PPh_3)_2CoN(SiMe_3)_2$ (56 mg, 0.075 mmol). An additional 2 mL toluene is used to rinse the vial and walls of the tube; the vessel is then sealed and removed from the glovebox. The reaction is then heated for 12 hours at 100˚C in a stirred oil bath. The reaction is then cooled and concentrated to dryness and isolated as specified for each product below.



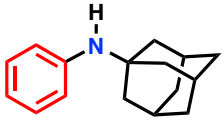
N-*phenylpiperidine (Table 3, Entry 1;* 22% conversion by GC-MS, 32 mg isolated, 0.2 mmol, 20%*)*. Off-white solid. Purified by preparative TLC using a mobile phase of 9:1 Ethyl Acetate/Hexanes. ^{1}H NMR (500 MHz, Benzene-d_6) δ 7.10−7.19 (m, 2H), 6.77−6.81 (m, 3H), 2.85 (t, J = 5.1 Hz, 4H), 1.34−1.42 (m, 4H), 1.21−1.27 (m, 2H); ^{13}C NMR (126 MHz, Benzene-d_6) δ 152.8, 129.3, 119.4, 117.0, 50.7, 26.1, 24.6. HRMS (EI) calcd for $C_{11}H_{15}N$ $[M]^+$: 161.1204, found: 161.1201.



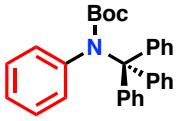
Diphenylamine (Table 3, Entry 2; 20% conversion by GC-MS, 25 mg isolated, 0.15 mmol, 15%*)*. Off-white solid. Deprotected and purified by Method A (see page S3) using a mobile phase of 9:1 Hexanes/Ethyl Acetate. ^{1}H NMR (500 MHz, Benzene-d_6) δ 7.10 (dd, J = 8.5, 7.2 Hz, 4H), 6.92 - 6.75 (m, 6H), 4.98 (s, 1H); ^{13}C NMR (126 MHz, Benzene-d_6) δ 143.52, 129.49, 121.10, 118.12. HRMS (EI) calcd for $C_{12}H_{11}N$ $[M]^+$: 169.0891 found: 169.0893.



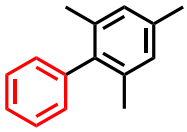
1,1-dimethyl-2,3,3-triphenyl-2,3-dihydro-1H-benzo[c][1,2]azasilole (*Table 3, Entry 3;* 100% conversion by GC-MS, 364 mg isolated, 0.93 mmol, 93%). Pale yellow air- and moisture-sensitive solid. Isolated by preparative TLC using a mobile phase of 9:1 Hexanes/Ethyl acetate. ^{1}H NMR (499 MHz, Benzene-d_6) δ 7.64 - 7.51 (m, 4H), 7.43 - 7.32 (m, 2H), 7.11 - 6.98 (m, 8H), 6.99 - 6.84 (m, 6H), 6.71 (tt, J = 6.7, 2.0 Hz, 1H), 0.56 (s, 6H). ^{13}C NMR (126 MHz, Benzene-d_6) δ 158.00, 145.29, 144.77, 134.28, 134.21, 134.05, 130.69, 130.16, 129.83, 127.06, 126.75, 126.70, 124.53, 121.12, 79.95, 1.37. HRMS (EI) calcd for $C_{27}H_{25}NSi$ $[M]^+$: 391.1756, found: 391.1756.



N-*adamantylaniline (Table 3, Entry 4;* 56% conversion by GC-MS, 102 mg isolated, 0.45 mmol, 45%*)*. Off-white solid. Deprotected and purified by Method A (see page S3) using a mobile phase of 7.5% Ethyl Acetate/Hexanes. ^{1}H NMR (500 MHz, Benzene-d_6) δ 6.83 (t, J = 7.2 Hz, 1H), 6.73 (dd, J = 8.5, 3.0 Hz, 2H), 3.02 (s, 1H), 1.88 – 1.93 (m, 3H), 1.74 (d, J = 3.0 Hz, 6H), 1.45 – 1.55 (m, 6H); ^{13}C NMR (126 MHz, Benzene-d_6) δ 146.76, 129.05, 119.12, 119.05, 51.95, 43.56, 36.65, 30.0. HRMS (EI) calcd for $C_{16}H_{21}N$ $[M]^+$: 227.1674, found: 227.1674.



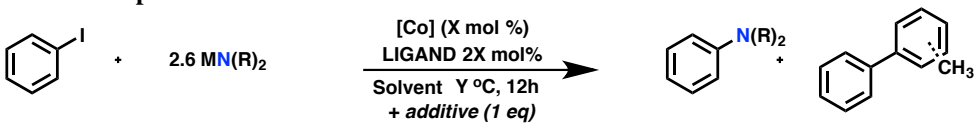
Tert-*butyl phenyl(trityl)carbamate* (*Table 3, Entry 5;* 60% conversion by GC-MS, 252 mg isolated, 0.58 mmol 58%). Pale yellow solid. Isolated by preparative TLC using a mobile phase of 9:1 Hexanes/Ethyl acetate. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.71 -7.64 (m, 6H), 7.48 - 7.34 (m, 8H), 7.30 (m, 3H), 7.22 (tt, J = 7.5, 2.1 Hz, 1H), 1.42 (s, 9H); ^{13}C NMR (125 MHz, Chloroform-*d*) δ 149.40, 142.64, 139.57, 131.73, 130.77, 129.21, 129.06, 127.91, 127.13, 80.22, 74.08, 28.16. HRMS (EI) calcd for $C_{30}H_{29}NO_2$ $[M]^+$: 435.2198, found: 435.2198.



2-phenylmesitylene (Table 3, Entry 6; 38% conversion by GC-MS, 61 mg, 0.31 mmol, 31%*)*. Colorless oil. Purified by preparative TLC using a mobile phase of 100% Hexanes. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.24 - 7.18 (m, 2H), 7.15 - 7.09 (m, 1H), 7.08 - 7.03 (m, 2H), 6.87 (s, 2H), 2.20 (s, 3H), 2.04 (s, 6H); ^{13}C NMR (126 MHz, Benzene-d_6) δ 141.78, 139.42, 136.46, 135.78, 129.58, 128.69, 128.51, 126.71, 21.08, 20.91. HRMS (EI) calcd for $C_{15}H_{16}$ $[M]^+$: 196.1252, found: 196.1252.

Optimization of Catalytic Reaction. *General procedure:* To a tared 20 mL vial in a glovebox is added solid ligand (0.132 mmol) and catalyst (58 mg, 0.066 mmol), followed by 3 mL toluene. The mixture is heated on a hot plate set to 85˚C and stirred for twenty minutes until a translucent ruddy brown solution forms. Meanwhile, iodobenzene (204 mg, 0.99 mmol) is added to a 35 mL tall Schlenck tube followed by nucleophile (2.62 mmol). The mixture is taken up in 2 mL toluene followed by the addition of additive (1 mmol), then the ligand/$(PPh_3)_3CoCl$ solution. Minimal toluene is used to rinse the vial and walls of the tube; the vessel is then sealed and heated for 12 hours at 100˚C in a stirred oil bath. The reaction is cooled before mesitylene (15 µL, 0.1 mmol) is added for GC-MS analysis. These results are presented in Table S1.

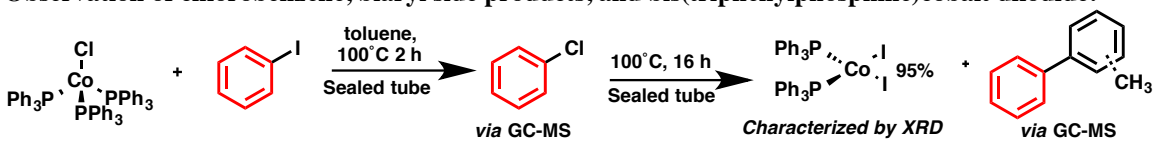
Table S1. Optimization.



	Entry #	Nucleophile	[Co] (X mol %)	Ligand	Additive	Solvent	Temp	% Conv.	% Amine	% Biaryl
Solvents	1	LiN(SiMe3)2	(PPh3)3CoCl (7.5%)	None	None	Toluene	100˚C	100%	77%	0%
	2	LiN(SiMe3)2	(PPh3)3CoCl (7.5%)	None	None	Benzene	100˚C	100%	53%	0%
	3	LiN(SiMe3)2	(PPh3)3CoCl (7.5%)	None	None	Hexanes	100˚C	100%	46%	0%
	4	LiN(SiMe3)2	(PPh3)3CoCl (7.5%)	DPEPhos	None	THF	100˚C	0%	0%	0%
	5	LiN(SiMe3)2	(PPh3)3CoCl (7.5%)	DPEPhos	None	Dioxane	100˚C	0%	0%	0%
	6	LiN(SiMe3)2	(PPh3)3CoCl (7.5%)	DPEPhos	None	DME	100˚C	0%	0%	0%
	7	LiN(SiMe3)2	(PPh3)3CoCl (7.5%)	DPEPhos	None	C6H5CF3	100˚C	60%	56%	0%
	8	LiN(SiMe3)2	(PPh3)3CoCl (7.5%)	DPEPhos	None	C6F6	100˚C	23%	23%	0%
Ligands	9	LiN(SiMe3)2	(PPh3)3CoCl (7.5%)*	DPEPhos	None	Toluene	100˚C	100%	79%	0%
	10	LiN(SiMe3)2	(PPh3)3CoCl (7.5%)	DPEPhos	None	Toluene	100˚C	100%	95%	0%
	11	LiN(SiMe3)2	(PPh3)3CoCl (7.5%)	dppe	None	Toluene	100˚C	100%	68%	0%
	12	LiN(SiMe3)2	(PPh3)3CoCl (7.5%)	dppf	None	Toluene	100˚C	100%	97%	0%
	13	LiN(SiMe3)2	(PPh3)3CoCl (7.5%)	BINAP	None	Toluene	100˚C	100%	98%	0%
Catalyst Loading	14	LiN(SiMe3)2	(PPh3)3CoCl (4%)	DPEPhos	None	Toluene	100˚C	99%	85%	0%
	15	LiN(SiMe3)2	(PPh3)3CoCl (2%)	DPEPhos	None	Toluene	100˚C	79%	60%	0%
	16	LiN(SiMe3)2	(PPh3)3CoCl (7.5%)	DPEPhos	Dark	Toluene	100˚C	100%	96%	0%
Other Alkali salts	17	NaN(SiMe3)2	(PPh3)3CoCl (7.5%)	DPEPhos	None	Toluene	100˚C	100%	28%	71%
	18	KN(SiMe3)2	(PPh3)3CoCl (7.5%)	DPEPhos	None	Toluene	100˚C	100%	0%	82%
	19	LiN(SiMe3)2	(PPh3)3CoCl (7.5%)	DPEPhos	KOtBu	Toluene	100˚C	73%	0%	45%
	20	LiN(SiMe3)2	(PPh3)3CoCl (7.5%)	DPEPhos	LiOtBu	Toluene	100˚C	100%	73%	15%
	21	LiN(SiMe3)2 (5.2 eq)	(PPh3)3CoCl (7.5%)	None	None	Toluene	100˚C	100%	99%	0%
	22	LiN(SiMe3)2	(PPh3)2CoN(SiMe3)2 (7.5%)	None	None	Toluene	100˚C	92%	80%	0%
Radical Traps	23	LiN(SiMe3)2	(PPh3)3CoCl (7.5%)	DPEPhos	1,1-diphenylethene	Toluene	100˚C	100%	96%	0%
	24	LiN(SiMe3)2	(PPh3)3CoCl (7.5%)	DPEPhos	BHT	Toluene	100˚C	100%	94%	0%
	25	LiN(SiMe3)2	(PPh3)3CoCl (7.5%)	DPEPhos	1,4-CHD	Toluene	100˚C	100%	93%	0%
	26	LiN(SiMe3)2	(PPh3)3CoCl (7.5%)	DPEPhos	TEMPO	Toluene	100˚C	40%	0%	0%
	27	LiN(SiMe3)2	(PPh3)3CoCl (7.5%)	DPEPhos	Ph3CCl	Toluene	100˚C	36%	22%	13%
Co(II) precatalysts	28	LiN(SiMe3)2	(DPEPhos)CoCl2 (7.5%)	None	None	Toluene	100˚C	100%	50%	50%
	29	LiN(SiMe3)2	[Co(N(SiMe3)2)2]2 (7.5%)	DPEPhos	None	Toluene	100˚C	100%	80%	15%
	30	LiN(SiMe3)2	[Co(N(SiMe3)2)2]2 (15%)	DPEPhos	None	Toluene	100˚C	100%	70%	30%
	31	LiN(SiMe3)2	(PPh3)3CoCl (7.5%)	DPEPhos	None	Durene	100˚C	48%	46%	0%
	32	LiN(SiMe3)2	(PPh3)3CoBr (7.5%)	DPEPhos	None	Toluene	100˚C	100%	97%	0%
CONTROL	33	LiN(SiMe3)2	None	None	None	Toluene	100˚C	0%	0%	0%
Temperature	34	LiN(SiMe3)2	(PPh3)3CoCl (7.5%)	DPEPhos	None	Toluene	RT	0%	0%	0%
	35	LiN(SiMe3)2	(PPh3)3CoCl (7.5%)	DPEPhos	None	Toluene	50˚C	6%	0%	5%
Other Nucleophiles	36	LiNH2	(PPh3)3CoCl (7.5%)	DPEPhos	None	Toluene	100˚C	0%	0%	0%
	37	NaNHPh	(PPh3)3CoCl (7.5%)	DPEPhos	None	Toluene	100˚C	40%	0%	30%
	38	LiNPh(SiMe3)	(PPh3)3CoCl (7.5%)	DPEPhos	None	Toluene	100˚C	40%	0%	20%
	39	LDA	(PPh3)3CoCl (7.5%)	DPEPhos	None	Toluene	100˚C	100%	0%	13%
	40	LiNtBu2	(PPh3)3CoCl (7.5%)	DPEPhos	None	Toluene	100˚C	100%	0%	48%
	41	LiPiperidide	(PPh3)3CoCl (7.5%)	DPEPhos	None	Toluene	100˚C	100%	0%	50%
	42	LiPiperidide (1 eq)	(PPh3)3CoCl (7.5%)	DPEPhos	LiN(SiMe3)2 (2.6 eq)	Toluene	100˚C	24%	10%	12%

All entries reported as the average of at least two runs.

Observation of chlorobenzene, biaryl side products, and bis(triphenylphosphine)cobalt diiodide.



In the glovebox, chlorotris(triphenylphosphine)cobalt (1 mmol, 881 mg) is added to a 15 mL Schlenck tube. To this is added toluene (10 mL), followed by iodobenzene (1 mmol, 204 mg). The mixture is removed from the glovebox and heated in a stirred oil bath at 100˚C for two hours, after which an aliquot is removed under inert atmosphere for GC-MS analysis. The reaction is heated further for 16 hours before being returned to the glovebox, where another aliquot is taken for GC-MS. The solution is then concentrated to incipient crystallization, filtered, and cooled to −35˚C overnight, yielding crystals suitable for X-ray diffraction. The mother liquor is concentrated further and again cooled to −35˚C, yielding 397 mg total crystalline product (95%). ^{1}H NMR (500 MHz, Benzene-*d6*) δ 15.21 (br, 12H), -4.01 (br, 12H), -5.49 (br, 6H); No peaks were observed in the ^{31}P spectrum that could be attributed to the metal complex. Anal. Calcd for $C_{36}H_{30}CoP_2I_2$: C, 51.64; H, 3.61. Found: C, 50.33; H, 3.48.

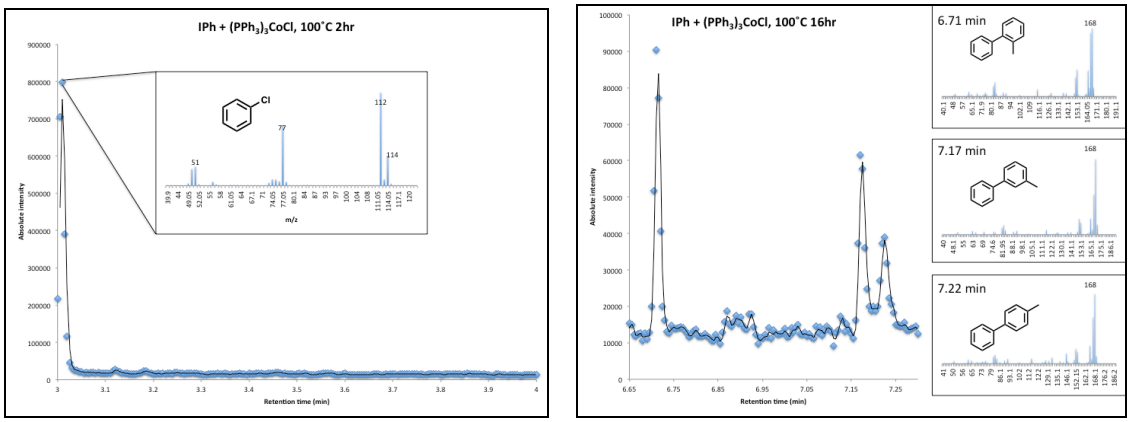
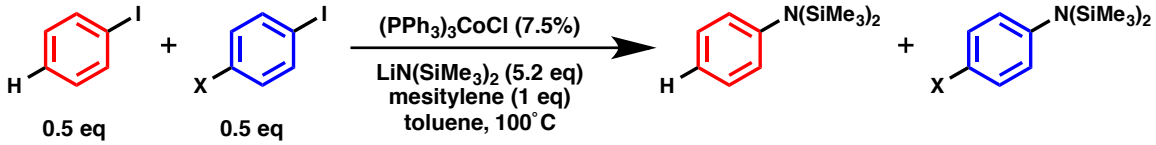


Figure S1. GC-MS trace illustrating the formation of cholorobenzene.

Linear Free Energy Study



In a glovebox, a 50 mL Schlenck flask is charged with a solution of iodobenzene (102 mg, 0.5 mmol), substituted aryl iodide (0.5 mmol), and mesitylene (120 mg, 1 mmol) in toluene (10 mL). To this is added solid lithium hexamethyldisilazide (878 mg, 5.2 mmol), and the solution is stirred at room temperature until all components have gone into solution. A 15 µL sample is removed and set aside for later analysis by GC as the 't_0' sample. Meanwhile, chlorotris(triphenylphosphine)cobalt (66 mg, 0.075 mmol) is weighed into a tared vial and taken up in toluene (2 mL). This solution is transferred to the Schlenck flask, which is sealed, removed from the glovebox, and heated to 100˚C in a well-stirred oil bath. Once each minute, 15 µL of solution is removed by pipette against a flow of argon in three evenly-spaced 5 µL aliquots over 15 seconds. These aliquots are used to prepare GC samples that are analyzed using a temperature program which ramps from 50˚C to 250˚C over 17 minutes with a three minute hold at 250˚C. The results are summarized in the following tables and charts.

Equation S1. $\ln\left(\frac{X_0}{X}\right) = k_{rel} \ln\left(\frac{H_0}{H}\right)$

Table S2. Summarized k_{rel} data

	S1		S2		S3		Averages			
X	Krel	logKrel	Krel	logKrel	Krel	logKrel	Krel	Stddev	logKrel	Stddev
OMe	1.49	0.17	1.39	0.14	1.39	0.14	1.42	0.06	0.15	0.02
Me	1.19	0.08	1.22	0.09	1.23	0.09	1.21	0.02	0.08	0.01
Ph	0.55	-0.26	0.50	-0.30	0.51	-0.30	0.52	0.03	-0.28	0.02
F	0.49	-0.31	0.44	-0.35	0.49	-0.31	0.47	0.03	-0.33	0.02
Cl	0.56	-0.25	0.56	-0.26	0.61	-0.21	0.58	0.03	-0.24	0.02
CF3	0.71	-0.15	0.72	-0.14	0.71	-0.15	0.71	0.004	-0.15	0.003

Table S3. Hammett σ parameters

	Closed Shell				Open Shell		
X	**σ**	**σ** $^{+}$	**σ** $^{-}$	**σ** ^{I}	**σ**$^{\bullet}$ (Creary)	**σ**$^{\bullet}$ (Arnold)	**σ**$^{\bullet}$ (Jiang)
OMe	-0.26	-0.78	-0.26	0.27	0.24	0.18	0.23
Me	-0.17	-0.31	-0.17	-0.05	0.11	0.15	0.15
Ph	-0.01	-0.18	0.02	0.1	0.46	NA	0.47
F	0.06	-0.07	-0.03	0.5	-0.08	-0.11	-0.02
Cl	0.23	0.11	0.19	0.46	0.12	0.11	0.22
CF3	0.54	0.61	0.65	0.42	0.08	-0.09	-0.01

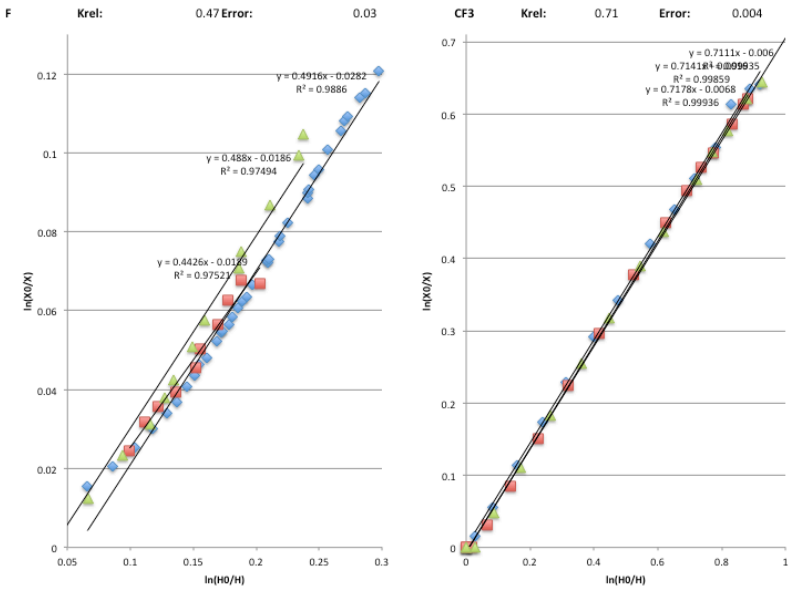


Figure S2. Relative rates for 1-fluoro-4-iodobenzene (left) and 1-iodo-4-(trifluoromethyl)benzene (right).

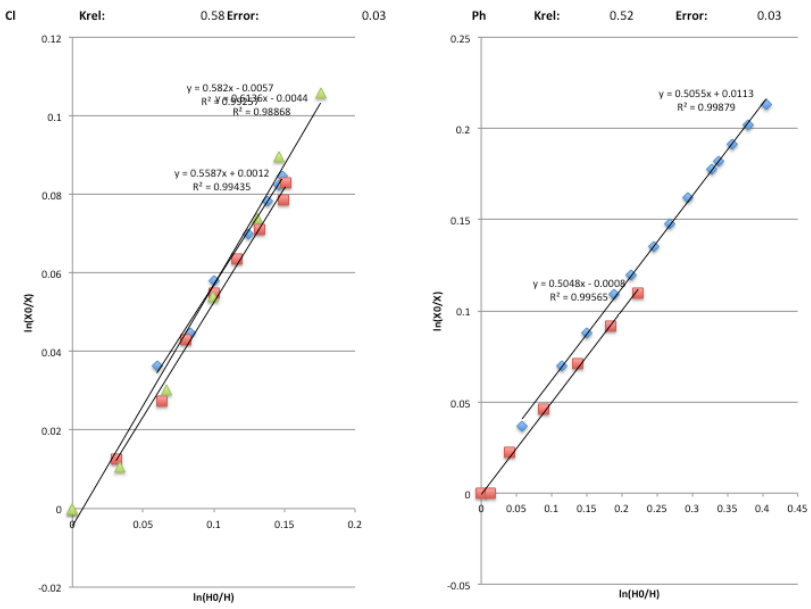


Figure S3. Relative rates for 1-chloro-4-iodobenzene (left) and 4-iodo-1,1'-biphenyl (right).

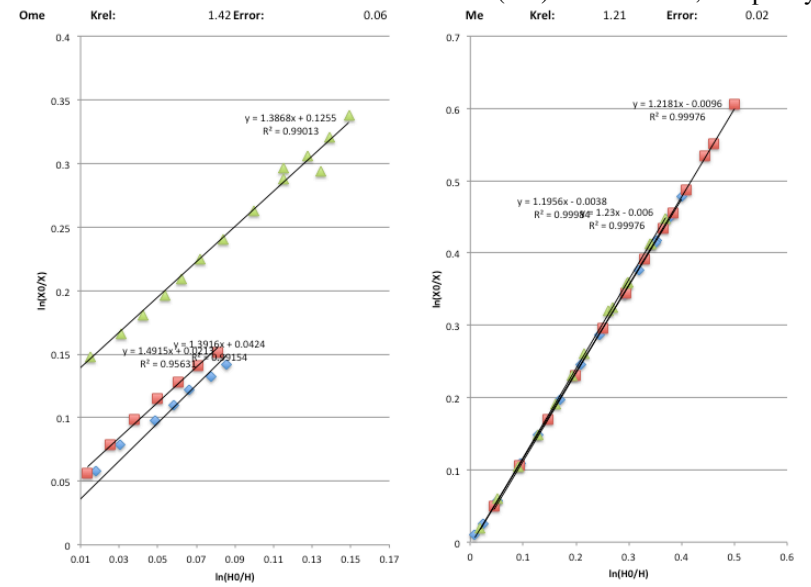


Figure S4. Relative rates for 1-iodo-4-methoxybenzene (left) and iodotoluene(right).

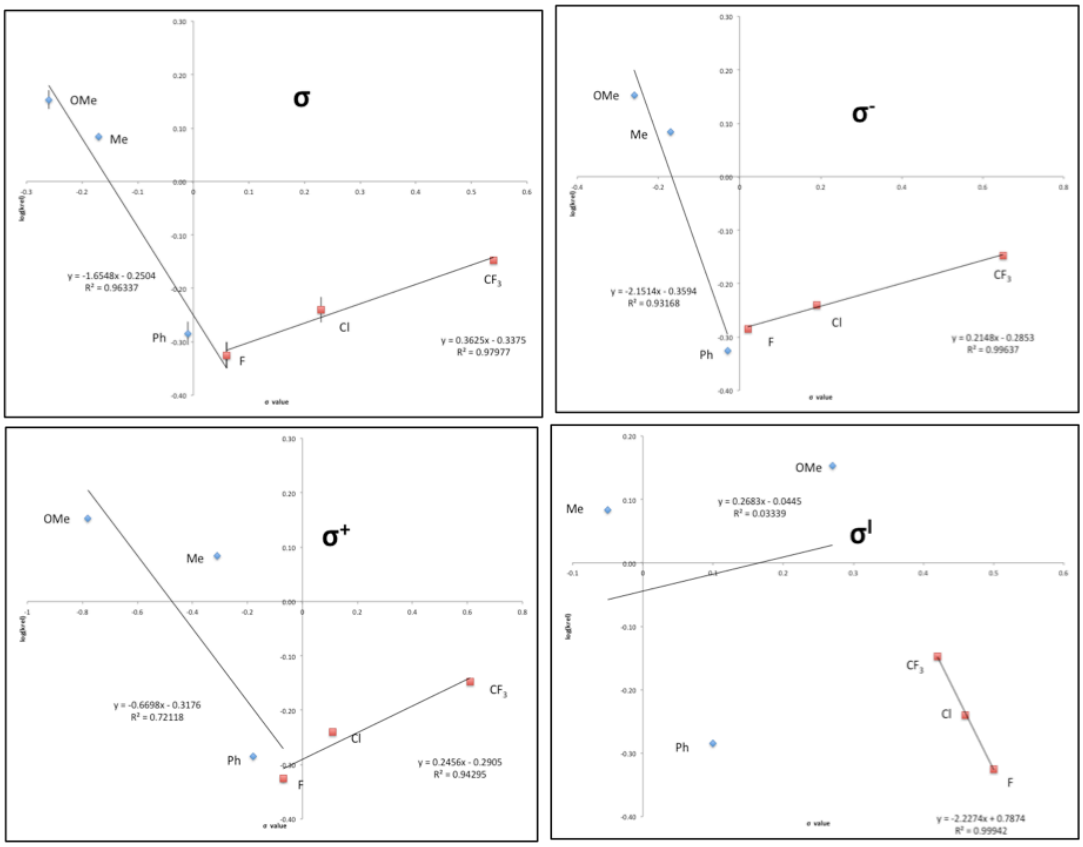


Figure S5. Closed-shell Hammett Plots

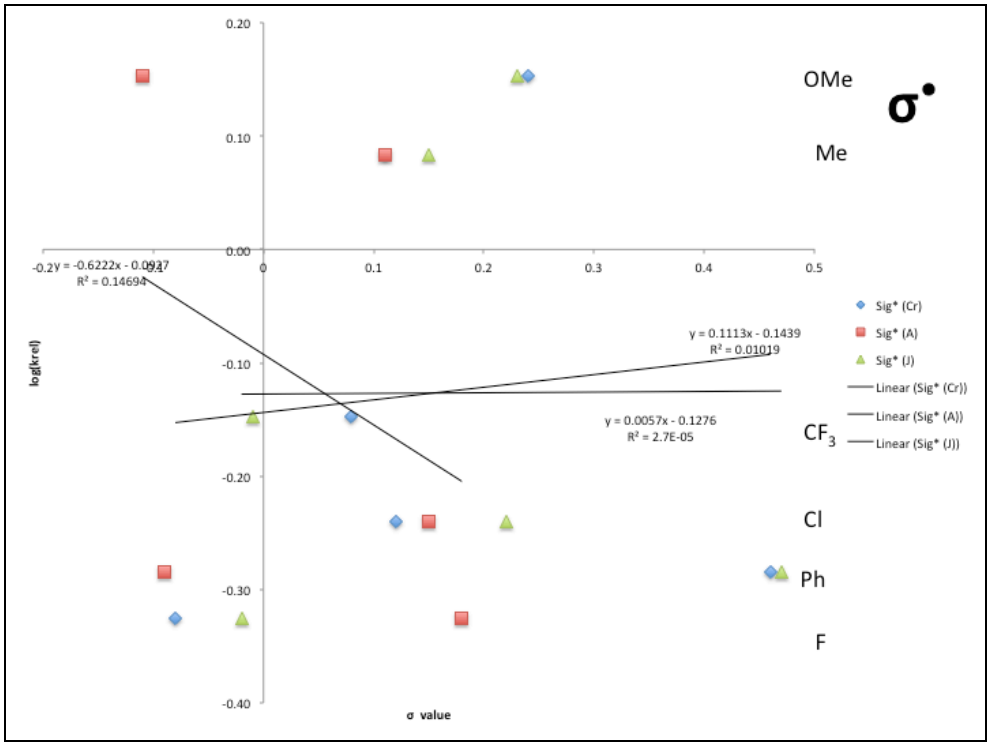


Figure S6. Open-shell Hammett Plots (Cr = Creary, A = Arnold, J = Jiang, See Table S3 for values)

Crystallographic data:

X-Ray Diffraction Techniques. All structures were collected on a Bruker three-circle platform goniometer equipped with an Apex II CCD and an Oxford cryostream cooling device. Radiation was from a graphite fine focus sealed tube Mo Kα (0.71073 Å) source. The crystal was mounted on a cryoloop using Paratone-N oil. Structures were collected at 168 K. Data was collected as a series of ϕ and/or ω scans. Data was integrated using SAINT[5] and scaled with either a numerical or multi-scan absorption correction using SADABS[5]. The structures were solved by direct methods or Patterson maps using SHELXS-97[6] and refined against F^2 on all data by full matrix least squares with SHELXL-97[6]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were either located or placed at idealized positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the atoms they are linked to (1.5 times for methyl groups). Further details on the structure is noted below.

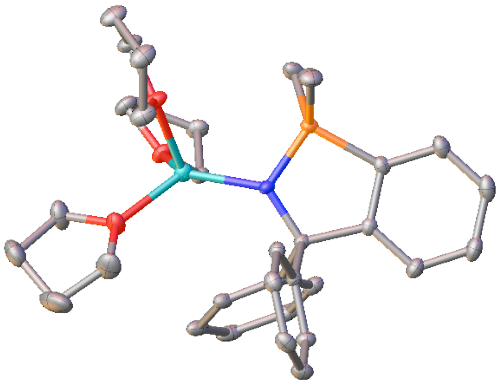


Figure S7. Crystal structure of Lithium silaazacycle (Table 3, Entry 3).

$(PPh_3)_3CoN(SiMe_3)_2$ (2). The structure was solved in the triclinic space group *P-1* with two molecule per unit cell and one in the asymmetric unit.

Lithium silaazaheterocycle. The structure was solved in the orthorhombic space group $Pna2_1$ with 4 molecules per unit cell and one in the asymmetric unit.

Table S4. Experimental Details for **2** and Lithium silaazaheterocycle**.**

	2	**Li-silaazaheterocycle**
Moiety Formula	$C_{42}H_{48}NSi_2P_2Co$	$C_{33}H_{44}NLiO_3Si$
FW	743.86	537.72
Crystal System	Triclinic	orthorhombic
Space Group (Z)	P-1	$Pna2_1$
a (Å)	9.280(2)	18.7063(12)
b (Å)	12.256(3)	11.4184(7)
c (Å)	18.651(4)	13.9803(10)
α (°)	98.324(3)	90
β (°)	91.537(3)	90
γ (°)	106.636(3)	90
Volume ($Å^3$)	2005.8(8)	2986.1(3)
Calc. ρ (g/cm^3)	1.232	1.196
μ (mm^{-1})	.597	0.112
Crystal Size (mm)	0.474 x 0.273 x 0.164	0.596 x 0.37 x 0.369
Reflections	23646	9165
Completeness (to 2θ)	98.8	100
GOF on F^2	1.038	1.061
R1, wR2	0.0504, 0.1305	0.0311, 0.0820

References:

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(S4) Bradley, D. C.; Chisholm, M. H. *Acc. Chem. Res.* **1976**, *9*, 273–280.

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