



Supporting Information

Accessing Ta/Cu Architectures via Metal-Metal Salt Metatheses: Heterobimetallic C–H Bond Activation Affords μ -Hydrides

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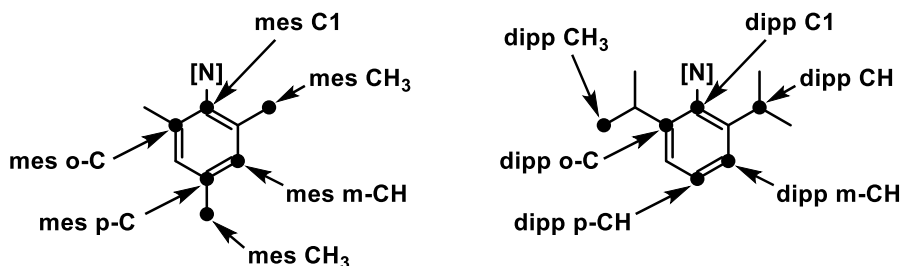
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Experimental Details

General Considerations

Unless otherwise specified, all operations were carried out in an MBraun drybox under a nitrogen atmosphere or using standard Schlenk and vacuum line techniques. All reaction glassware for air- and moisture-sensitive chemistry was dried at 140 °C for a minimum of 8 hours and cooled in either an evacuated glovebox antechamber or under vacuum on a Schlenk/vacuum line. Solvents for air- and moisture-sensitive reactions were dried over sodium benzophenone ketyl or by the method of Grubbs.^[1] Deuterated solvents were purchased from Cambridge Isotope Laboratories and vacuum transferred from sodium benzophenone ketyl. Solvents, once dried and degassed, were vacuum transferred directly prior to use or stored under inert atmosphere over activated 4 Å molecular sieves (Fischer Scientific—activated under vacuum at 300 °C for 72 hours). SiMesCuCl,^[2] SiPrCuCl,^[2] EtCAACuCl,^[3] and [Na(THF)][Ta(naph)₃]^[4] were prepared according to literature procedures. [Na(THF)][Ta(naph-*d*₈)₃] was prepared analogously, employing Na[naph-*d*₈]. The latter was prepared from deuterated naphthalene purchased from Sigma Aldrich and sublimed before use. Commercial reagents were purchased from standard vendors and used without further purification unless noted otherwise.

¹H and ¹³C{¹H} spectra were recorded on a Bruker Avance Neo 500 MHz (Prodigy BBO Cryoprobe), Varian Vnmrs 600 MHz (PFF AutoX Dual Broadband probe), or Varian Vnmrs 400 MHz (PFG AutoX Dual Broadband probe) spectrometer with shifts reported in parts per million (ppm). ²H spectra were recorded on a Varian Vnmrs 700 MHz (PFG AutoX Broadband Probe) spectrometer with shifts reported in parts per million (ppm). ¹H, ²H, and ¹³C{¹H} spectra are referenced to residual solvent peaks.^[5] Multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, dt = doublet of triplets, td = triplet of doublets, qq = quartet of quartets, vt = virtual triplet, d vt = doublet of virtual triplets, m = multiplet, br = broad, and v br = very broad (multiplicity assignments are omitted for “v br” assignments due to poor resolution). Mesityl (mes) and diisopropyl phenyl (dipp) ring positions are labeled as outlined below:

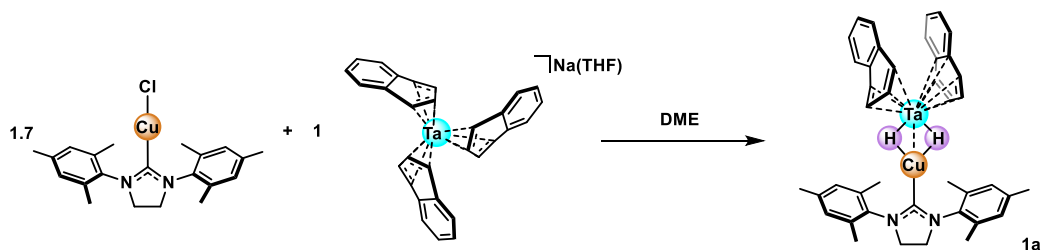


The bulk purity of diamagnetic complexes was established via qNMR^[6] rather than combustion analysis.^[7] Previous work in our lab has shown that this technique correlates with combustion analysis results for related multinuclear clusters.^[8] In each qNMR assay, a hexamethyldisiloxane (HMDSO) standard was added to a C₆D₆ solution of each analyte. ¹H NMR spectra (1 scan) were collected with a 90° pulse angle, no steady state scans, and no autogain. The relative peak integration of the standard ($\delta_{\text{HMDSO}} = 0.12$ ppm) and

that of each baseline-resolved compound ligand proton signal was recorded; these values were used to determine the percent purity employing the formula below (n = number of protons giving rise to the integral, Int = integral value, MW = molecular weight, m = exact weight of sample, ic = internal standard, t = target analyte).

$$P [\%] = \frac{n_{ic} * Int_t * MW_t * m_{ic}}{n_t * Int_{ic} * MW_{ic} * m_t}$$

Synthesis of 1a



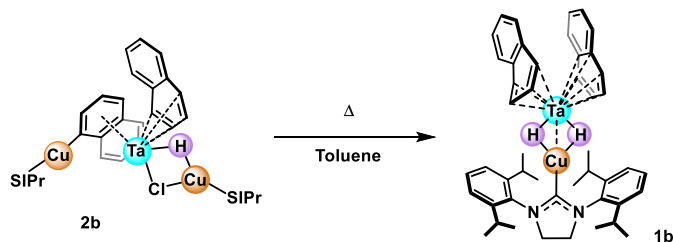
A 20 mL scintillation vial was charged with a DME (10 mL) solution of SIMesCuCl (120.2 mg, 0.30 mmol) and a stir bar. A solution of $[\text{Ta}(\text{C}_{10}\text{H}_8)_3]^-$ (111.5 mg, 0.17 mmol) in DME (6 mL) was added dropwise, with stirring. The reaction mixture was left to stir at room temperature for 16 hours, affording an orange/brown solution with a dark brown precipitate. At this time, volatiles were removed *in vacuo* and the resulting residue was triturated with hexanes (2 x 5 mL). The solids were washed with hexanes (20 mL) and diethyl ether (20 mL). The diethyl ether was filtered through a sintered glass frit packed with a bed of Celite and the solids were further extracted until the washes ran clear (~50 mL, total). The bright orange filtrate was dried under reduced pressure, affording $(\text{CuSIMes})\text{TaH}_2(\text{C}_{10}\text{H}_8)_2$ as an orange solid (17.3 mg, 0.021 mmol, 12%). X-ray quality crystals were grown via vapor diffusion of pentane into a concentrated diethyl ether solution of $(\text{CuSIMes})\text{TaH}_2(\text{C}_{10}\text{H}_8)_2$.

^1H (500 MHz, C_6D_6 , 25 °C) δ (ppm): 6.75 (s, 4H, mesityl m-CH), 6.36 (m, 8H, naphthyl-CH), 4.95 (m, 4H, naphthyl-CH), 4.19 (s, 4H, naphthyl-CH), 2.95 (s, 4H, carbene- CH_2), 2.11 (d, $J = 5.4$ Hz, 18 H, mesityl- CH_3), -7.07 (s, 2H, Ta-H-Cu).

$^{13}\text{C}\{^1\text{H}\}$ (126 MHz, C_6D_6 , 25 °C) δ (ppm): 208.25 (s, carbene-C), 138.62 (s, mesityl p-C), 136.02 (m, overlapping, mesityl o-C and mesityl C1 [corroborated by HSQC and HMBC]), 132.59 (s, naphthyl-C_{bridge}), 129.51 (s, mesityl m-C), 126.25 (s, naphthyl-CH), 125.17 (s, naphthyl-CH), 94.19 (s, naphthyl-CH), 66.29 (s, naphthyl-CH), 49.99 (s, carbene- CH_2), 20.92 (s, mesityl- CH_3), 17.79 (s, mesityl- CH_3).

qNMR (^1H NMR, 400MHz, C_6D_6 with HMDSO standard 25 °C): 99%

Synthesis of 1b



A Teflon-stoppered Schlenk tube was charged with a toluene (8 mL) solution of $(\text{SIPrCu})_2\text{HTaCl}(\text{C}_{10}\text{H}_7)(\text{C}_{10}\text{H}_8)$ (37.5 mg, 0.027 mmol) and a stir bar, sealed, and placed in an oil bath preheated to 110 °C. The reaction mixture was stirred at 110 °C for 16 hours,

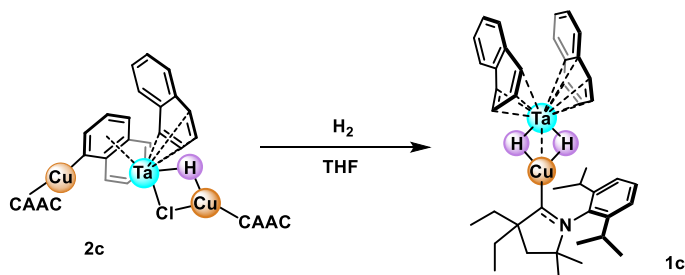
at which time the reaction was cooled and solvent was removed under reduced pressure. The solids were triturated with hexanes (2 x 10 mL), affording a brown residue. Extraction into hexanes (15 mL), filtration through Celite, and removal of volatiles afforded (SIPrCu)TaH₂(C₁₀H₈)₂ as an orange powder (15.8 mg, 0.018 mmol, 66%). X-ray quality crystals were grown via vapor diffusion of pentane into a toluene solution of (SIPrCu)TaH₂(C₁₀H₈)₂ at –35 °C.

¹H (500 MHz, C₆D₆, 25 °C) δ (ppm): 7.22 (t, 2H, *J* = 7.8 Hz, dipp p-CH), 7.06 (d, 4H, *J* = 7.7 Hz, dipp m-CH), 6.36 (d, 8H, *J* = 23.1 Hz, naphthyl-CH), 4.79 (s, 4H, naphthyl-CH), 4.11 (s, 4H, naphthyl-CH), 3.15 (s, 4H, carbene-CH₂), 2.93 (m, 4H, dipp-CH), 1.45 (d, 12H, *J* = 16.1 Hz, dipp-CH₃), 1.15 (d, 12H, *J* = 15.3 Hz, dipp-CH₃), –7.17 (s, 2H, Ta–H–Cu).

¹³C{¹H} (126 MHz, C₆D₆, 25 °C) δ (ppm): 147.27 (s, dipp o-C), 132.61 (s, naphthyl-C_{bridge}), 129.99 (s, dipp p-CH), 126.25 (s, naphthyl-CH), 125.22 (s, naphthyl-CH), 124.59 (s, dipp m-CH), 95.12 (naphthyl-CH), 66.06 (s, naphthyl-CH), 53.00 (s, carbene-CH₂), 29.04 (s, dipp-CH), 24.65 (s, dipp-CH₃). Note: The SIPr carbene carbon was not clearly observed given the low signal/noise ratio of the spectrum despite collecting 3072 scans on a cryoprobe equipped spectrometer (see instrument details above).

qNMR (¹H NMR, 400MHz, C₆D₆ with HMDSO standard 25 °C): 97%

Synthesis of 1c



A Schlenk tube was charged with a deep red THF (10 mL) solution of (E^tCAACCu)₂HTaCl(C₁₀H₇)(C₁₀H₈) (109.7 mg, 0.089 mmol) and a stir bar. The tube was sealed, degassed via three freeze-pump-thaw cycles, and backfilled with H₂ (1 atm). The reaction was stirred vigorously for 16 hours at room temperature, during which time the color changed from deep red to orange. Solvent was removed *in vacuo*. The resultant orange solids were extracted into pentane (30 mL) and filtered through Celite. The filtrate was dried under reduced pressure, affording (E^tCAACCu)TaH₂(C₁₀H₈)₂ as an orange solid (34.3 mg, 0.042 mmol, 47%). X-ray quality crystals were grown from a concentrated hexamethyldisiloxane (HMDSO) solution at –35 °C.

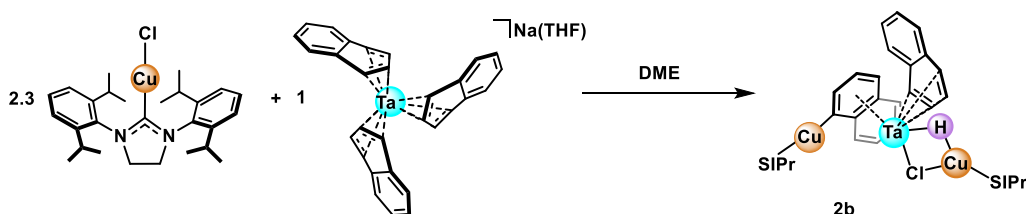
¹H (500 MHz, C₆D₆, 25 °C) δ (ppm): 7.18 (m, 1H, Dipp p-CH), 7.02 (d, 2H, *J* = 7.8 Hz, Dipp m-CH), 6.44 (m, 8H, naphthyl-CH), 5.26 (s, 4H, naphthyl-CH), 4.29 (s, 4H, naphthyl-CH), 2.70 (m, 2H, Dipp CH), 1.59 (m, 2H, ethyl-CH₂), 1.47 (m, 2H, ethyl-CH₂), 1.43 (d,

6H, $J = 6.7$ Hz, Dipp CH_3), 1.36 (s, 2H, carbene- CH_2), 1.08 (d, 6H, $J = 6.7$ Hz, Dipp CH_3), 0.89 (m, 12H, overlapping, ethyl- CH_3 and carbene- CH_3 [corroborated by HSQC and HMBC]), -6.79 (s, 2H, Ta-H-Cu).

$^{13}\text{C}\{^1\text{H}\}$ (126 MHz, C_6D_6 , 25 °C) δ (ppm): 254.46 (s, carbene-C), 145.63 (s, dipp o-C), 132.85 (s, naphthyl-C_{bridge}), 129.76 (s, dipp p-C), 126.34 (naphthyl-CH), 125.45 (s, dipp m-C), 125.36 (naphthyl-CH), 95.73 (naphthyl-CH), 79.16 (s, carbene- $\text{C}(\text{C}_2\text{H}_5)_2$), 66.60 (s, naphthyl-CH), 62.13 (s, carbene- $\text{C}(\text{CH}_3)_2$), 43.57 (s, carbene- CH_2), 31.49 (s, ethyl- CH_2), 29.22 (s, dipp-CH), 29.08 (s, carbene- CH_3), 26.05 (s, dipp- CH_3), 23.74 (s, dipp- CH_3), 9.38 (s, ethyl- CH_3).

qNMR (^1H NMR, 400MHz, C_6D_6 with HMDSO standard 25 °C): 96%

Synthesis of 2b



A 100 mL round bottom flask was charged with a DME (15 mL) solution of SIPrCuCl (308.7 mg, 0.63 mmol) and a stir bar. A separate scintillation vial was charged with a DME (15 mL) solution of $[\text{Ta}(\text{C}_{10}\text{H}_8)_3]^-$ (178.2 mg, 0.27 mmol). The $[\text{Ta}(\text{C}_{10}\text{H}_8)_3]^-$ solution was added dropwise to the stirring SIPrCuCl solution. Following complete addition, the reaction mixture was stirred at room temperature for 16 hours. At this time, solvent was removed *in vacuo*, resulting in a red-brown residue that was triturated with hexanes (3 x 5 mL). The resulting solids were washed with hexanes (20 mL), extracted into diethyl ether, and filtered over a pad of Celite. The filter cake was washed with diethyl ether until the rinses ran clear (~75 mL, total). Drying the filtrate under reduced pressure afforded $(\text{SIPrCu})_2\text{HTaCl}(\text{C}_{10}\text{H}_7)(\text{C}_{10}\text{H}_8)$ as a red-brown solid (143.3 mg, 0.10 mmol, 37%). X-ray quality crystals were grown via slow evaporation of an ether solution of $(\text{SIPrCu})_2\text{HTaCl}(\text{C}_{10}\text{H}_7)(\text{C}_{10}\text{H}_8)$ at -35 °C.

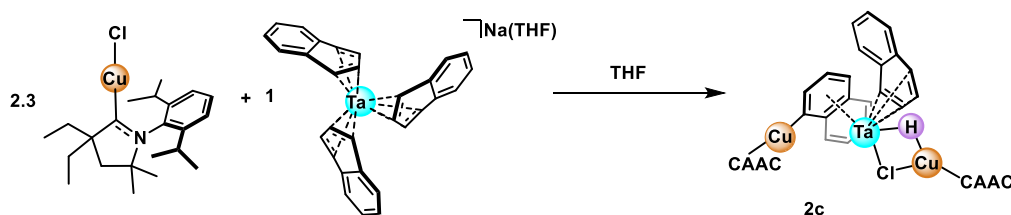
^1H (500 MHz, C_6D_6 , 25 °C) δ (ppm): 7.35 (t, $J = 7.7$ Hz, 2H, dipp p-CH), 7.26 (m, 4H, overlapping, dipp p-CH and dipp m-CH [corroborated by HSQC]), 7.19 (m, 2H, dipp m-CH), 7.10 (dd, $J = 1.6$ Hz, 2H, dipp m-CH), 6.74 (td, $J = 7.3, 1.2$ Hz, 1H, naphthyl-CH), 6.59 (td, $J = 7.3, 1.2$ Hz, 1H, naphthyl-CH), 6.26 (dd, $J = 7.2, 1.2$ Hz, 1H, naphthyl-CH), 6.16 (m, 3H, overlapping, naphthyl-CH [corroborated by HSQC]), 5.50 (ddd, $J = 7.3, 5.5, 2.0$ Hz, 1H, naphthyl-CH), 5.44 (ddd, $J = 8.0, 6.7, 1.2$ Hz, 1H, naphthyl-CH), 5.10 (d, $J = 7.7$ Hz, 2H, overlapping, naphthyl-CH [corroborated by HSQC]), 4.26 (m, 1H, naphthyl-CH), 4.14 (dd, $J = 7.1, 1.6$ Hz, 1H, naphthyl-CH), 3.38 (dd, $J = 7.2, 2.1$ Hz, 1H, naphthyl-CH), 3.27 (m, 8H, carbene- CH_2), 3.16 (m, 2H, dipp-CH), 3.07 (m, 6H, overlapping, dipp-CH [corroborated via HSQC]), 2.91 (m, 1H, naphthyl-CH), 2.75 (dd, $J = 6.4, 2.0$ Hz, 1H,

naphthyl-CH), 1.61 (dd, $J = 15.6, 6.8$ Hz, 12H, dipp-CH₃), 1.52 (d, $J = 6.8$ Hz, 6H, dipp-CH₃), 1.45 (d, $J = 6.8$ Hz, 6H, dipp-CH₃), 1.27 (dd, $J = 14.6, 6.9$ Hz, 12H, dipp-CH₃), 1.21 (dd, $J = 6.9, 2.1$ Hz, 12H, dipp-CH₃), -4.73 (s, 1H, Ta-H).

¹³C{¹H} (126 MHz, C₆D₆, 25 °C) δ (ppm): 211.80 (s, carbene-C), 205.95 (s, carbene-C), 150.52 (s, naphthyl-C_{bridge}), 147.73 (s, dipp o-C), 147.43 (s, dipp o-C), 147.29 (s, dipp o-C), 147.26 (s, dipp-C1), 146.38 (s, naphthyl-C_{bridge}), 136.41 (s, dipp-C1), 135.78 (s, dipp o-C), 134.98 (s, naphthyl-CH), 131.32 (s, naphthyl-C_{bridge}), 129.82 (s, dipp p-CH), 129.68 (s, dipp p-CH), 129.07 (s, naphthyl-CH), 126.58 (s, naphthyl-CH), 125.91 (s, naphthyl-CH), 125.00 (s, dipp m-CH), 124.86 (s, dipp m-CH), 124.54 (s, dipp m-CH), 124.34 (s, dipp m-CH), 121.09 (s, naphthyl-C-Cu), 120.88 (s, naphthyl-CH), 120.84 (s, naphthyl-CH), 120.14 (s, naphthyl-CH), 119.85 (s, naphthyl-CH), 118.72 (s, naphthyl-CH), 116.20 (s, naphthyl-CH), 105.58 (s, naphthyl-CH), 93.89 (s, naphthyl-CH), 79.40 (s, naphthyl-CH), 71.46 (s, naphthyl-CH), 60.79 (s, naphthyl-CH), 53.24 (s, carbene-CH₂), 53.18 (s, carbene-CH₂), 29.33 (s, dipp-CH), 29.30 (s, dipp-CH), 29.01 (s, dipp-CH), 28.99 (s, dipp-CH), 26.03 (s, dipp-CH₃), 25.68 (s, dipp-CH₃), 25.36 (s, dipp-CH₃), 25.01 (s, dipp-CH₃), 24.93 (s, dipp-CH₃), 24.75 (s, dipp-CH₃), 24.05 (s, dipp-CH₃).

qNMR (¹H NMR, 400MHz, C₆D₆ with HMDSO standard 25 °C): 97%

Synthesis of 2c



A 100 mL round bottom flask was charged with a THF (20 mL) solution of EtCAACCuCl (340.7 mg, 0.83 mmol) and a stir bar. A 20 mL scintillation vial was charged with a THF (20 mL) solution of [Ta(C₁₀H₈)₃]⁻ (233.5 mg, 0.35 mmol). With stirring, the [Ta(C₁₀H₈)₃]⁻ solution was added to the EtCAACCuCl solution dropwise, affording a red/brown homogenous solution. Stirring continued at room temperature for 16 hours, at which time solvent was removed *in vacuo*. The residue was triturated with hexanes (20 mL) and dried under reduced pressure. The resultant solids were extracted into diethyl ether and filtered through Celite. The filter cake was washed until the rinses ran clear (~30 mL, total). Drying the filtrate under reduced pressure afforded crude (EtCAACCu)₂TaHCl(C₁₀H₇)(C₁₀H₈) as a deep red powder (309.8 mg, 0.25 mmol, 71%). The solids were further purified by repeatedly extracting the product with HMDSO, concentrating the solution, and placing it in a -35 °C freezer overnight. The resulting solids demonstrated higher spectroscopic purity but had minor impurities that were inseparable from **2c**.

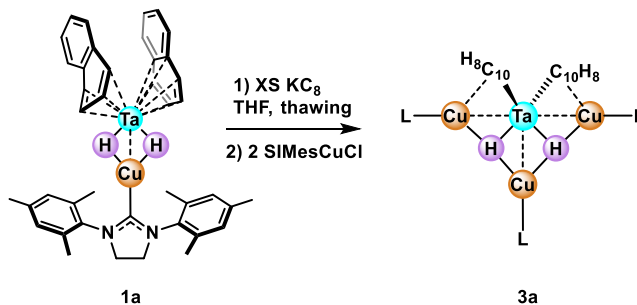
¹H (500 MHz, C₆D₆, 25 °C) δ (ppm): 7.21-7.17 (m, 2H, dipp p-CH), 7.13-7.05 (m, 4H, dipp m-CH), 6.98 (impurity), 6.89 (m, 1H, naphthyl-CH), 6.79 (t, 1H $J = 7.3$ Hz, naphthyl-CH),

6.68 (d, 3H, $J = 7.4$ Hz, naphthyl-CH), 6.58 (d, 2H, $J = 4.0$ Hz, naphthyl-CH), 6.38 (m, 1H, naphthyl-CH), 6.02 (m, 1H, naphthyl-CH), 5.66 (m, 1H, naphthyl-CH), 4.49 (dd, 1H, $J = 7.1, 1.5$ Hz, naphthyl-CH), 4.34 (m, 2H, naphthyl-CH), 3.15 (dd, 1H, $J = 7.1, 5.8$ Hz, naphthyl-CH), 2.91 (m, 4H, dipp-CH), 2.85 (m, 1H, naphthyl-CH), 2.70 (impurity), 2.04-1.80 (m, 4H, ethyl-CH₂), 1.62 (m, 9H, dipp-CH₃), 1.53 (d, 3H, $J = 6.7$ Hz, dipp-CH₃), 1.50-1.31 (m, 8H, overlapping, ethyl-CH₂ and carbene-CH₂ [corroborated by HSQC]), 1.20 (d, 3H, $J = 6.7$ Hz, dipp-CH₃), 1.16 (m, 9H, dipp-CH₃), 1.08 (m, 6H, ethyl-CH₃), 1.02-0.94 (m, 9H, overlapping, ethyl-CH₃ and carbene-CH₃ [corroborated by HSQC]) 0.91 (s, 6H, carbene-CH₃), 0.87-0.77 (m, 3H, overlapping, ethyl-CH₃ and impurity [corroborated by HSQC]), -4.52 (s, 1H, Ta-H).

$^{13}\text{C}\{^1\text{H}\}$ (126 MHz, C₆D₆, 25 °C) δ (ppm): 261.19 (s, carbene-C), 255.10 (s, carbene-C), 149.98 (s, naphthyl-C_{bridge}), 146.60 (s, naphthyl-C_{bridge}), 146.02 (s, dipp o-C), 145.94 (s, dipp o-C), 145.74 (s, dipp o-C), 145.33 (s, dipp o-C), 136.74 (s, dipp C1), 136.63 (s, naphthyl-CH), 135.79 (s, dipp C1), 130.24 (s, impurity), 130.00 (s, impurity), 129.61 (s, dipp p-CH), 129.53 (s, dipp p-CH), 128.82 (s, naphthyl-CH), 127.07 (s, naphthyl-CH), 126.13 (s, naphthyl-CH), 125.49 (s, dipp m-CH), 125.32 (s, dipp m-CH), 124.89 (s, dipp m-CH), 124.80 (s, dipp m-CH), 123.16 (s, naphthyl-C-Cu), 121.27 (s, naphthyl-CH), 120.84 (s, naphthyl-CH), 120.63 (naphthyl-CH), 119.76 (s, naphthyl-CH), 119.17 (s, naphthyl-CH), 114.88 (s, naphthyl-CH), 106.10 (naphthyl-CH), 98.40 (s, naphthyl-C_{bridge}), 95.62 (s, naphthyl-CH), 79.53 (s, impurity), 79.47 (s, naphthyl-CH), 70.20 (s, naphthyl-CH), 63.52 (s, carbene-C(C₂H₅)₂), 62.68 (s, carbene-C(C₂H₅)₂), 61.16 (s, naphthyl-CH), 42.65 (s, carbene-CH₂), 41.47 (s, carbene-CH₂), 32.08 (s, ethyl-CH₂), 31.95 (s, ethyl-CH₂), 31.75 (s, ethyl-CH₂), 31.17 (s, ethyl-CH₂), 29.58 (s, dipp CH), 29.49 (s, dipp CH), 29.39 (s, overlapping dipp CH), 29.35 (s, carbene-CH₃), 29.26 (s, carbene-CH₃), 29.01 (s, carbene-C(CH₃)₂), 28.97 (s, carbene-C(CH₃)₂), 28.78 (s, overlapping carbene-CH₃), 27.91 (s, dipp CH₃), 27.78 (s, dipp CH₃), 27.16 (s, dipp CH₃), 26.58 (s, impurity), 24.05 (s, dipp CH₃), 23.62 (s, dipp CH₃), 22.76 (s, dipp CH₃), 22.68 (s, dipp CH₃), 22.37 (s, dipp CH₃), 10.13 (s, 10.12 ethyl-CH₃), 9.78 (s, ethyl-CH₃), 9.74 (s, ethyl-CH₃), 9.70 (s, ethyl-CH₃), 9.62 (s, impurity).

qNMR: Due to the inability to separate **2c** from unknown impurities (see Figs. S21 – S25) satisfactory qNMR data were not obtained.

Synthesis of 3a



A 20 mL scintillation vial was charged with a THF (4 mL) solution of (CuSImes)TaH₂(C₁₀H₈)₂ (30.0 mg, 0.037 mmol) and a stir bar. A second scintillation vial was charged with a THF (4 mL) solution of SImesCuCl (29.1 mg, 0.072 mmol) and a stir bar. Both vials were placed in a liquid nitrogen (LN₂) chilled cold well and the contents frozen. The (CuSImes)TaH₂(C₁₀H₈)₂ solution was removed from the cold well, and upon thawing, solid KC₈ was added. The mixture was stirred cold for three minutes, then quickly filtered through a pre-cooled (rinsed with just-thawed THF) pad of Celite into the thawing SImesCuCl solution. Immediately upon mixing, the solution turned orange/brown. The reaction was slowly warmed to room temperature, with stirring, and left for 16 hours. Solvent was removed *in vacuo* and the resulting residue was triturated with hexanes (5 mL) and dried under reduced pressure. The solids were washed with hexanes (10 mL) and extracted into THF (*ca.* 5 mL). Filtering the THF extract through Celite provided a dark orange solution that, upon drying under reduced pressure, afforded (CuSImes)₃TaH₂(C₁₀H₈)₂ as an orange solid (41.6 mg, 0.026 mmol, 70%). X-ray quality crystals were grown via vapor diffusion of pentane into a concentrated THF solution of (CuSImes)₃TaH₂(C₁₀H₈)₂.

¹H (500 MHz, C₆D₆, 25 °C) δ (ppm): 7.18 (s, 2H, mesityl m-CH), 7.02 (s, 2H, mesityl m-CH), 6.79 (s, 4H, mesityl m-CH), 6.75 (s, 4H, mesityl m-CH), 6.33 (m, 4H, naphthyl-CH), 6.24 (td, *J* = 7.2, 1.3 Hz, 2H, naphthyl-CH), 5.58 (d, *J* = 7.1 Hz, 2H, naphthyl-CH), 4.49 (m, 2H, naphthyl-CH), 3.22 (m, 4H, carbene-CH₂), 3.02 (m, 8H, carbene-CH₂), 2.46 (m, 2H, naphthyl-CH), 2.43 (s, 6H, mesityl-CH₃), 2.37 (s, 12H, mesityl-CH₃), 2.31 (s, 6H, mesityl-CH₃), 2.21 (s, 6H, mesityl-CH₃), 2.18 (s, 12H, mesityl-CH₃), 2.12 (s, 12H, mesityl-CH₃), 1.79 (d, *J* = 7.5 Hz, 2H, naphthyl-CH), 1.43 (m, 2H, naphthyl-CH), -3.38 (s, 2H, Ta-H-Cu).

¹³C{¹H} (126 MHz, C₆D₆, 25 °C) δ (ppm): 208.23 (s, carbene-C), 206.66 (s, carbene-C), 157.27 (s, naphthyl-C_{bridge}), 146.96 (s, naphthyl-C_{bridge}), 137.67 (s, mesityl p-C), 137.47 (s, mesityl o-C), 137.29 (s, mesityl p-C), 137.13 (s, mesityl o-C), 137.08 (s, mesityl o-C), 136.41 (s, mesityl o-C), 135.67 (s, mesityl-C1), 135.38 (s, mesityl-C1), 131.02 (s, mesityl m-CH), 130.38 (s, mesityl m-CH), 129.54 (s, mesityl m-CH), 129.11 (s, mesityl m-CH), 120.71 (s, naphthyl-CH), 119.79 (s, naphthyl-CH), 119.13 (s, naphthyl-CH), 117.63 (s, naphthyl-CH), 70.75 (s, naphthyl-CH), 61.34 (s, naphthyl-CH), 51.03 (s, carbene-CH₂), 50.93 (s, naphthyl-CH), 50.67 (s, carbene-CH₂), 35.17 (s, naphthyl-CH), 21.28 (s, mesityl-CH₃), 21.16 (s, mesityl-CH₃), 19.41 (s, mesityl-CH₃), 19.25 (s, mesityl-CH₃), 18.91 (s, mesityl-CH₃), 18.82 (s, mesityl-CH₃).

qNMR (¹H NMR, 400MHz, C₆D₆ with HMDSO standard 25 °C): 97%

NMR Spectra

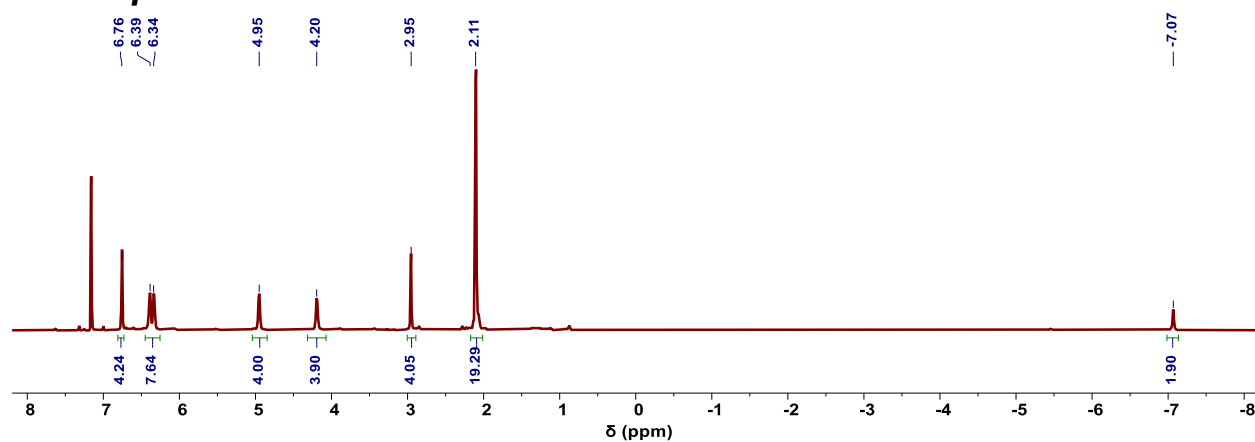


Figure S1 – ¹H NMR Spectrum of **1a** (500 MHz, C₆D₆, 25 °C).

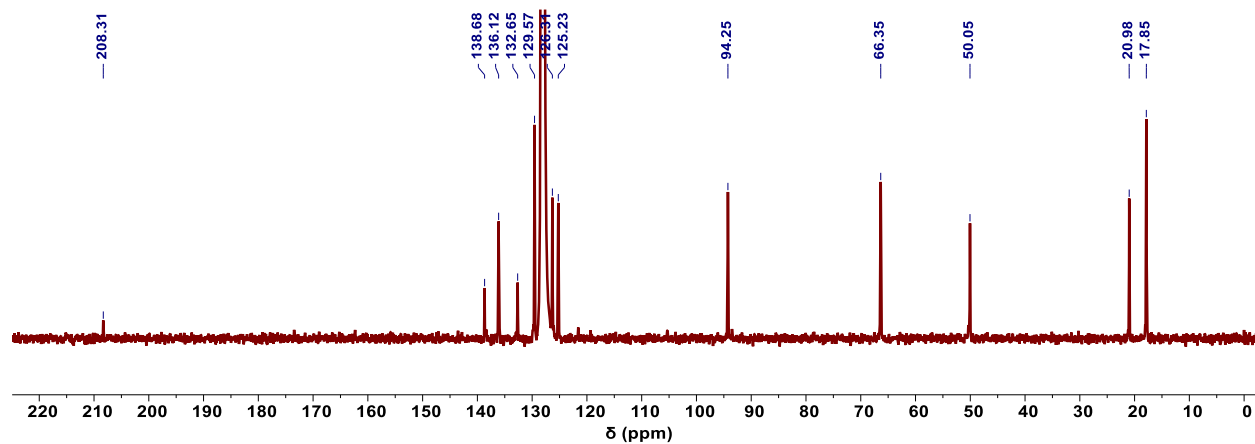


Figure S2 – ¹³C{¹H} NMR Spectrum of **1a** (126 MHz, C₆D₆, 25 °C).

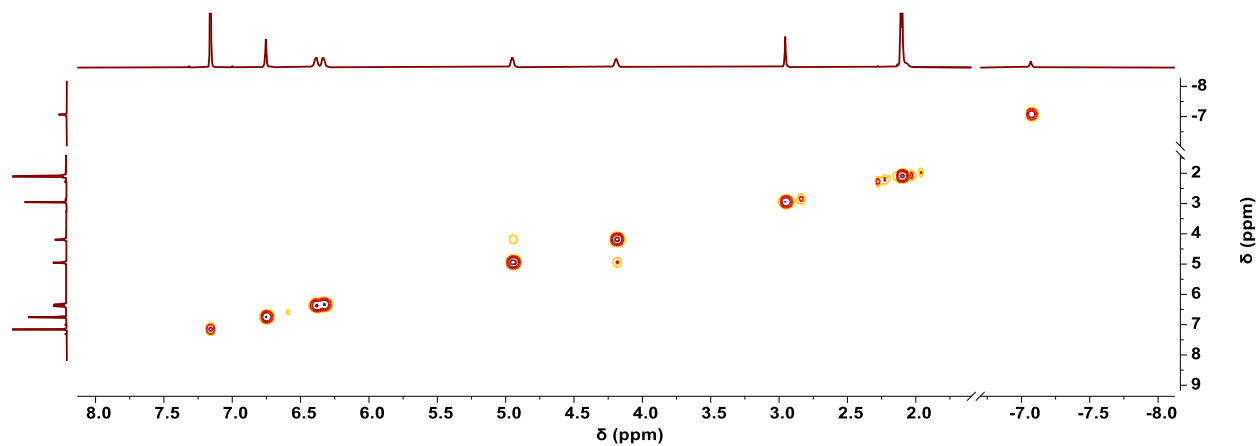


Figure S3 – Partial ¹H/¹H COSY NMR Spectrum of **1a** (500 MHz, C₆D₆, 25 °C).

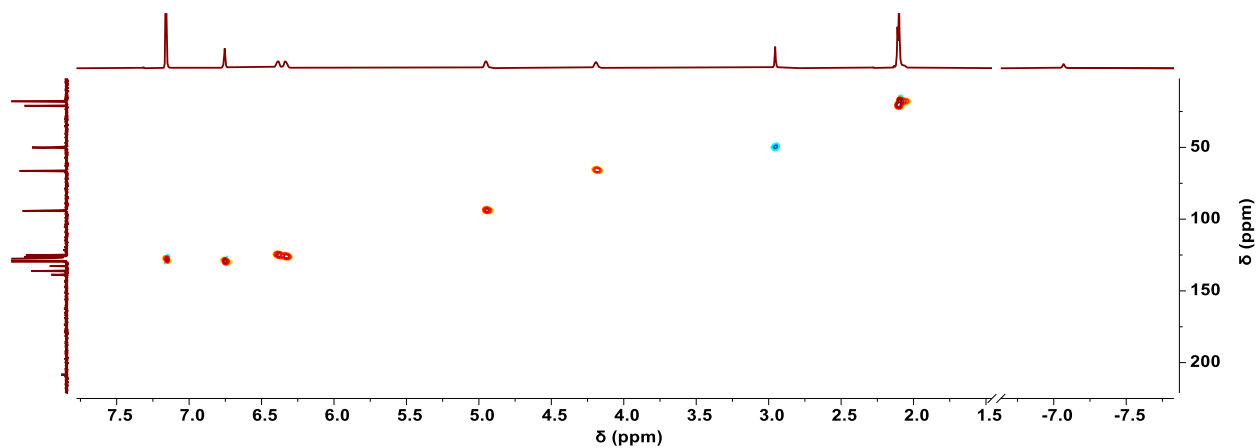


Figure S4 – Partial $^1\text{H}/^{13}\text{C}$ HSQC NMR Spectrum of **1a** (500/126 MHz, C_6D_6 , 25 $^\circ\text{C}$).

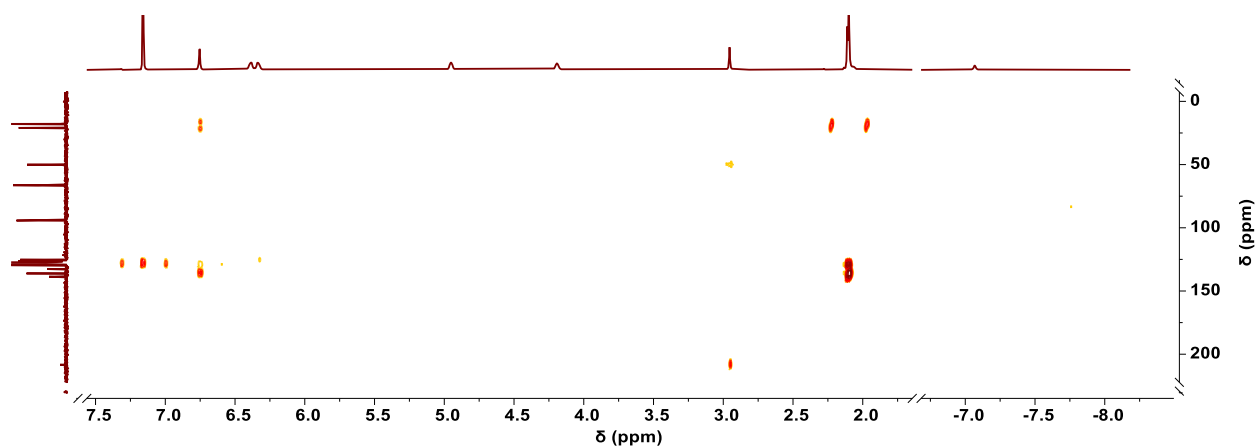


Figure S5 – Partial $^1\text{H}/^{13}\text{C}$ HMBC NMR Spectrum of **1a** (500/126 MHz, C_6D_6 , 25 $^\circ\text{C}$).

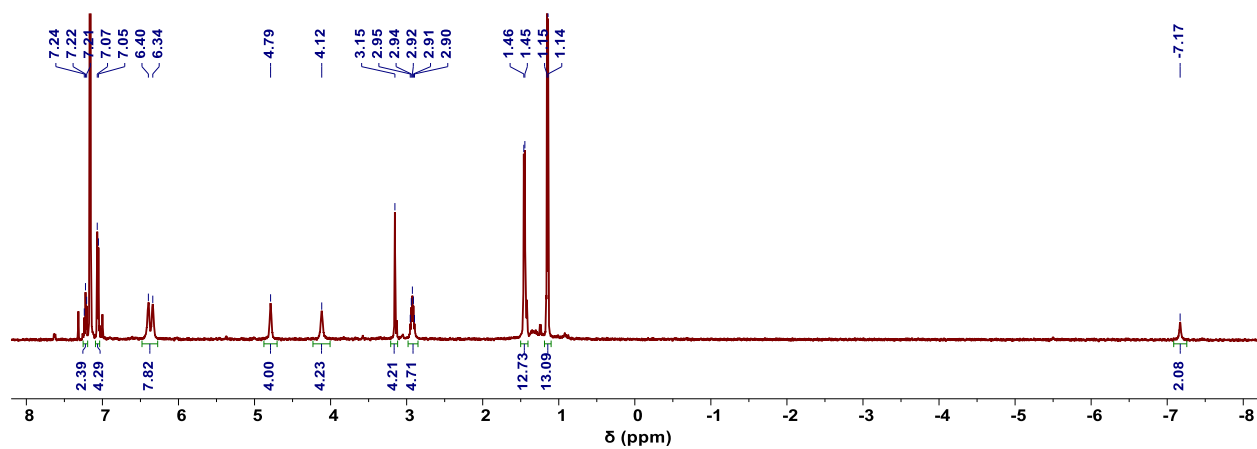


Figure S6 – ^1H NMR Spectrum of **1b** (500 MHz, C_6D_6 , 25 $^\circ\text{C}$).

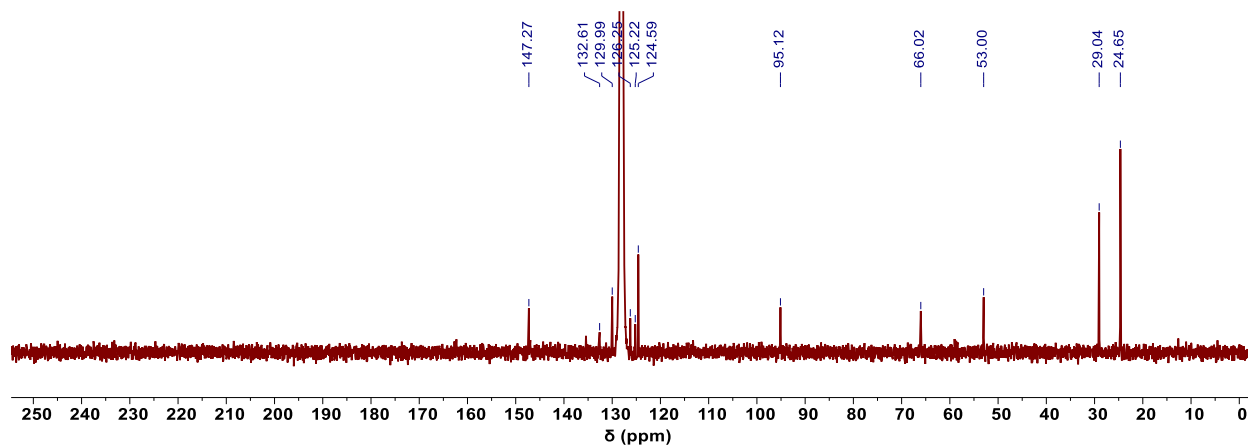


Figure S7 – $^{13}\text{C}\{^1\text{H}\}$ NMR Spectrum of **1b** (126 MHz, C_6D_6 , 25 °C). Note: The SIPr carbene carbon was not clearly observed given the low signal/noise ratio of the spectrum

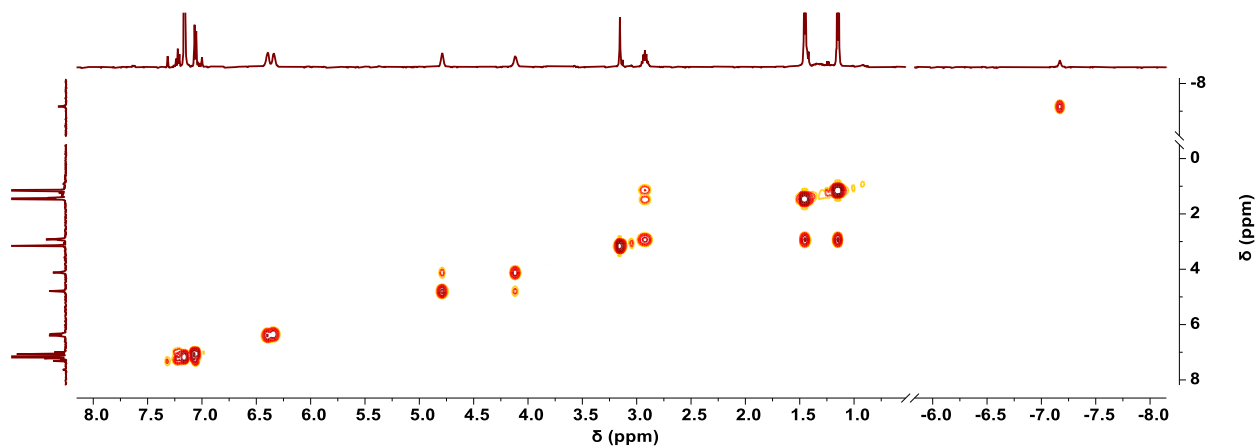


Figure S8 – Partial $^1\text{H}/^1\text{H}$ COSY NMR Spectrum of **1b** (500 MHz, C_6D_6 , 25 °C).

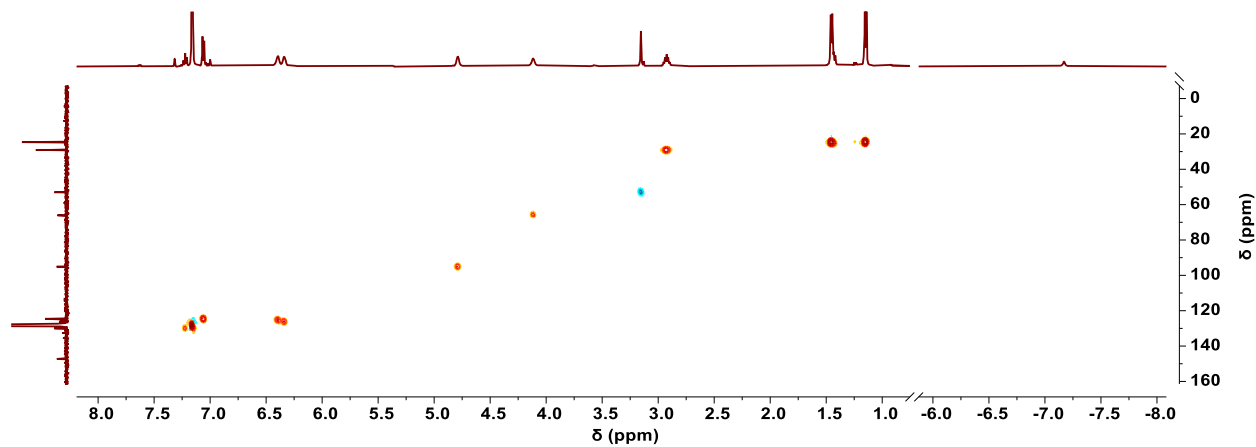


Figure S9 – Partial $^1\text{H}/^{13}\text{C}$ HSQC NMR Spectrum of **1b** (500/126 MHz, C_6D_6 , 25 °C).

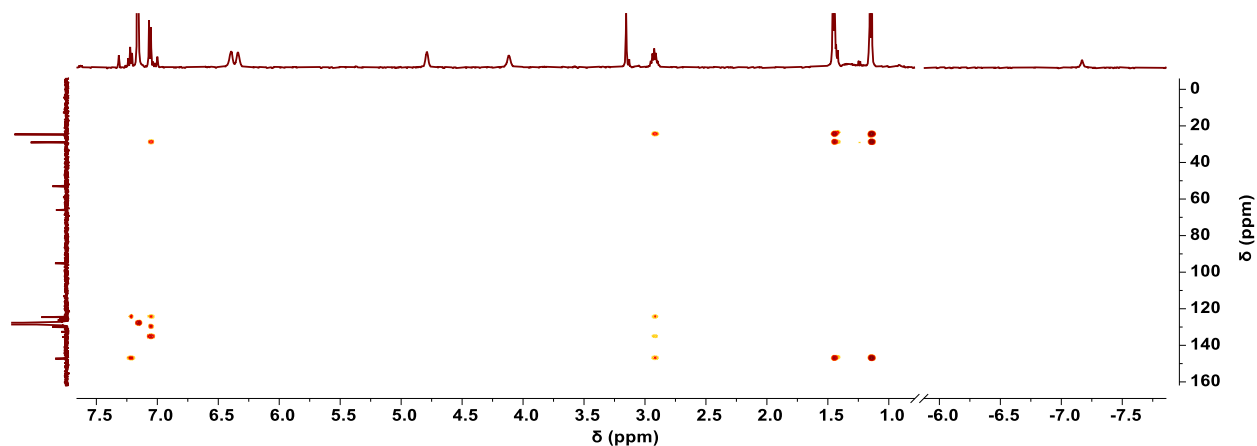


Figure S10 – Partial $^1\text{H}/^{13}\text{C}$ HMBC NMR Spectrum of **1b** (500/126 MHz, C_6D_6 , 25 $^\circ\text{C}$).

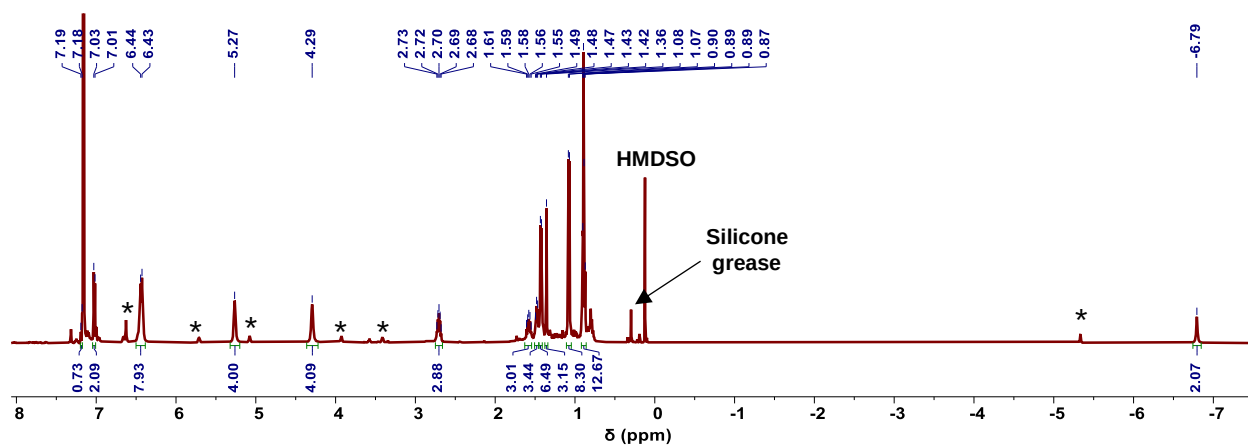


Figure S11 – ^1H NMR Spectrum of **1c** (500 MHz, C_6D_6 , 25 $^\circ\text{C}$). Signals corresponding to the minor conformation are designated with an asterisk.

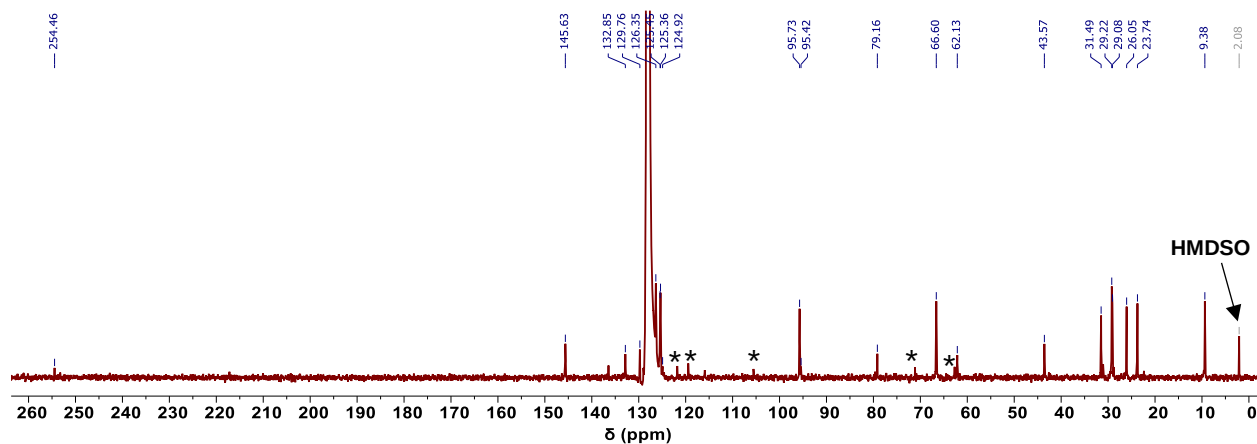


Figure S12 – $^{13}\text{C}\{^1\text{H}\}$ NMR Spectrum of **1c** (126 MHz, C_6D_6 , 25 $^\circ\text{C}$). Signals corresponding to the minor conformation are designated with an asterisk.

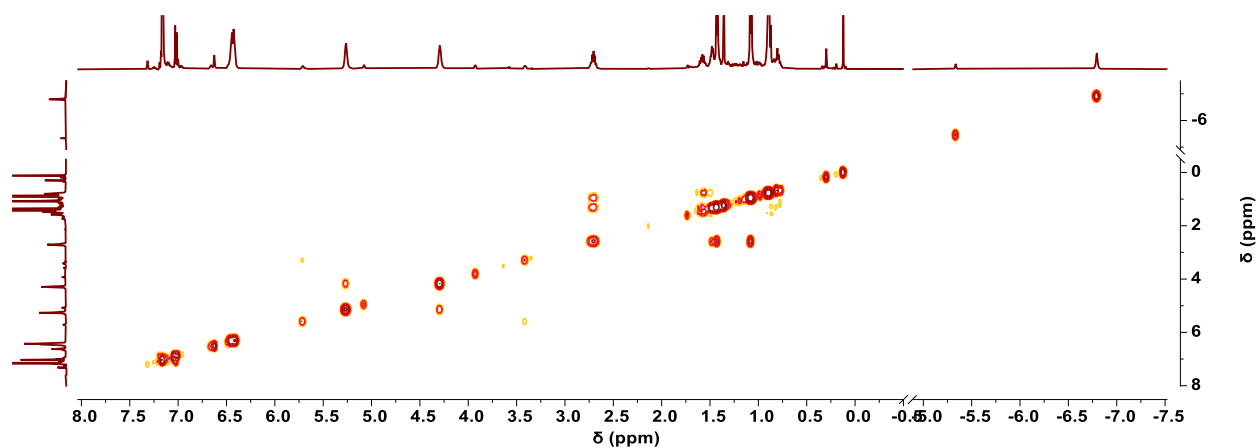


Figure S13 – Partial $^1\text{H}/^1\text{H}$ COSY NMR Spectrum of **1c** (500 MHz, C_6D_6 , 25 $^\circ\text{C}$).

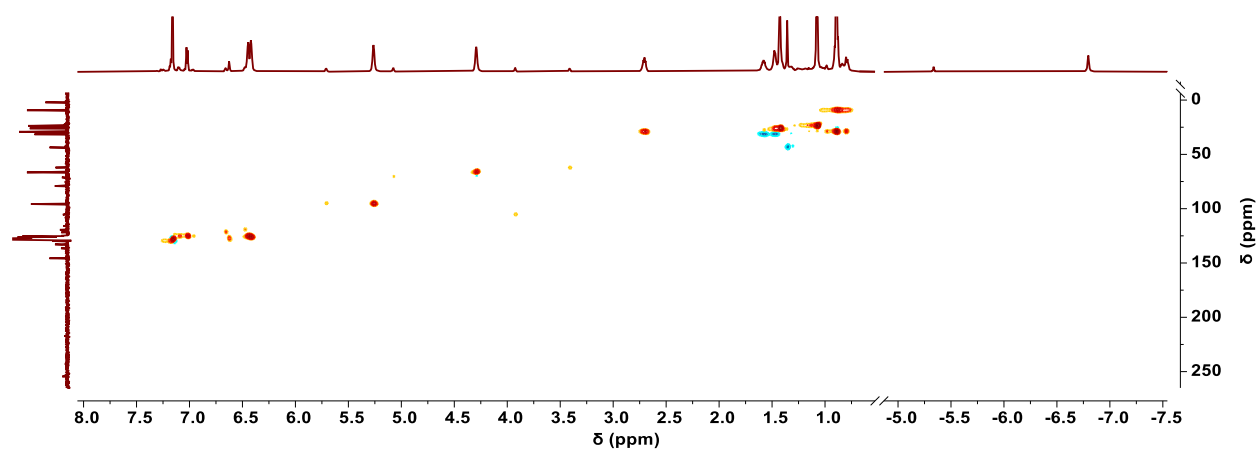


Figure S14 – Partial $^1\text{H}/^{13}\text{C}$ HSQC NMR Spectrum of **1c** (500/126 MHz, C_6D_6 , 25 $^\circ\text{C}$).

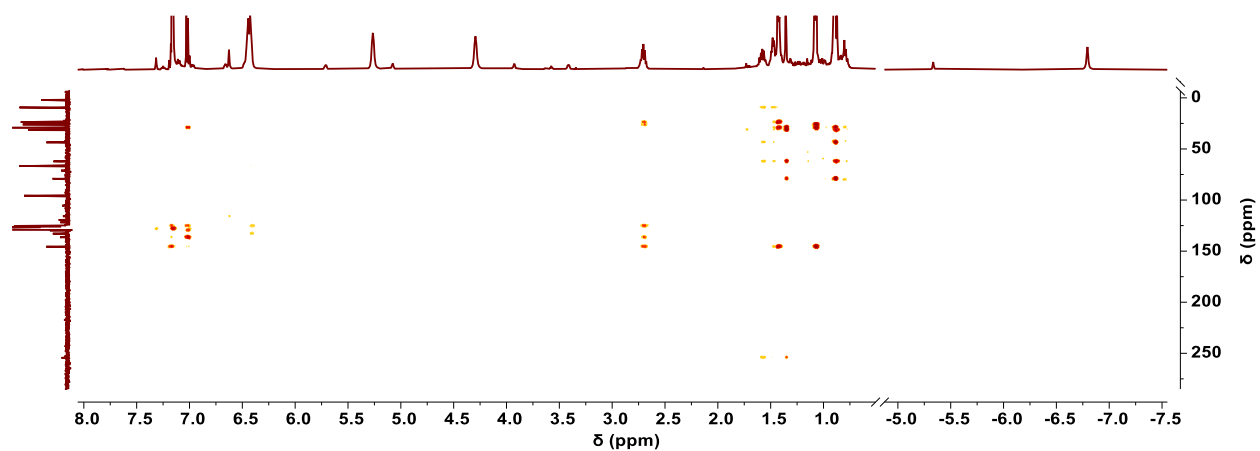


Figure S15 – Partial $^1\text{H}/^{13}\text{C}$ HMBC NMR Spectrum of **1c** (500/126 MHz, C_6D_6 , 25 $^\circ\text{C}$).

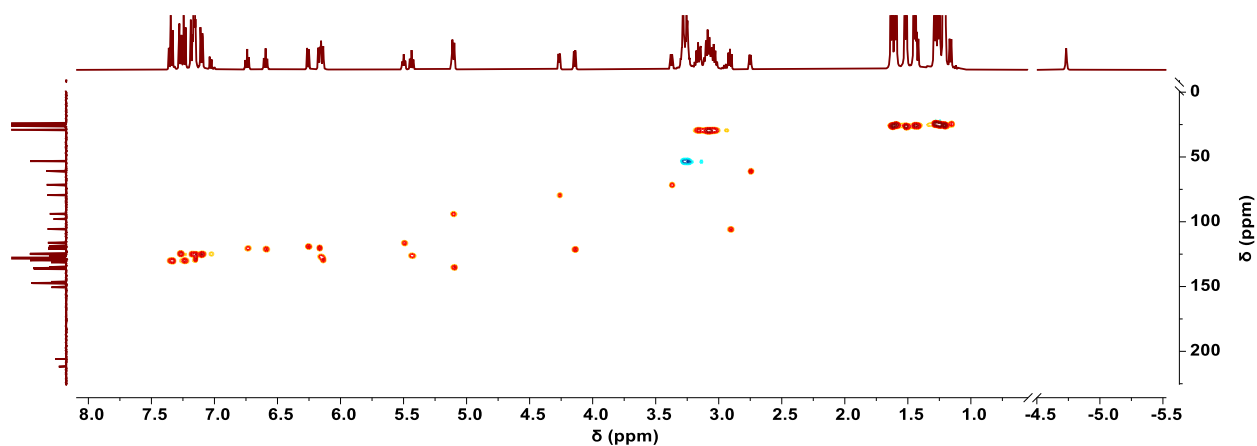


Figure S19 – Partial $^1\text{H}/^{13}\text{C}$ HSQC NMR Spectrum of **2b** (500/126 MHz, C_6D_6 , 25 °C).

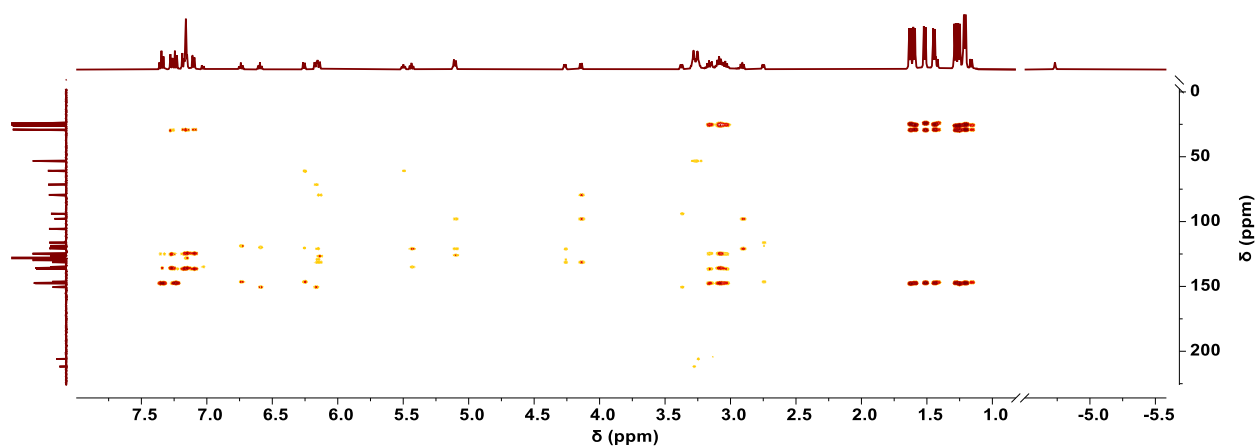


Figure S20 – Partial $^1\text{H}/^{13}\text{C}$ HMBC NMR Spectrum of **2b** (500/126 MHz, C_6D_6 , 25 °C).

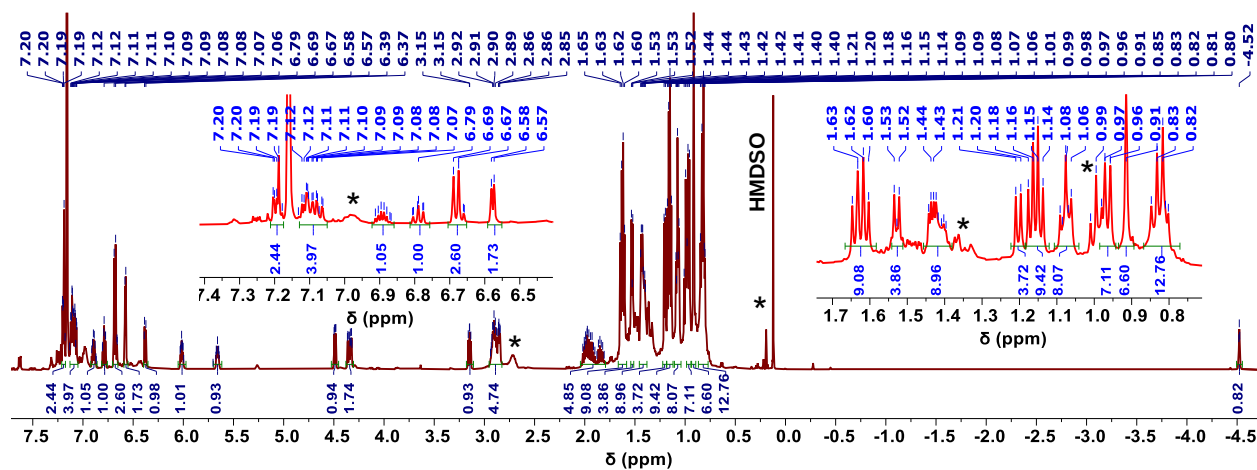


Figure S21 – ^1H NMR Spectrum of **2c** (500 MHz, C_6D_6 , 25 °C). Unidentified impurities are labeled with an asterisk.

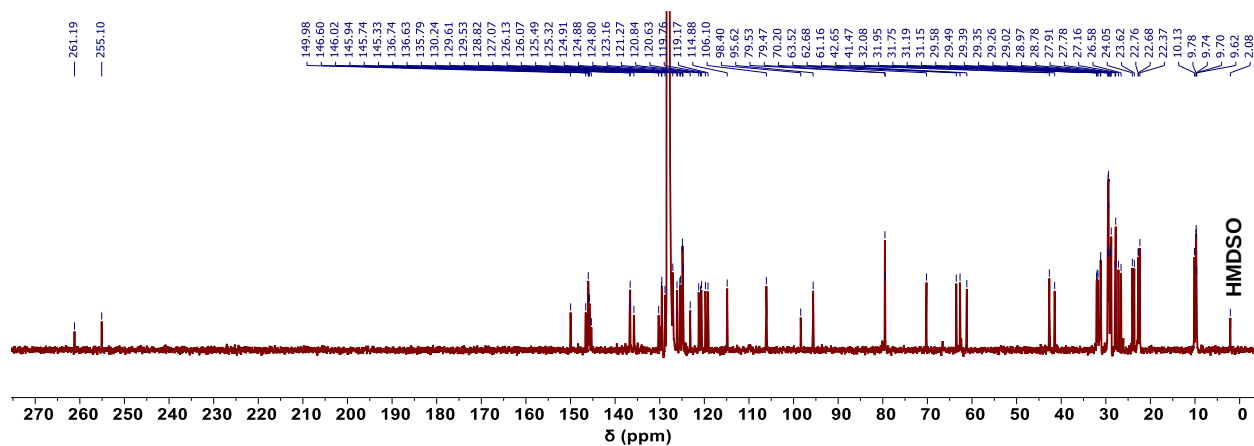


Figure S22 – $^{13}\text{C}\{^1\text{H}\}$ NMR Spectrum of **2c** (126 MHz, C_6D_6 , 25 °C).

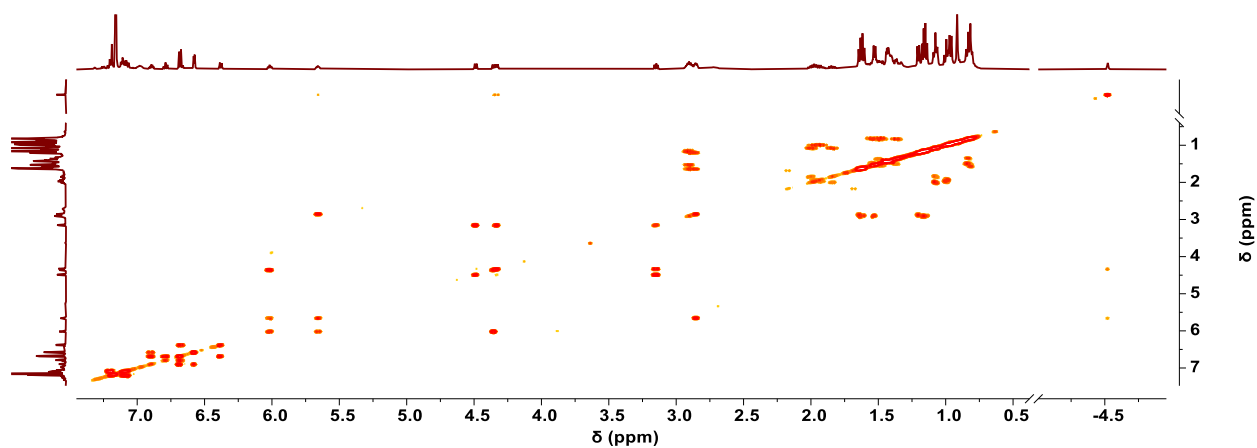


Figure S23 – Partial $^1\text{H}/^1\text{H}$ COSY NMR Spectrum of **2c** (500 MHz, C_6D_6 , 25 °C).

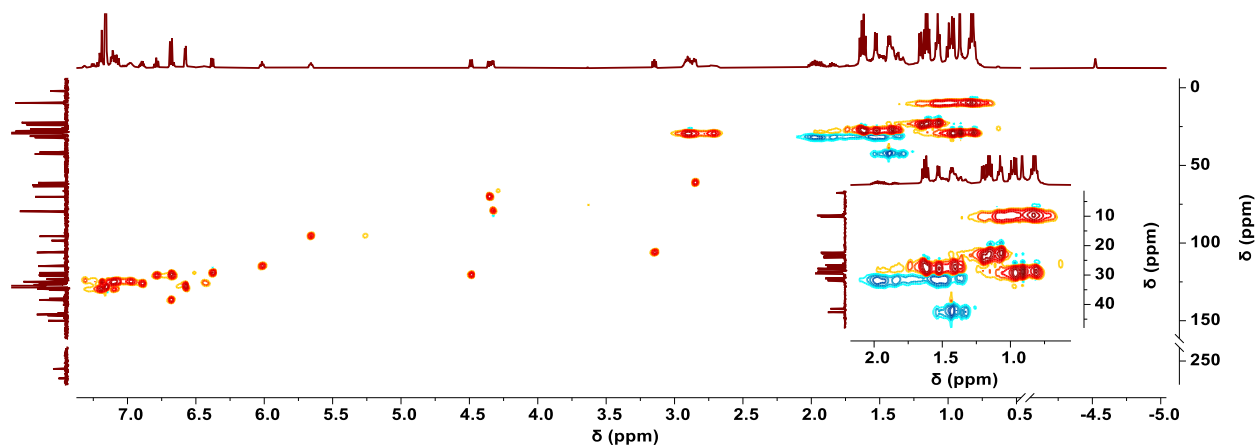


Figure S24 – Partial $^1\text{H}/^{13}\text{C}$ HSQC NMR Spectrum of **2c** (500/126 MHz, C_6D_6 , 25 °C). The insets show enlargements of the aliphatic region of the spectrum.

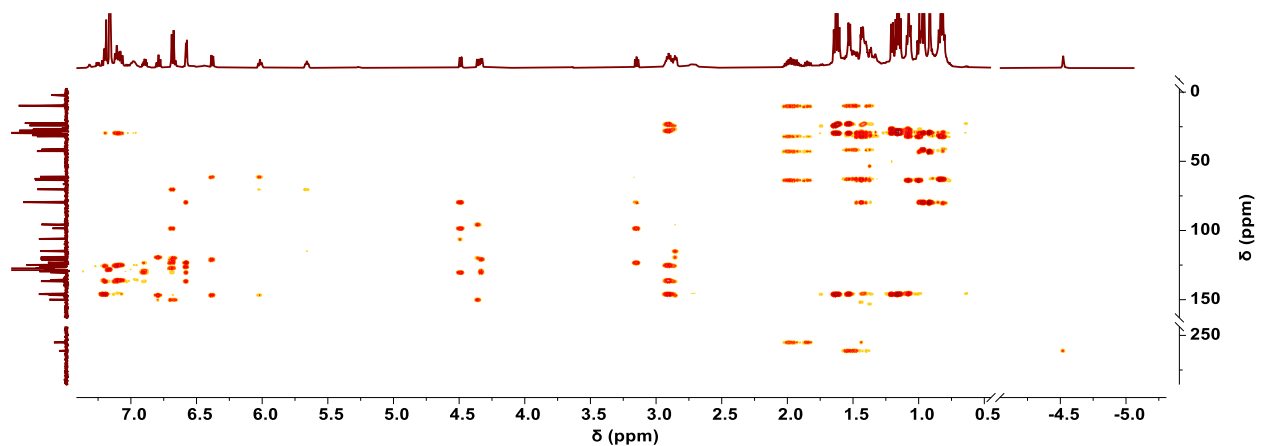


Figure S25 – Partial $^1\text{H}/^{13}\text{C}$ HMBC NMR Spectrum of **2c** (500/126 MHz, C_6D_6 , 25 $^\circ\text{C}$).

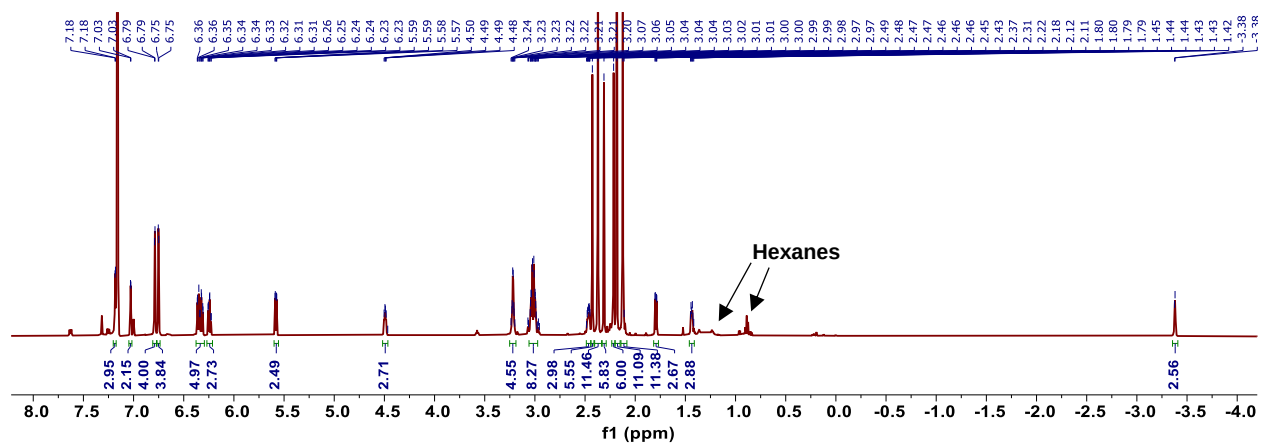


Figure S26 – ^1H NMR Spectrum of **3a** (500 MHz, C_6D_6 , 25 $^\circ\text{C}$).

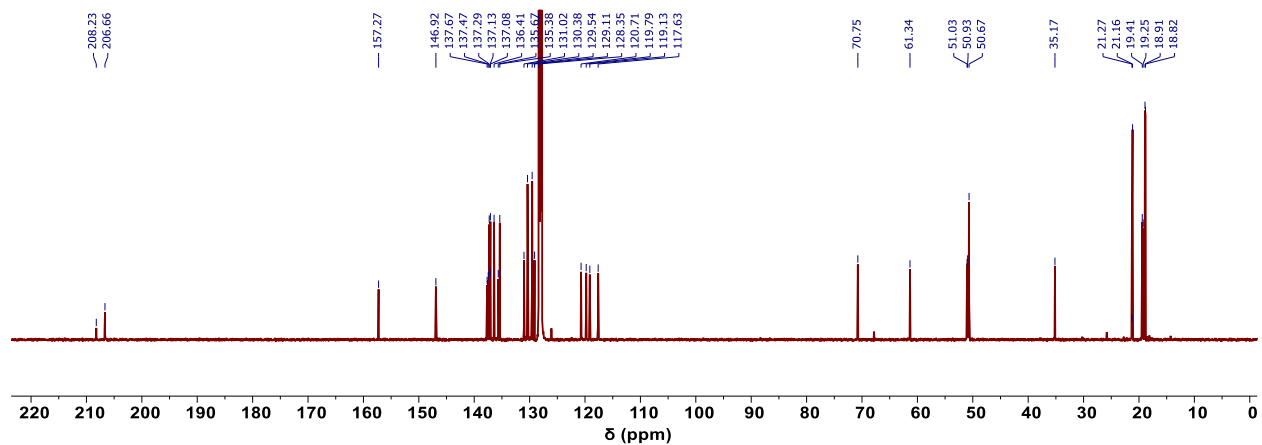


Figure S27 – $^{13}\text{C}\{^1\text{H}\}$ NMR Spectrum of **3a** (126 MHz, C_6D_6 , 25 $^\circ\text{C}$).

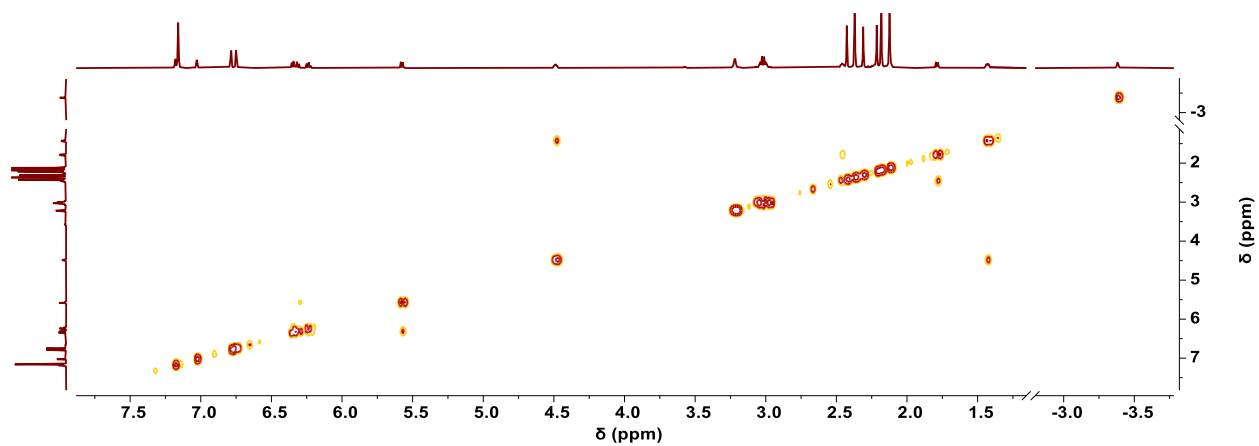


Figure S28 – Partial $^1\text{H}/^1\text{H}$ COSY NMR Spectrum of **3a** (500 MHz, C_6D_6 , 25 °C).

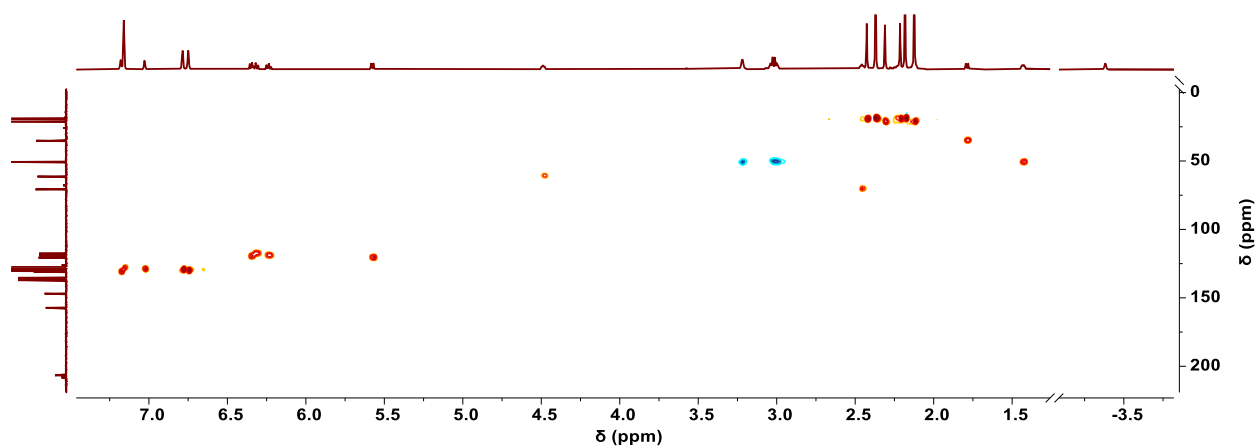


Figure S29 – Partial $^1\text{H}/^{13}\text{C}$ HSQC NMR Spectrum of **3a** (500/126 MHz, C_6D_6 , 25 °C).

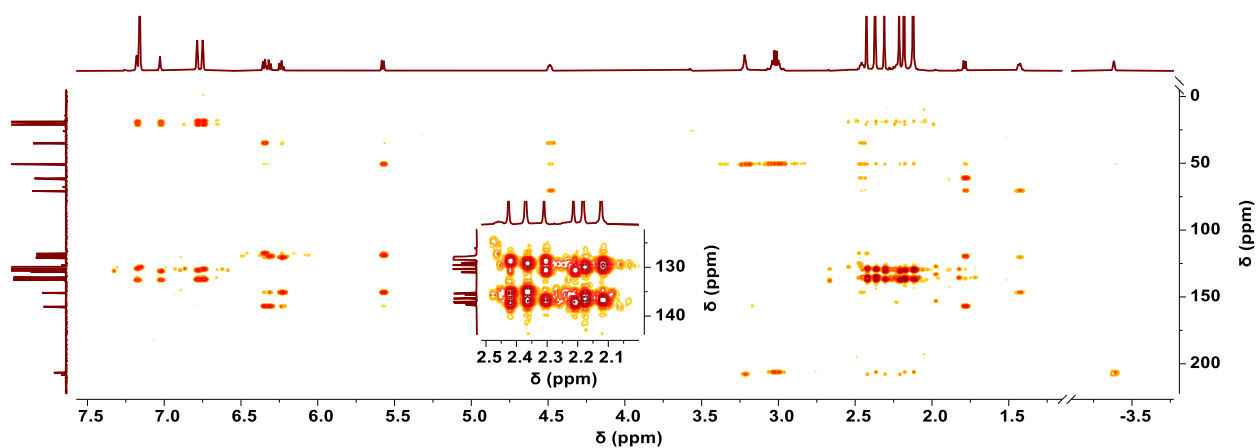


Figure S30 – Partial $^1\text{H}/^{13}\text{C}$ HMBC NMR Spectrum of **3a** (500/126 MHz, C_6D_6 , 25 °C). The insets show enlargements of the aliphatic region of the spectrum.

Naphthalene Dynamics, Exchange, and Isotopic Labeling Experiments

Syn/Anti Isomerism in **1a** and **1c**

To investigate the proposed isomerization of the naphthalene rings in **1a**, a sample was heated to 80 °C in C₇D₈. As the temperature was increased (Fig. S31, bottom to top), a broadening and then coalescence of the signals was observed (viz. 60 °C). Upon cooling, the same relative ratio of the C_s and C_{2v} isomers was obtained. Note that no H₂ was observed during the course of the reaction (conducted in a sealed J. Young style NMR tube), suggesting that hydrides are required for structural integrity.

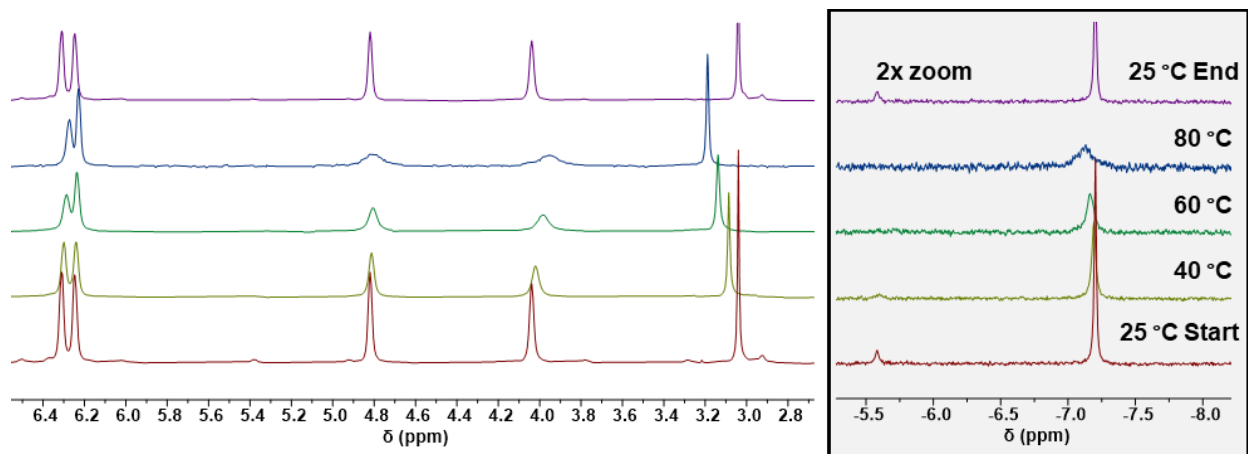


Figure S31 – Variable temperature partial ¹H NMR spectra of **1a** (600 MHz, toluene-d₈) ranging from 25 °C (bottom) to 80 °C (top). The high-field spectral region was enlarged (x2) for clarity.

A similar experiment was performed for **1c**, once again showing exchange that is intermediate on the NMR timescale upon heating, and no release of H₂. The room temperature spectra collected before and after heating are indistinguishable.

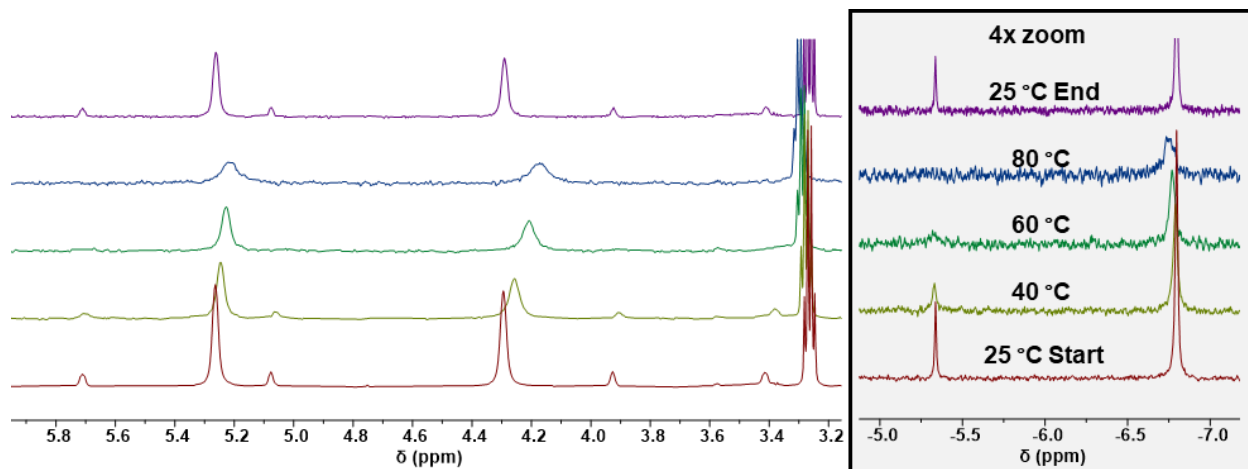
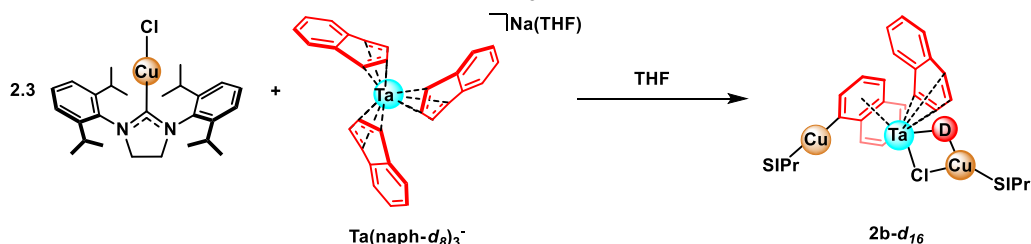


Figure S32 – Variable temperature partial ¹H NMR spectra of **1c** (600 MHz, C₆D₆) ranging from 25 °C (bottom) to 80 °C (top). The high-field spectral region was enlarged (x4) for clarity.

Preparation and Characterization of **2b-d₁₆**



A 100 mL round bottom flask was charged with a THF (10 mL) solution of SIPrCuCl (104.8 mg, 0.21 mmol) and a stir bar. A scintillation vial was charged with a THF (10 mL) solution of $[\text{Ta(naph-d}_8\text{)}_3]^-$ (63.1 mg, 0.096 mmol). The $[\text{Ta(naph-d}_8\text{)}_3]^-$ solution was added dropwise to the stirring SIPrCuCl solution. The reaction mixture was stirred at room temperature for 16 hours, and solvent was removed *in vacuo*, resulting in a residue that was triturated with hexanes (2 x 5 mL). The resulting solids were washed with hexanes (15 mL), extracted into diethyl ether, and filtered through a pad of Celite. The filter cake was washed with diethyl ether until the rinses ran clear (ca. 20 mL, total). Drying the filtrate under reduced pressure afforded **2b-d₁₆** as a red-brown solid.

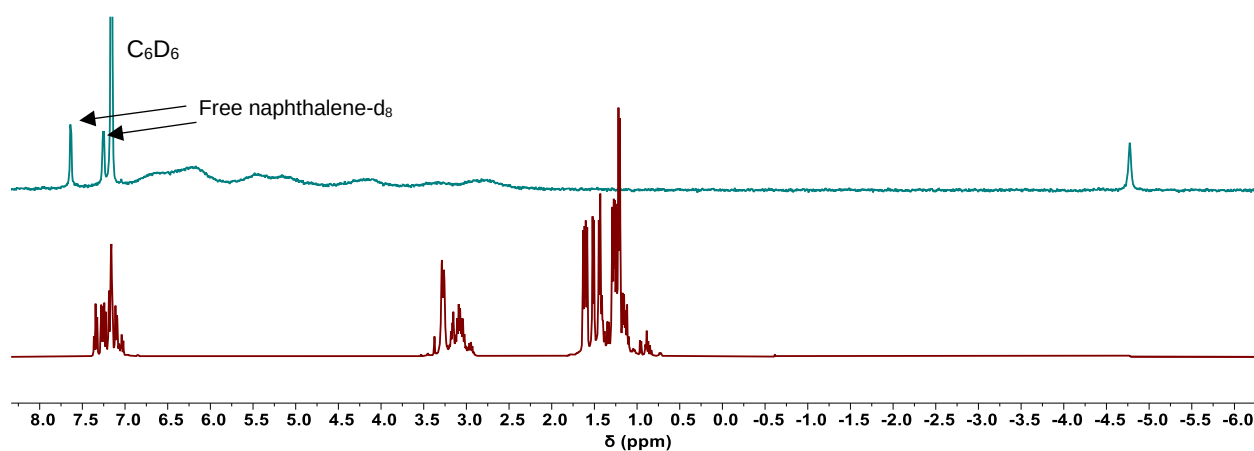
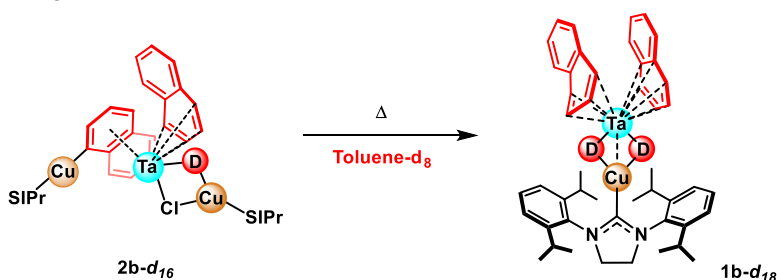


Figure S33 – Preparation of **2b-d₁₆**. Both ^2H (top; 107 MHz, 25 °C, C_6H_6 with a C_6D_6 standard) and ^1H (bottom; 400 MHz, 25 °C, C_6D_6) NMR spectra corroborate exclusive deuteride formation following C–D activation.

Formation of **1b-d₁₈**



A J-Young style NMR tube was charged with a toluene- d_8 (0.6 mL) solution of **2b-d₁₆** (10.0 mg, 0.0072 mmol). The tube was sealed and placed in an oil bath preheated to 110 °C for 16 hours. Upon cooling to room temperature, solvent was removed under reduced pressure. The resultant solids were extracted into hexanes (5 mL) and filtered through a pad of Celite. The filtrate was dried *in vacuo*, affording **1b-d₁₈** as an orange powder.

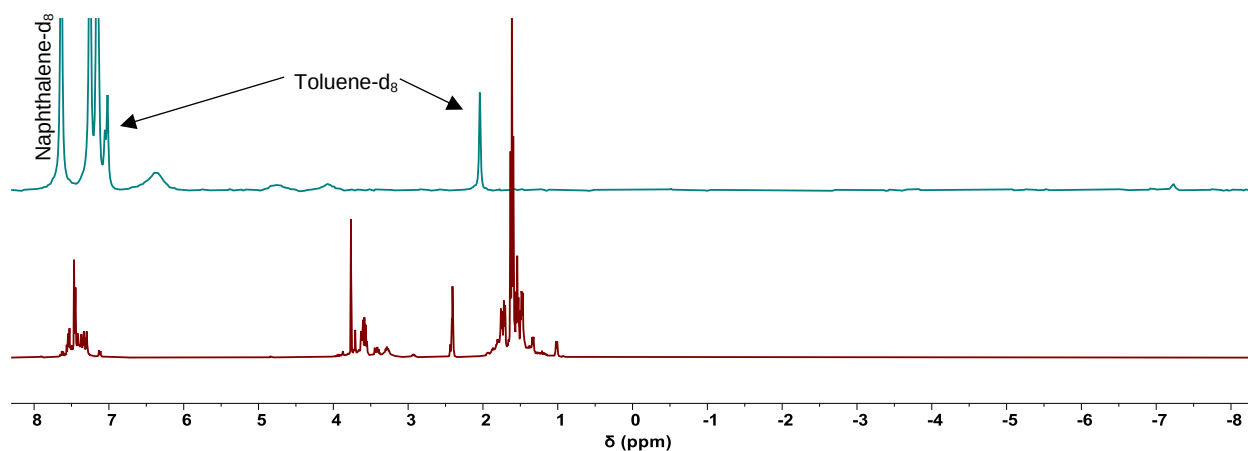
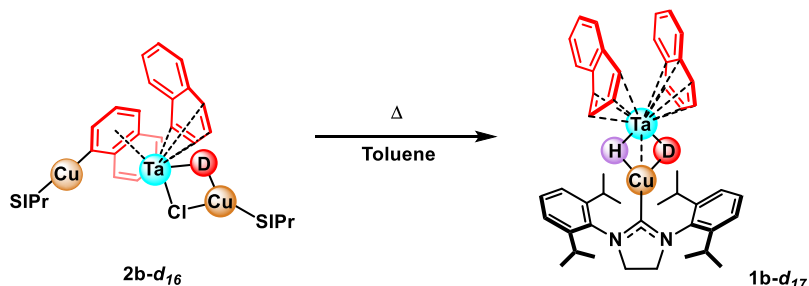


Figure S34 – Formation of **1b-d₁₈**. The ^2H (top; 107 MHz, 25 °C, C_6H_6 with a C_6D_6 standard) and ^1H (bottom; 400 MHz, 25 °C, C_7D_8) NMR spectra corroborate exclusive generation of the bimetallic dideuteride.

Formation of **1b-d₁₇**



A J-Young style NMR tube was charged with a toluene (0.6 mL) solution of **2b-d₁₆** (11.2 mg, .0080 mmol). The tube was sealed and placed in an oil bath preheated to 110 °C for 16 hours. Upon cooling to room temperature, solvent was removed under reduced pressure. The resultant solids were extracted into hexanes (5 mL) and filtered through a pad of Celite. The filtrate was dried *in vacuo*, resulting in **1b-d₁₇** as an orange powder.

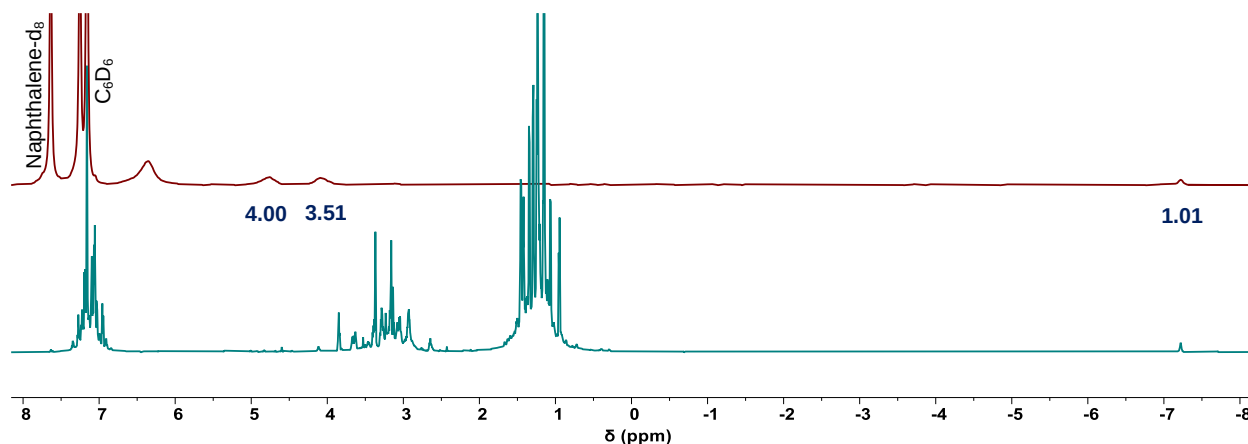
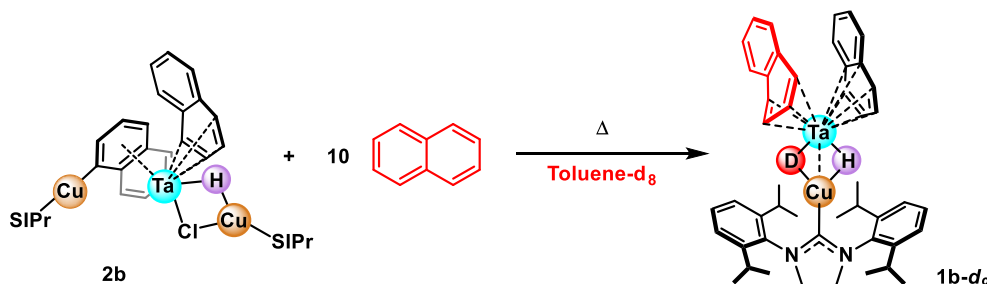


Figure S35 – Formation of **1b-d₁₇**. The ²H (top; 107 MHz, 25 °C, C₆H₆ with a C₆D₆ standard) and ¹H (bottom; 400 MHz, 25 °C, C₆D₆) NMR spectra corroborate generation of the mixed hydride/deuteride. Relative integration of the ²H NMR spectrum is consistent with formation of a monodeuteride.

Investigating Naphthalene Exchange at 110 °C



A J-Young style NMR tube was charged with a toluene-*d*₈ (0.6 mL) solution of **2b** (9.4 mg, 0.0068 mmol) and 10 equivalents of naphthalene-*d*₈ (9.3 mg, 0.068 mmol). The tube was sealed and placed in an oil bath preheated to 110 °C for 16 hours, mirroring the reaction conditions for the generation of the bimetallic species above. Upon cooling to room temperature, solvent was removed under reduced pressure and the resultant solids were extracted into hexanes (5 mL) and filtered through a pad of Celite. The filtrate was dried *in vacuo* and the resulting residue was analyzed by multinuclear NMR spectroscopy. Both ¹H (Fig. S36, bottom) and ²H (Fig. S36, top) NMR spectroscopy evidence naphthalene exchange (gray box).

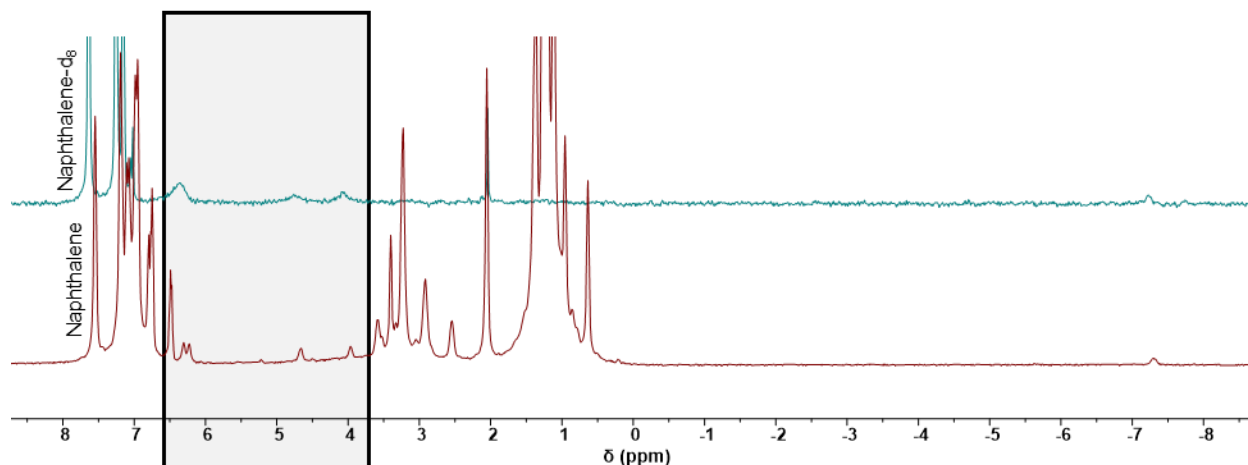
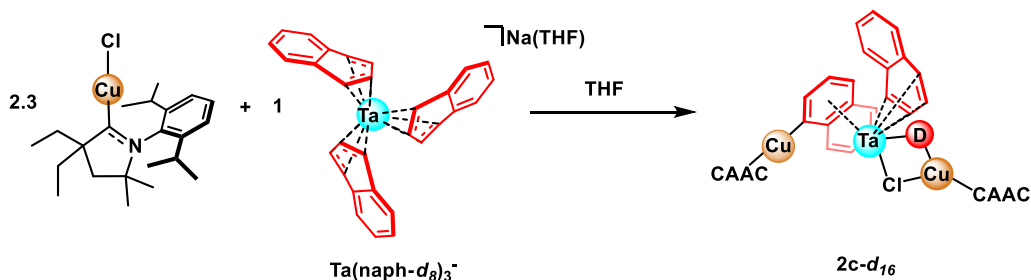


Figure S36 – Naphthalene exchange from **2b**. The ^2H (top; 107 MHz, 25 °C, C_6H_6 with a C_6D_6 standard) and ^1H (bottom; 400 MHz, 25 °C, C_7D_8) NMR spectra are consistent with naphthalene exchange under the reaction conditions.

Preparation and Characterization of **2c-d₁₆**



A 20 mL scintillation vial was charged with a THF (8 mL) solution of EtCAACCuCl (113.1 mg, 0.27 mmol) and a stir bar. A separate scintillation vial was charged with a THF (8 mL) solution of $[\text{Ta}(\text{naph-}d_8)_3]^-$ (80.8 mg, 0.12 mmol). With stirring, the $[\text{Ta}(\text{naph-}d_8)_3]^-$ solution was added to the EtCAACCuCl solution dropwise. Stirring continued at room temperature for 16 hours, at which time solvent was removed *in vacuo*. The deep red residue was triturated with hexanes (2 x 5 mL) and dried under reduced pressure. The resultant solids were extracted into diethyl ether and filtered through Celite; the filter cake was washed until the rinses ran clear (~15 mL, total). Drying the filtrate under reduced pressure afforded **2c-d₁₆** as a deep red solid.

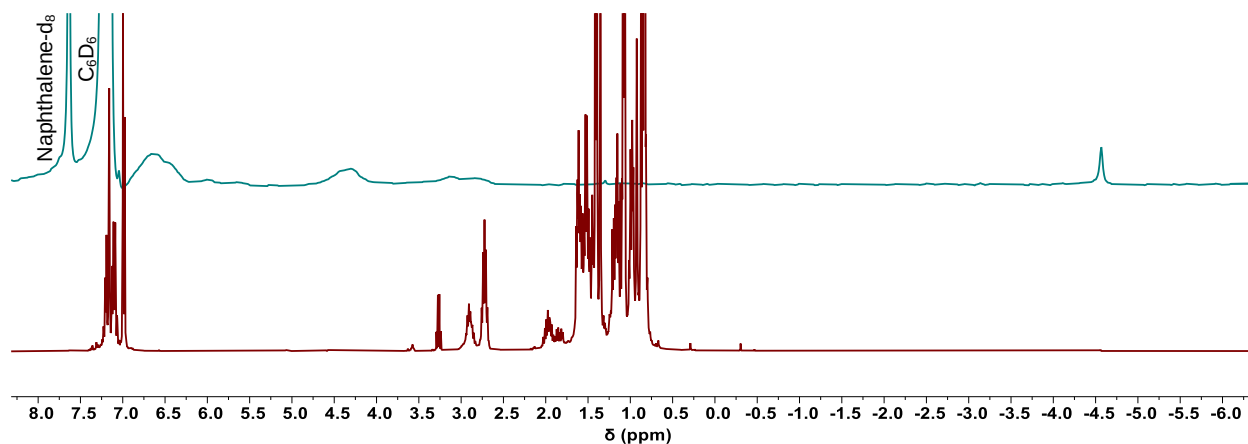
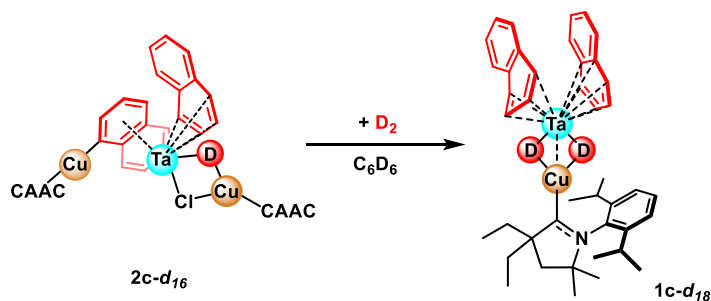


Figure S37 – Formation of **2c-d₁₆**. Both ²H (top; 107 MHz, 25 °C, C₆H₆ with a C₆D₆ standard) and ¹H (bottom; 400 MHz, 25 °C, C₆D₆) NMR spectra corroborate exclusive deuteride formation following C–D activation.

Formation of **1c-d₁₈**



A J-Young style NMR tube was charged with a C₆D₆ (0.6 mL) solution of **2c-d₁₆** (12.1 mg, 0.0098 mmol). The tube was sealed, degassed via three freeze-pump-thaw cycles, and backfilled with D₂ (1 atm). The reaction was mixed via inversion at room temperature for 16 hours, at which time solvent was removed *in vacuo*. The resultant orange solids were extracted into HMDSO (5 mL) and filtered through Celite. The filtrate was dried under reduced pressure, affording **1c-d₁₈** as an orange solid.

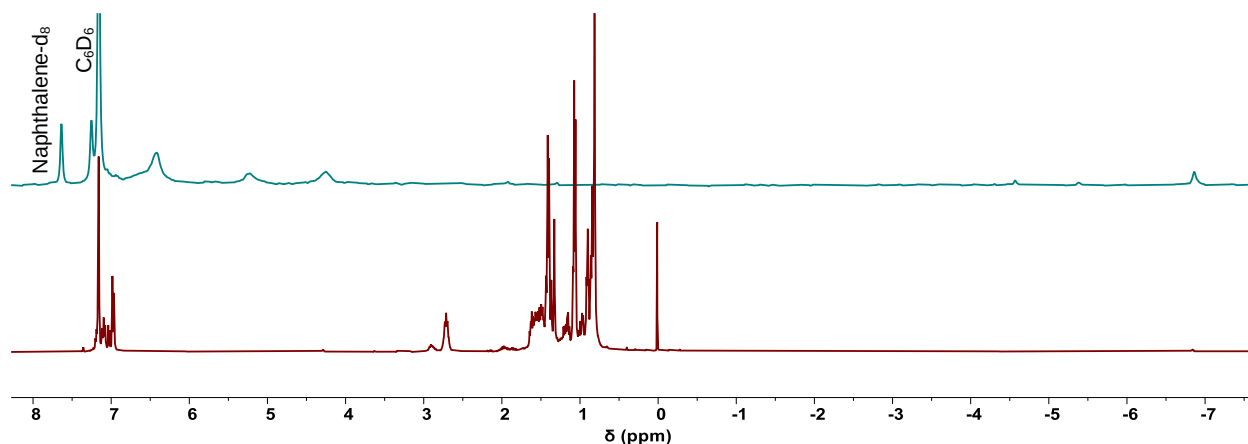
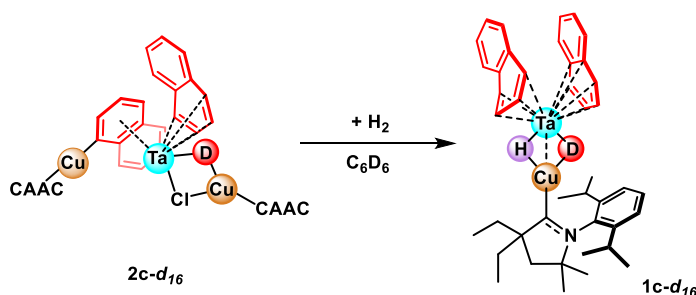


Figure S38 – Formation of **1c-d₁₈**. The ²H (top; 107 MHz, 25 °C, C₆H₆ with a C₆D₆ standard) and ¹H (bottom; 400 MHz, 25 °C, C₆D₆) NMR spectra corroborate exclusive generation of the bimetallic dideuteride.

Formation of **1c-d₁₆**



A J-Young style NMR tube was charged with a C₆D₆ (0.6 mL) solution of **2c-d₁₆** (12.6 mg, 0.010 mmol). The tube was sealed, degassed via three freeze-pump-thaw cycles, and backfilled with H₂ (1 atm). The reaction was mixed via inversion at room temperature for 16 hours, at which time solvent was removed *in vacuo*. The resultant orange solids were extracted into HMDSO (5 mL) and filtered through Celite. The filtrate was dried under reduced pressure, affording **1c-d₁₆** as an orange solid.

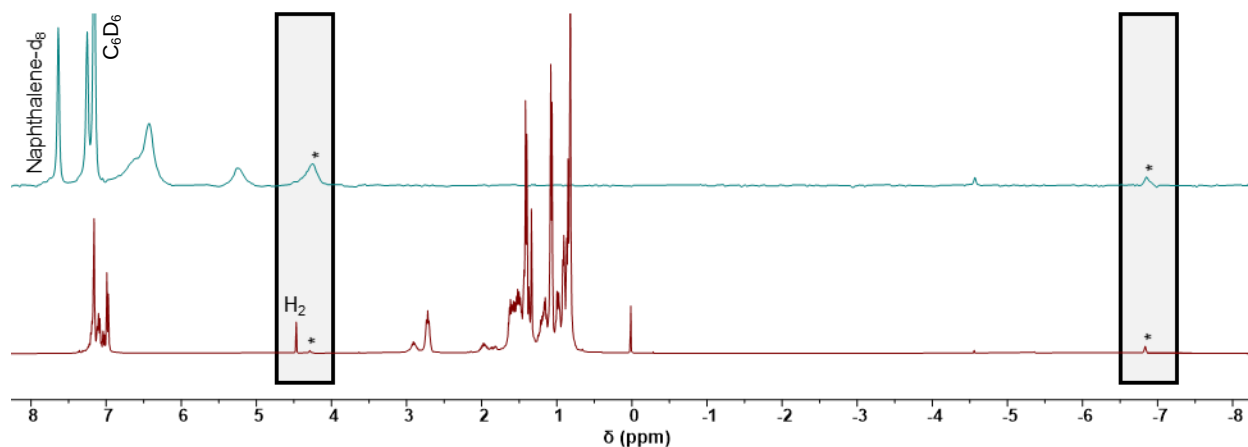


Figure S39 – Formation of **1c-d₁₆** via H₂ addition. The ²H (top; 107 MHz, 25 °C, C₆H₆ with a C₆D₆ standard) and ¹H (bottom; 400 MHz, 25 °C, C₆D₆) NMR spectra show formation of a mixed hydride/deuteride bimetallic core and incorporation of an H-atom into one of the coordinated naphthyl rings; the gray boxes highlight the salient spectral features.

The incorporation of an H-atom into the bound naphthyl ring was further corroborated by comparing ¹H NMR spectra of the starting **2c-d₁₆** and the product of H₂ addition. Note that under these milder reaction conditions, no naphthyl exchange is observed (*vide infra*).

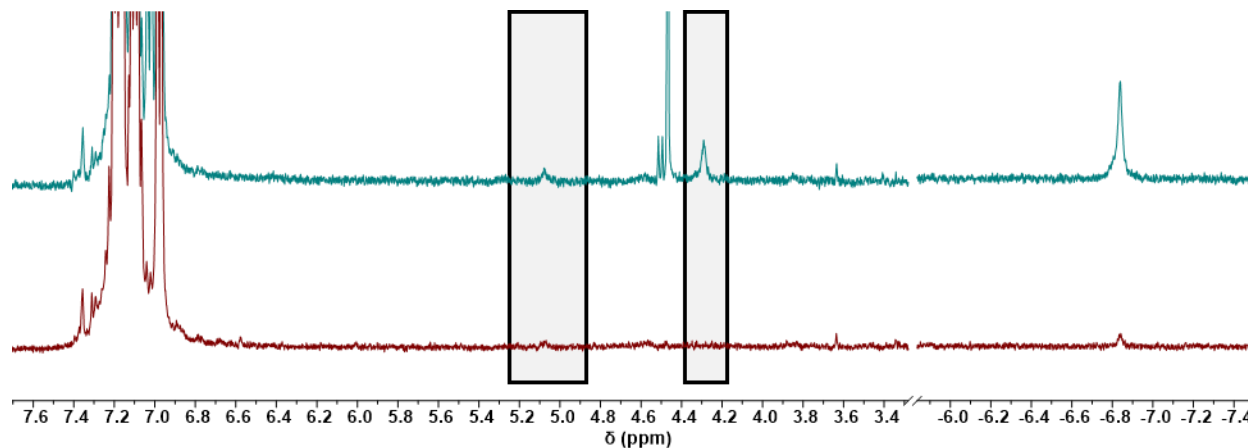
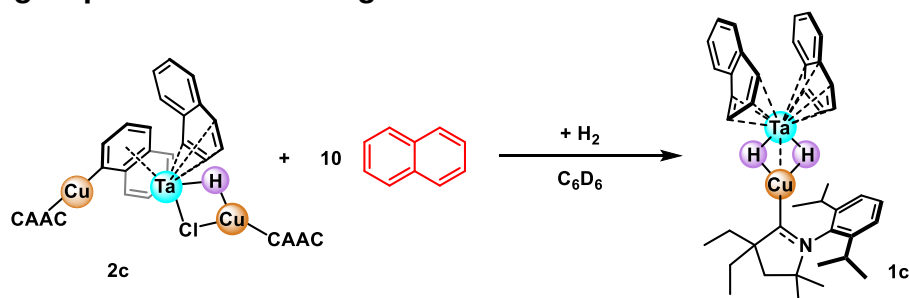


Figure S40 – Naphthyl C–H bond formation from H₂ addition to **2c-d₁₆**. Partial ¹H NMR spectra (400 MHz, 25 °C, C₆D₆) before (bottom) and after (top) H₂ addition to a degassed C₆D₆ solution of **2c-d₁₆**. The resonances in the gray boxes show partial H-atom incorporation into the naphthyl rings that is not present in the starting material.

Investigating Naphthalene Exchange Under H₂



A J-Young style NMR tube was charged with a benzene (0.6 mL) solution of **2c** (11.9 mg, 0.0097 mmol), naphthalene-d₈ (13.3 mg, 0.097 mmol), and a C₆D₆ standard. The tube was sealed, degassed via three freeze-pump-thaw cycles, and backfilled with H₂ (1 atm). The reaction was mixed via inversion at room temperature for 16 hours and characterized *in situ* via ¹H NMR spectroscopy.

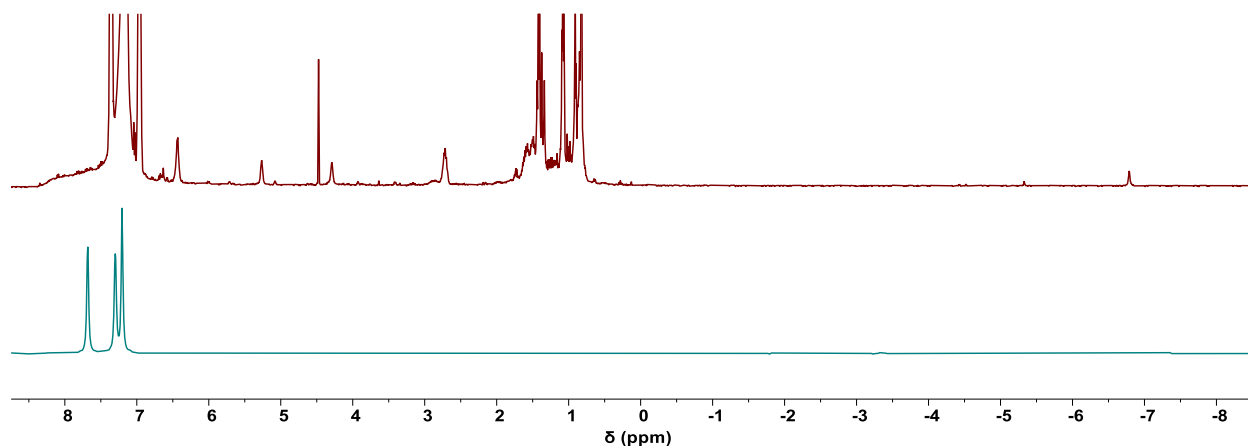
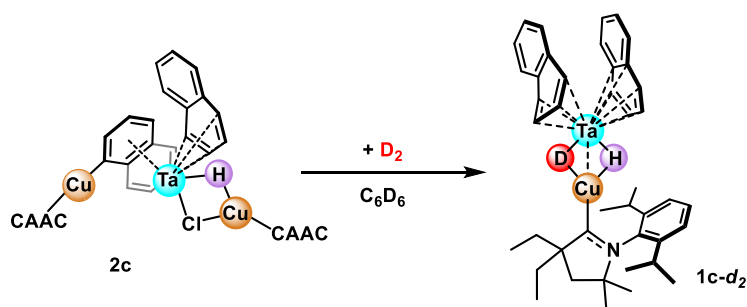


Figure S41 – Attempted naphthyl exchange from **2c-d₁₆**. The ¹H (bottom; 400 MHz, 25 °C, C₆D₆) and ²H (top; 107 MHz, 25 °C, C₆H₆ with a C₆D₆ standard) NMR spectra show no evidence of naph-d₈ incorporation into the product, **1c**.

Formation of **1c-d₂**



A J-Young style NMR tube was charged with a C₆D₆ (0.6 mL) solution of **2c** (10.7 mg, 0.0087 mmol). The tube was sealed, degassed via three freeze-pump-thaw cycles, and backfilled with D₂ (1 atm). The reaction was mixed via inversion for 16 hours at room

temperature, at which time solvent was removed *in vacuo*. The resultant orange solids were extracted into HMDSO (5 mL) and filtered through Celite. The filtrate was dried under reduced pressure, affording **1c-d₂** as an orange solid.

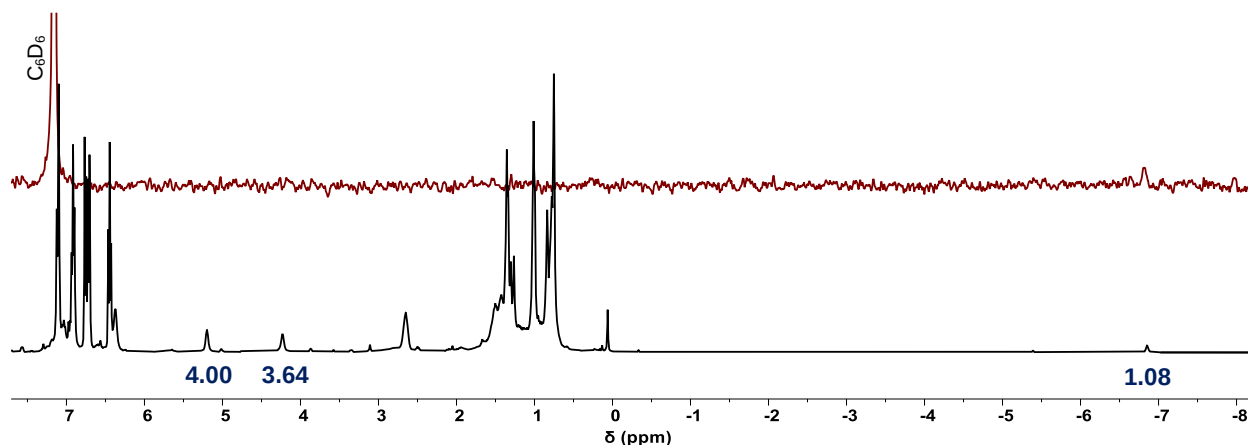
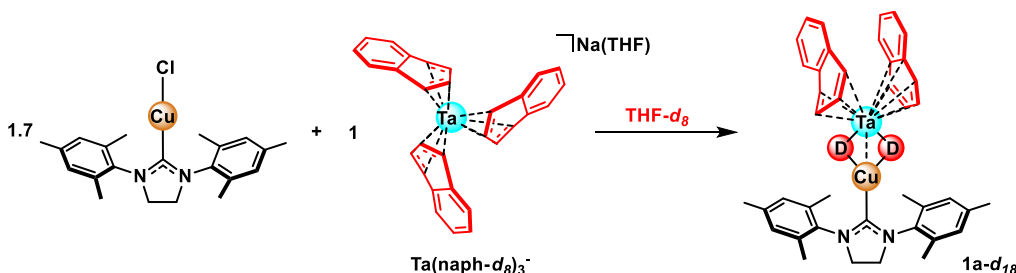


Figure S42 – Formation of **1c-d₂** via D₂ addition to **2c**. The ²H (top; 107 MHz, 25 °C, C₆H₆ with a C₆D₆ standard) and ¹H (bottom; 400 MHz, 25 °C, C₆D₆) NMR spectra are consistent with the results described above for H₂ addition to **2c-d₁₆**. The signal to noise ratio of the ²H NMR spectrum prohibits definitive assignment of the naphthyl deuterium, but the integrations in the ¹H NMR spectrum are consistent with a mixed H/D bimetallic core and partial naphthyl C–D bond formation.

Preparation of **1a-d₁₈**



A J-Young style NMR tube was charged with SIMesCuCl (10.5 mg, 0.026 mmol) and [Ta(naph-d₈)₃][−] (10.1 mg, 0.015 mmol). The tube was degassed and THF-d₈ (0.6 mL) was added via vacuum transfer. The reaction was mixed via inversion for 16 hours at room temperature, at which time solvent was removed *in vacuo*. The resultant orange solids were extracted into diethyl ether (5 mL) and filtered through a pad of Celite. The filtrate was dried under reduced pressure, affording **1a-d₁₈** as an orange powder.

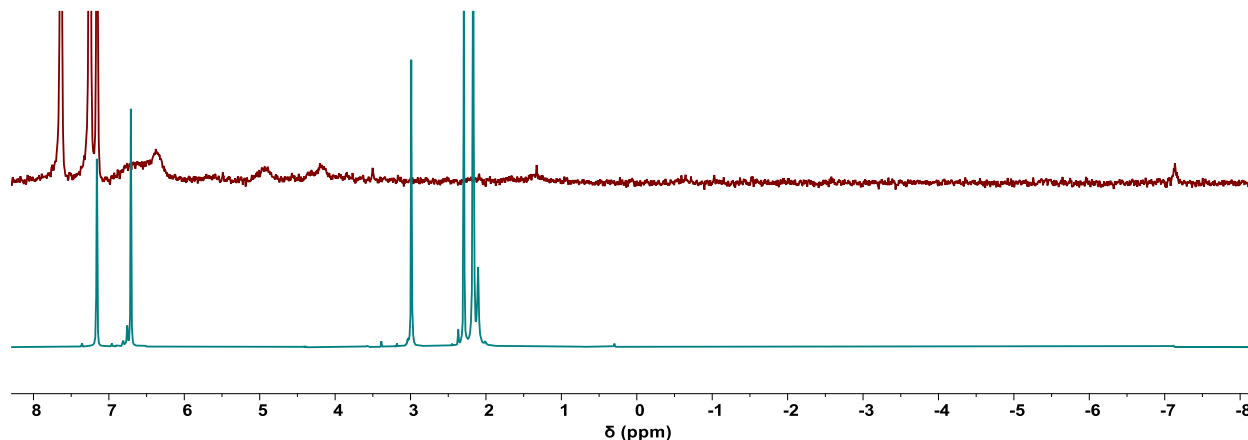
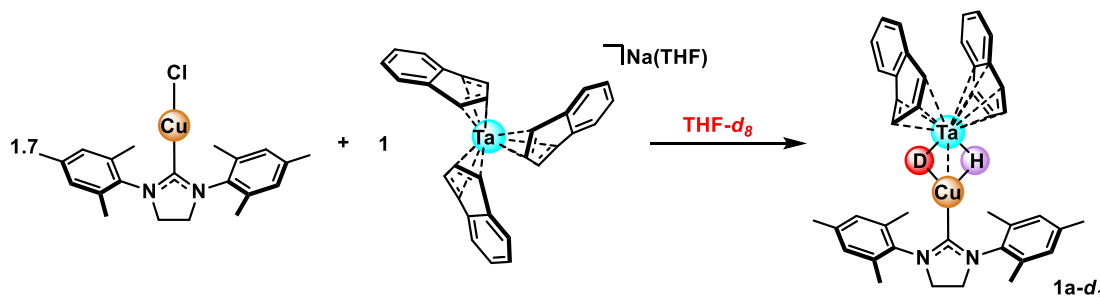


Figure S43 – Formation of **1a-d₁₈** using [Ta(naph-*d*₈)₃]⁻ and THF-*d*₈. The ²H (top; 107 MHz, 25 °C, C₆H₆ with a C₆D₆ standard) and ¹H (bottom; 400 MHz, 25 °C, C₆D₆) NMR spectra show exclusive formation of the dideuteride bimetallic core.

Preparation of **1a-d₁** in THF-*d*₈



A J-Young style NMR tube was charged with SIMesCuCl (11.6 mg, 0.029 mmol) and [Ta(naph)₃]⁻ (10.8 mg, 0.016 mmol). The tube was degassed and THF-*d*₈ (0.6 mL) was added via vacuum transfer. The reaction was mixed via inversion for 16 hours at room temperature, at which time solvent was removed *in vacuo*. The resultant orange solids were extracted into diethyl ether (5 mL) and filtered through a pad of Celite. The filtrate was dried under reduced pressure, affording **1a-d₁** as an orange powder.

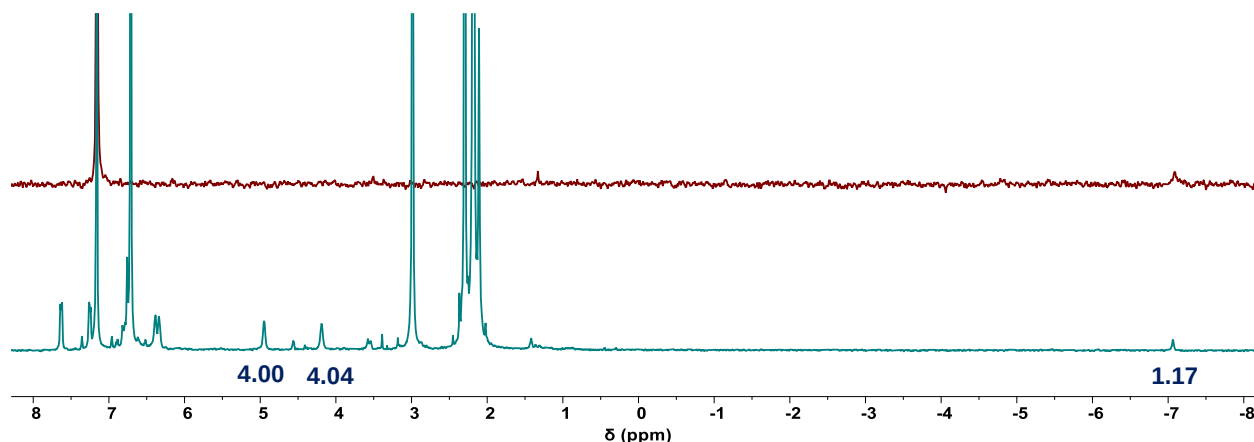
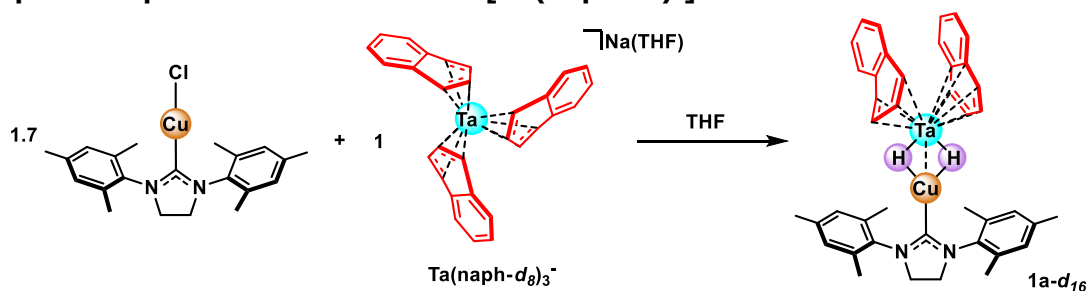


Figure S44 – Formation of **1a-d₁** using THF-*d*₈. The ²H (top; 107 MHz, 25 °C, C₆H₆ with a C₆D₆ standard) and ¹H (bottom; 400 MHz, 25 °C, C₆D₆) NMR spectra are consistent with a mixed bimetallic core.

Attempted Preparation of **1a-d₁₆** with [Ta(naph-*d*₈)₃][–]



A J-Young style NMR tube was charged with SIMesCuCl (9.9 mg, 0.024 mmol) and [Ta(naph-*d*₈)₃][–] (9.6 mg, 0.015 mmol). The tube was degassed and THF (0.6 mL) was added via vacuum transfer. The reaction was mixed via inversion for 16 hours at room temperature, at which time solvent was removed *in vacuo*. The resultant orange solids were extracted into diethyl ether (5 mL) and filtered through a pad of Celite. The filtrate was dried under reduced pressure, affording **1a-d₁₆** as an orange powder. Despite prolonged experiments, no ²H NMR signal was observed for a bridging deuteride. This may reflect H/D exchange processes occurring during the formation of the bimetallic.

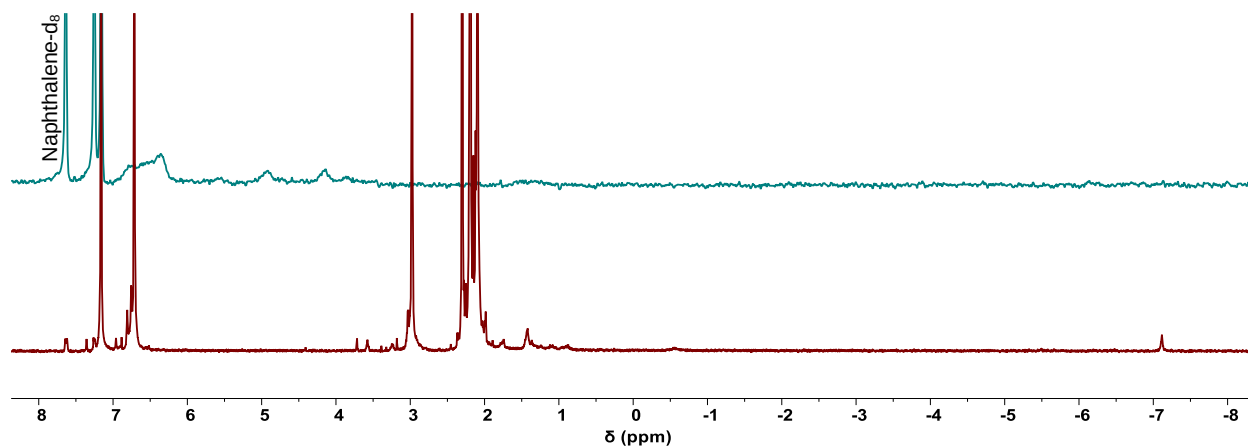
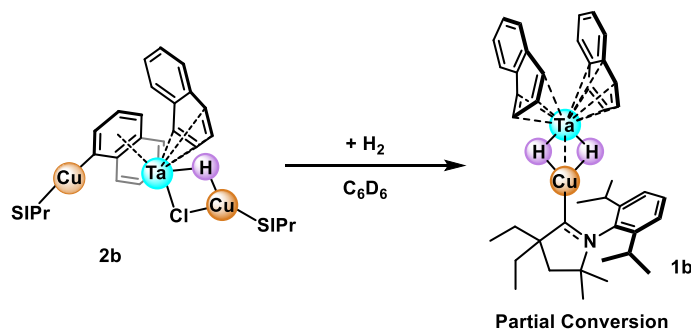


Figure S45 – Formation of **1a-d₁₆** using [Ta(naph-*d*₈)₃][–] and THF. The ²H (top; 107 MHz, 25 °C, C₆H₆ with a C₆D₆ standard) and ¹H (bottom; 400 MHz, 25 °C, C₆D₆) NMR spectra show naph-*d*₈ rings bound to tantalum, but do not provide conclusive evidence for a bridging deuteride.

Dihydrogen addition to trimetallic **2b**



A J-Young style NMR tube was charged with a C₆D₆ (0.6 mL) solution of **2b** (11.3 mg, 0.0082 mmol). The tube was sealed, degassed via three freeze-pump-thaw cycles, and backfilled with H₂ (1 atm). The reaction was mixed at room temperature for 48 hours, during which time reaction progress was monitored via ¹H NMR spectroscopy. The sluggish reaction observed required more forcing reaction conditions (heating in toluene); however, the associated control reaction showed equivalent conversion of **2b** to **1b** in toluene at 110 °C with or without H₂ (*vide supra*).

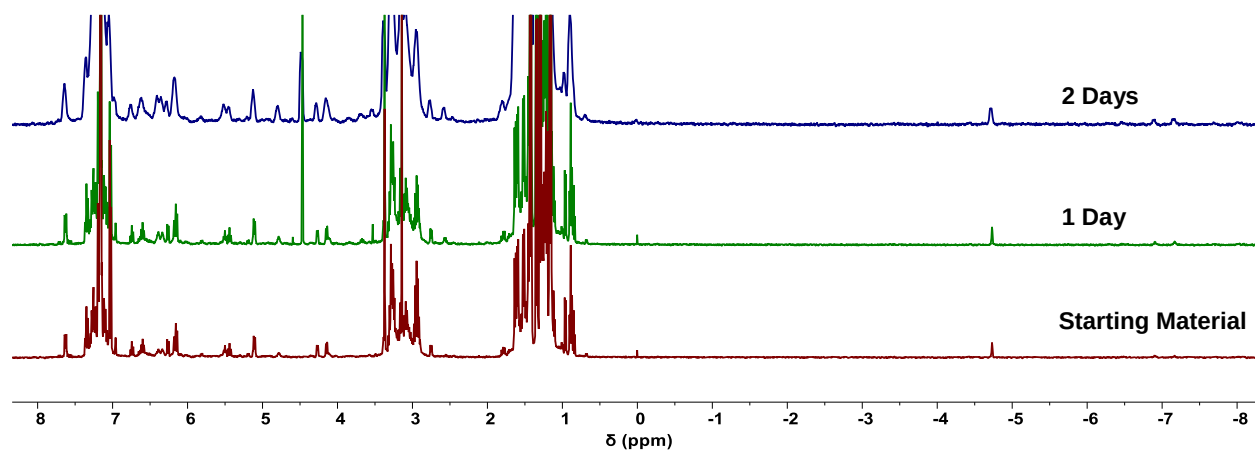
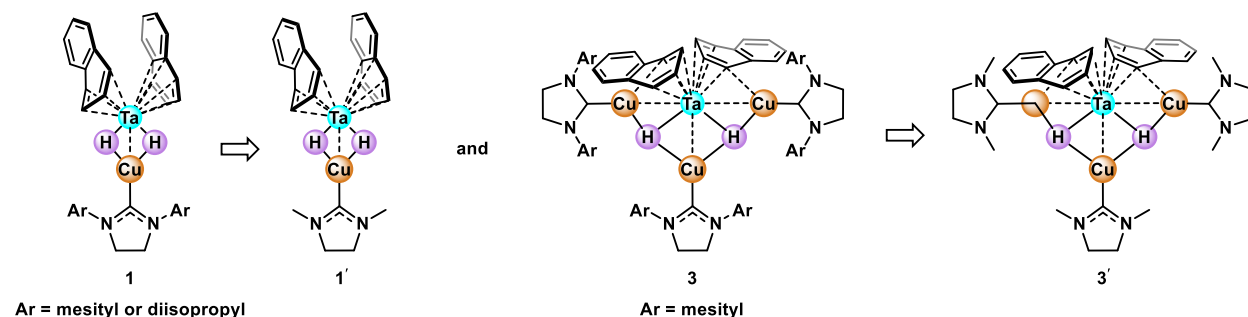


Figure S46 – Stacked ^1H NMR spectra showing partial conversion of **2b** to **1b** following H_2 addition (^1H NMR, 400 MHz, C_6D_6).

Computational Details

All calculations were performed using spin-restricted DFT within the Gaussian 16 software suite.^[9] Initial geometries were sourced from single-crystal XRD structures and truncated as shown below:



Geometry optimizations were performed using the parameter-free PBE0 functional,^[10] with the def2/TZVPP basis set on all atoms, including a quasi-relativistic small core pseudopotential for Ta.^[11] Similar levels of theory have been successfully applied to related heteromultimetallic systems in the literature.^[12] Further, the computed bond metrics are in close agreement with those found experimentally in the solid-state (Table S2 and Table S4). Grimme's D3 dispersion correction^[13] was employed in each case and calculated structures were confirmed as minima by the absence of imaginary vibrational frequencies. Multiwfn^[14] was utilized (starting from optimized geometries) to calculate bond critical points for the QTAIM analysis. Representations of the results were plotted through Multiwfn (2D projection, Figure 4) or VMD^[15] (3D representation, Figures S47 and S48). Orbital contours were plotted with a 0.04 eA⁻³ isosurfaces and visualized using GaussView5.^[16]

Table S1. Optimized Cartesian coordinates for 1'

C	-4.263534	0.237809	-0.000265	C	2.797008	1.595447	0.702460
C	-6.533536	-0.365674	0.083236	C	3.994159	1.790035	0.392325
H	6.881315	-0.651052	1.093338	H	3.992816	1.790066	0.485648
H	7.199085	-0.838056	-0.653639	C	5.195604	1.969171	0.688973
C	6.425679	1.154806	-0.084068	H	6.131282	2.099547	0.236701
H	6.729763	1.486578	-1.094047	C	5.194415	-1.966942	0.704713
H	-7.017802	1.716367	0.652880	H	6.129159	-2.095625	1.254438
C	1.466665	1.401184	0.329190	C	3.991781	-1.785593	1.405463
H	1.441008	1.329248	0.419315	H	3.988580	-1.782230	2.498780
C	0.378404	2.117248	0.695146	C	0.847778	-1.865865	-1.410407
H	-0.434680	2.567938	1.264498	H	0.846998	-1.875616	-2.498947
C	0.377019	-2.114705	0.703604	C	-0.278966	-2.411595	-0.693128
H	-0.437898	2.562457	-1.272588	H	-1.175040	-2.708445	-1.238696
C	1.464503	-1.396607	1.336791	C	-0.281525	-2.408112	0.700657
H	1.437025	-1.320779	2.426605	H	-1.180346	-2.700721	1.243883
C	2.795806	-1.593172	0.712974	C	0.843758	-1.859953	1.418714

H	0.839728	-1.864852	2.507284
C	2.138252	-1.847298	0.722307
C	2.140329	-1.849589	-0.710155
C	3.372709	-1.756008	-1.390372
H	3.367721	-1.743144	-2.482395
C	4.565891	-1.653740	-0.693544
H	5.506739	-1.554873	-1.236462
C	4.563878	-1.651734	0.711881
H	5.503259	-1.551565	1.257122
C	3.368751	-1.751930	1.405686
H	3.360693	-1.735954	2.497653
Cu	-2.365069	0.115133	-0.001364
N	-4.985956	1.375969	0.106946

N	-5.139300	-0.787700	-0.107861
Ta	0.301398	-0.165266	-0.000138
C	-4.425018	2.705417	0.025513
H	-3.343604	2.638791	0.201817
H	-4.595397	3.155353	-0.968458
H	-4.873902	3.359907	0.788289
C	-4.770885	-2.182002	-0.022986
H	-3.689899	-2.265527	-0.194419
H	-5.006484	-2.602875	0.970589
H	-5.303091	-2.769150	-0.787102
H	-1.159926	0.105976	-1.166486
H	-1.160430	0.110812	1.164327

Table S2. Comparison of Salient Metrical Parameters for 1a and 1'

	XRD (1a)	DFT (1')
Cu1 – C _{NHC}	1.895	1.902
Ta1 – Cu1	2.654	2.681
Ta1 – C1	2.331	2.362
Ta1 – C2	2.352	2.387
Ta1 – C3	2.372	2.387
Ta1 – C4	2.338	2.362
Ta1 – C11	2.251	2.276
Ta1 – C12	2.387	2.421
Ta1 – C13	2.395	2.421
Ta1 – C14	2.259	2.276
Ta1 – C15	2.548	2.593
Ta1 – C20	2.511	2.593
C1 – C2	1.447	1.449
C2 – C3	1.375	1.399
C3 – C4	1.449	1.449
C4 – C5	1.478	1.483
C5 – C10	1.405	1.415
C10 – C1	1.478	1.483
C11 – C12	1.431	1.443
C12 – C13	1.391	1.394
C13 – C14	1.432	1.443
C14 – C15	1.471	1.470
C15 – C20	1.414	1.432
C20 – C11	1.452	1.470

Table S3. Optimized Cartesian coordinates for 3'

C	-4.377175	0.274978	1.115257	H	2.311972	-2.524231	1.608078
C	-6.537069	1.140588	0.774809	C	0.455590	-1.656013	2.286359
H	-7.386266	0.746163	0.197369	H	0.076824	-2.594365	2.692897
H	-6.607058	2.244370	0.774270	C	-0.249717	-0.429337	2.452763
C	-6.448571	0.564129	2.193560	H	-1.133587	-0.352553	3.087444
H	-6.779064	1.269232	2.970719	C	0.475506	0.755089	1.940881
H	-7.036670	-0.366156	2.304104	H	-0.063093	1.697062	2.113837
C	0.370693	3.389671	-0.996199	C	1.913786	0.794884	2.311040
C	1.015481	5.563107	-1.626687	C	2.614299	-0.426789	2.154729
H	1.784602	5.591403	-2.421421	C	3.968128	-0.497074	2.495450
H	1.074416	6.505798	-1.063002	H	4.500178	-1.446099	2.381110
C	-0.383590	5.275833	-2.183929	C	4.650799	0.642453	2.949613
H	-1.168446	5.855784	-1.662974	H	5.715282	0.582222	3.188447
H	-0.472415	5.476196	-3.261902	C	3.962820	1.847569	3.104772
C	4.281902	-1.171967	-0.949487	H	4.485171	2.736038	3.466998
C	6.506866	-0.430772	-1.011555	C	2.591927	1.912193	2.807741
H	6.929044	-0.278728	-0.000751	H	2.043396	2.846821	2.959321
H	7.072340	0.192742	-1.719250	Cu	-2.582108	-0.251317	0.713959
C	6.465948	-1.911920	-1.404541	Cu	0.363113	1.612568	-0.295427
H	6.666089	-2.064074	-2.482065	Cu	2.426845	-1.101044	-0.488784
H	7.171674	-2.533437	-0.834277	H	1.171513	0.117020	-0.865410
C	-1.976092	-2.444027	0.143421	H	-1.264473	0.599994	-0.103834
H	-2.492741	-2.831984	1.030773	N	-5.258377	0.715023	0.193750
C	-0.678667	-3.086960	-0.115249	N	-5.014412	0.268300	2.311942
H	-0.305497	-3.903154	0.505399	N	1.236151	4.402579	-0.753442
C	0.012705	-2.642652	-1.270891	N	-0.535603	3.845090	-1.892799
H	0.902852	-3.151956	-1.645834	N	5.079823	-0.082878	-1.010438
C	-0.682388	-1.554870	-1.972516	N	5.073482	-2.260580	-1.093007
H	-0.135340	-1.087243	-2.795727	Ta	-0.084449	-0.890983	0.223710
C	-2.126805	-1.752495	-2.186377	C	4.578093	-3.601160	-1.293515
C	-2.830718	-2.258721	-1.063466	H	3.521142	-3.622487	-0.997382
C	-4.194232	-2.543476	-1.162492	H	4.657828	-3.910356	-2.351289
H	-4.723934	-2.949319	-0.295638	H	5.141292	-4.319241	-0.676893
C	-4.891518	-2.270872	-2.351353	C	4.648858	1.256500	-0.670908
H	-5.963925	-2.470339	-2.413142	H	3.556023	1.303858	-0.771526
C	-4.211035	-1.736869	-3.446927	H	4.911345	1.511969	0.370006
H	-4.750396	-1.514390	-4.370832	H	5.111172	1.984823	-1.355993
C	-2.829139	-1.497022	-3.369729	C	-4.935086	1.017082	-1.181733
H	-2.291570	-1.107596	-4.239189	H	-4.911151	2.109065	-1.351354
C	1.785486	-1.562061	1.659135	H	-3.952932	0.589051	-1.417608

H	-5.673168	0.562863	-1.858439
C	-4.495934	-0.365659	3.500506
H	-5.007731	-1.324550	3.700877
H	-3.427888	-0.563319	3.345804
H	-4.621323	0.286402	4.379302
C	-1.732436	3.134202	-2.282987
H	-1.635663	2.085643	-1.970701

H	-2.628197	3.564995	-1.800282
H	-1.866933	3.179634	-3.374986
C	2.475237	4.257744	-0.026777
H	2.606264	5.086023	0.687427
H	2.452374	3.311355	0.527630
H	3.342643	4.250272	-0.711953

Table S4. Comparison of Salient Metrical Parameters for 3a and 3'

	XRD (3a)	DFT (3')
Ta1 – Cu1	2.636	2.624
Cu1 – C _{NHC}	1.926	1.913
Ta1 – Cu3	2.610	2.596
Cu2 – C _{NHC}	1.918	1.910
Ta1 – Cu2	2.631	2.619
Cu3 – C _{NHC}	1.915	1.913
Ta1 – C1	2.411	2.449
Ta1 – C2	2.257	2.300
Ta1 – C3	2.276	2.305
Ta1 – C4	2.345	2.371
Ta1 – C11	2.414	2.451
Ta1 – C12	2.245	2.265
Ta1 – C13	2.268	2.282
Ta1 – C14	2.356	2.444
C1 – C2	1.475	1.471
C2 – C3	1.413	1.418
C3 – C4	1.476	1.469
C4 – C5	1.479	1.473
C5 – C10	1.390	1.419
C10 – C1	1.484	1.490
C11 – C12	1.468	1.473
C12 – C13	1.398	1.425
C13 – C14	1.477	1.480
C14 – C15	1.465	1.486
C15 – C20	1.410	1.417
C20 – C15	1.479	1.490
Cu1 – C1	2.351	2.354
Cu2 – C11	2.331	2.289

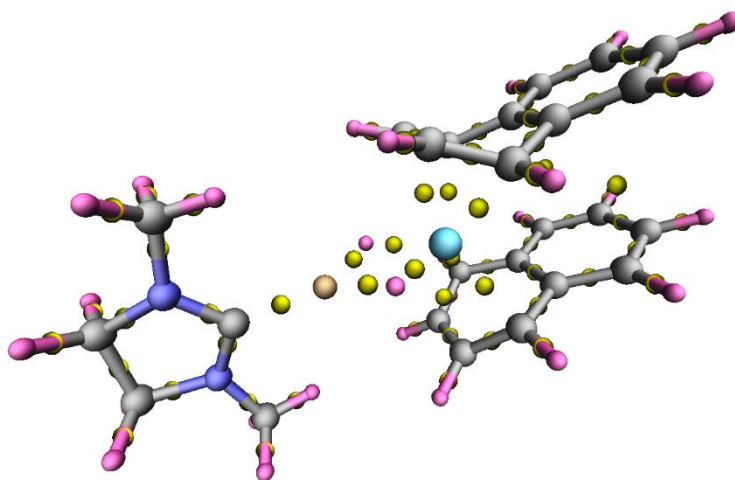


Figure S47 – Calculated bond critical points (3, -1) for **1'**.

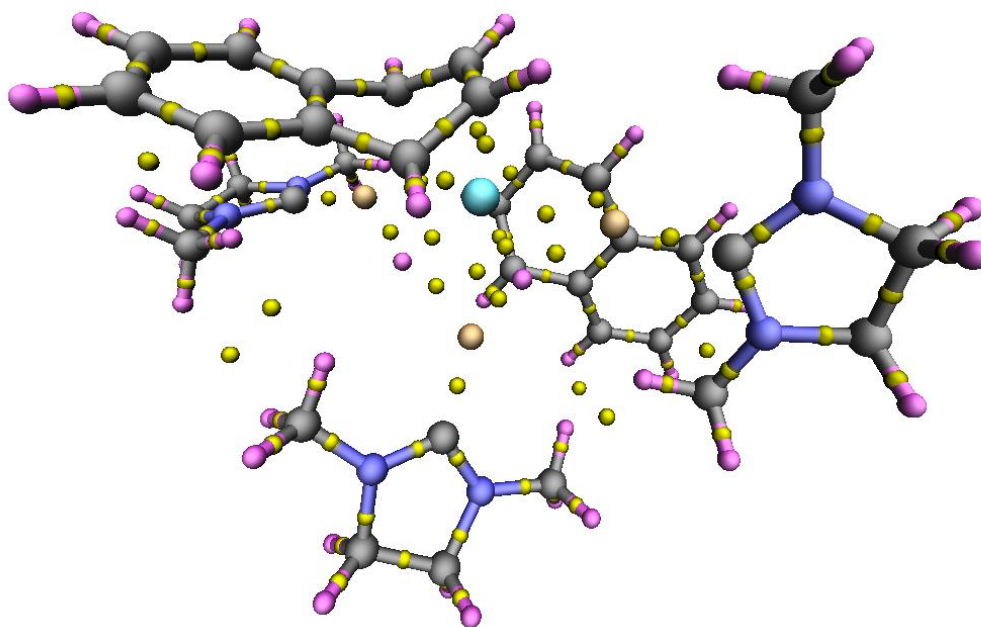


Figure S48 – Calculated bond critical points (3, -1) for **3'**. Critical points were computed between each Cu atom and Ta, and along each M-H bond vector for the μ^3 hydrides.

Crystallographic Information

Refinement Details

In each case, crystals were mounted on a MiTeGen loop, using Paratone oil, then placed on a Rigaku AFC10K Saturn 944+ CCD-based X-ray diffractometer equipped with a low temperature cryostream and a Mircomax-007HF Cu-target micro-focus rotating anode ($\lambda = 1.54187 \text{ \AA}$) operated at 1.2 kW power (40 kV 30 mA). The X-ray intensities were measured at 85(1) K with the detector located at a distance of 42.00 mm from the crystal. Rigaku d*trek images were exported to CrysAlisPro^[17] for processing and corrected for absorption using spherical harmonics, as implemented in the SCALE3 ABSPACK scaling algorithm.^[18] Space groups were determined on the basis of systematic absences and intensity statistics and the structures were solved using SHELXTL intrinsic phasing (XT)^[19] as incorporated into the Olex2 software interface.^[20] Solutions were refined (SHELXL)^[21] by full-matrix least squares on F^2 to convergence. All non-hydrogen atoms were refined using anisotropic displacement parameters and hydrogen atoms were placed in the idealized positions and refined using a riding model, unless noted otherwise. Graphical representations of structures with 50% probability thermal anisotropic displacement ellipsoids were generated as Poscript vector images via Olex2.

Table S5—Crystal and refinement data for complexes **1a**, **1b**, **1c**, **2b**, and **3a**.

	1a	1b	1c	2b	3a
CCDC Number ^[22]	2287351	2287354	2287355	2287353	2287352
Internal ID Code	mm171e	mm2131	mm228	mm2109a	mm177e
Empirical formula	C ₄₁ H ₄₂ CuN ₂ Ta	C ₁₀₁ H ₁₂₀ Cu ₂ N ₄ Ta ₂	C _{49.5} H _{70.5} CuNTa	C ₇₄ H ₉₁ ClCu ₂ N ₄ Ta	C _{88.1} H _{107.9} Cu ₃ N ₆ Ta
Formula weight	807.25	1878.98	924.05	1379.98	1622.47
T (K)	85	153	85	153	85
a, Å	7.2773(2)	23.6992(3)	28.3073(3)	19.5157(6)	36.4619(1)
b, Å	17.4982(6)	18.9938(3)	16.1736(2)	19.7513(6)	36.4619(1)
c, Å	26.8110(9)	19.5107(2)	22.4262(2)	23.6353(6)	11.3713(1)
α, °	90	90	90	109.902(2)	90
β, °	97.708(3)	91.7930(10)	125.2390(10)	94.315(2)	90
γ, °	90	90	90	117.716(3)	90
Volume, Å ³	3383.25(19)	8778.2(2)	8385.93(18)	7278.8(4)	15117.81(16)
Z	4	4	8	4	8
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic	Tetragonal
Space group	P2 ₁ /n	C2/c	C2/c	P-1	I-4
d _{calc} , g/cm ³	1.585	1.422	1.464	1.259	1.426
2θ range, °	6.048 to 139.4	5.964 to 138.9	6.818 to 138.7	5.33 to 138.8	3.426 to 139.7
μ, mm ⁻¹	6.861	5.367	5.594	4.016	3.913
Abs. Correction	Multi-scan	Multi-scan	Multi-scan	Multi-scan	Multi-scan
GOF	1.028	1.037	1.098	0.980	1.083
R ₁ , ^a wR ₂ ^b [I>2 σ(I)]	0.0480, 0.1210	0.0378, 0.1001	0.0269, 0.0738	0.0692, 0.1676	0.0324, 0.0791
Radiation Type	Cu Kα (λ = 1.54178)	Cu Kα (λ = 1.54178)	Cu Kα (λ = 1.54178)	Cu Kα (λ = 1.54178)	Cu Kα (λ = 1.54178)

^a $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$. ^b $wR_2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{1/2}$

Structure Determination of Complex 1a

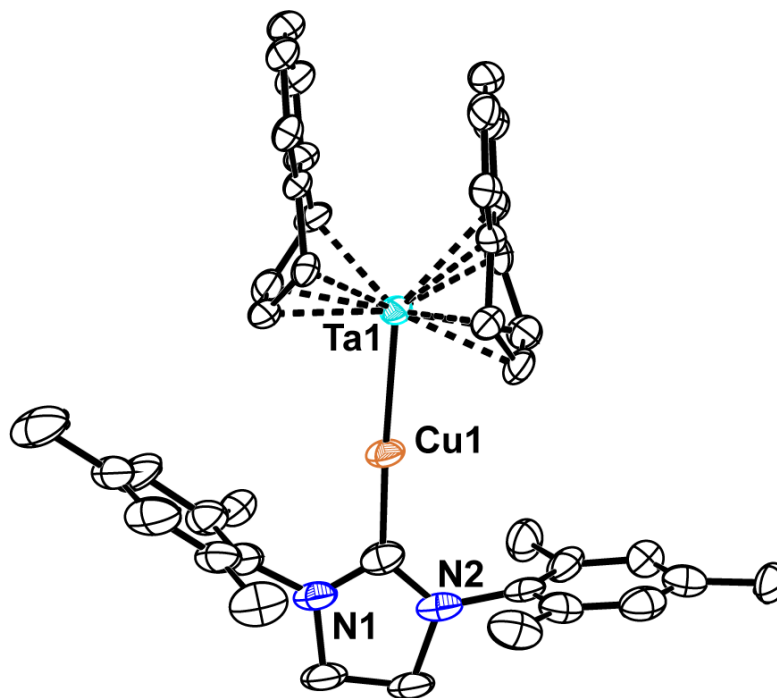


Figure S49 – Structural drawing of **1a** with 50% probability anisotropic displacement ellipsoids. H-atoms are omitted for clarity. Note that the hydride ligands in this case were not resolved in the Fourier map and have not been included in the structural depiction.

Special Refinement Details: Both of the mesityl substituents of the N-heterocyclic carbene ligand (C25 > C28 C31 C32 and C33 > C41) suffered from positional disorder. This was modeled satisfactorily over two discrete positions in 62:38 and 73:27 population ratios for each aryl ring, respectively. One of the methyl groups for the first mesityl ring (C32) was refined with U_{ij} similarity restraints. We elected to refine the minor component (27%) of the second (C33 > C41) mesityl ring isotropically, in lieu of employing distance similarity and enhanced rigid bond restraints.

Structure Determination of Complex 1b

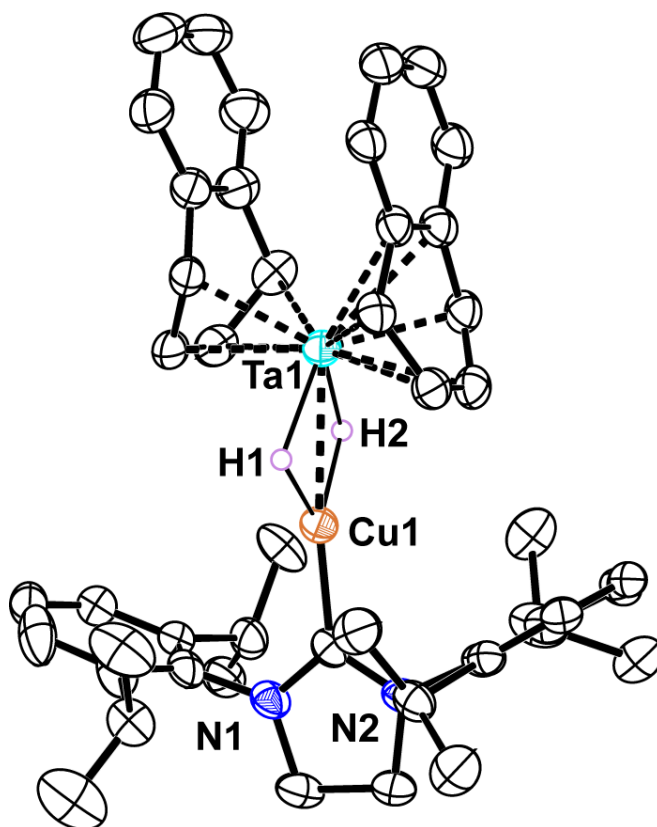


Figure S50 – Structural drawing of **1b** with 50% probability anisotropic displacement ellipsoids. The hydride hydrogens were discernable in the Fourier map and refined freely. Non-hydride H-atoms are omitted for clarity.

Special Refinement Details: Two of the isopropyl moieties on the diisopropylphenyl groups displayed positional disorder. The first (C30 C31 C32) was satisfactorily modeled over two discrete positions, in a 50:50 population ratio. The second was satisfactorily modeled with a split methyl carbon (C44) in a 65:45 relative ratio. The structure refined stably without restraints.

Structure Determination of Complex 1c

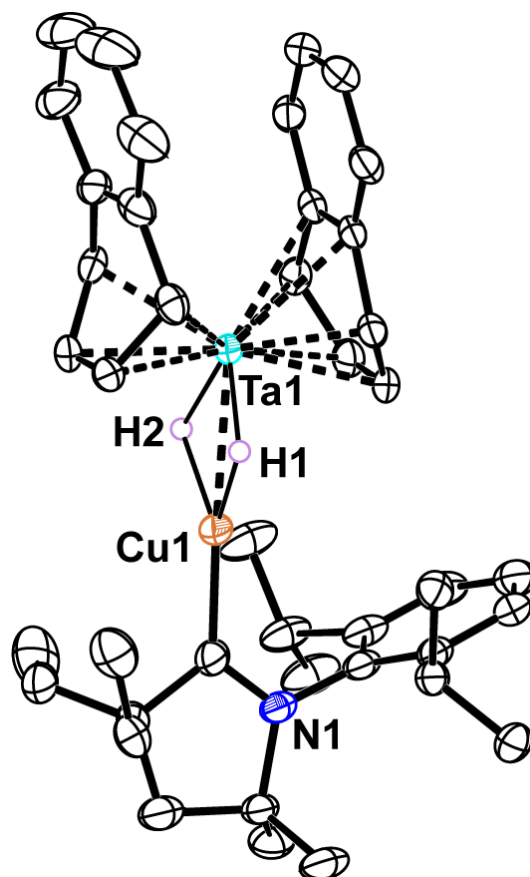


Figure S51 – Structural drawing of **1c** with 50% probability anisotropic displacement ellipsoids. The hydride hydrogens were discernable in the Fourier map and refined freely. Non-hydride H-atoms are omitted for clarity.

Special Refinement Details: The ethyl groups of the cyclic (alkyl)(amino)carbene ligand (C24 C39 C40 C41 C42) were disordered and satisfactorily modeled over two discrete positions in a 66:34 relative population ratio. These groups were refined with 1,2- and 1,3-distance similarity restraints. Additionally, there were hexane solvate molecules present in the asymmetric unit. One of these solvent molecules (C43 C44 C45) occupied a symmetry special position and was modeled discretely without restraints (0.5 hexane [C₆H₁₄]). The second was highly disordered and treated with a solvent mask via the BYPASS feature in Olex2. A solvent mask was calculated and 280 electrons were found in a volume of 968 Å³ in a single void per unit cell. This is consistent with the presence of 0.75 hexane [C₆H₁₄] molecules per asymmetric unit, accounting for 300 electrons per unit cell.

Structure Determination of Complex 2b

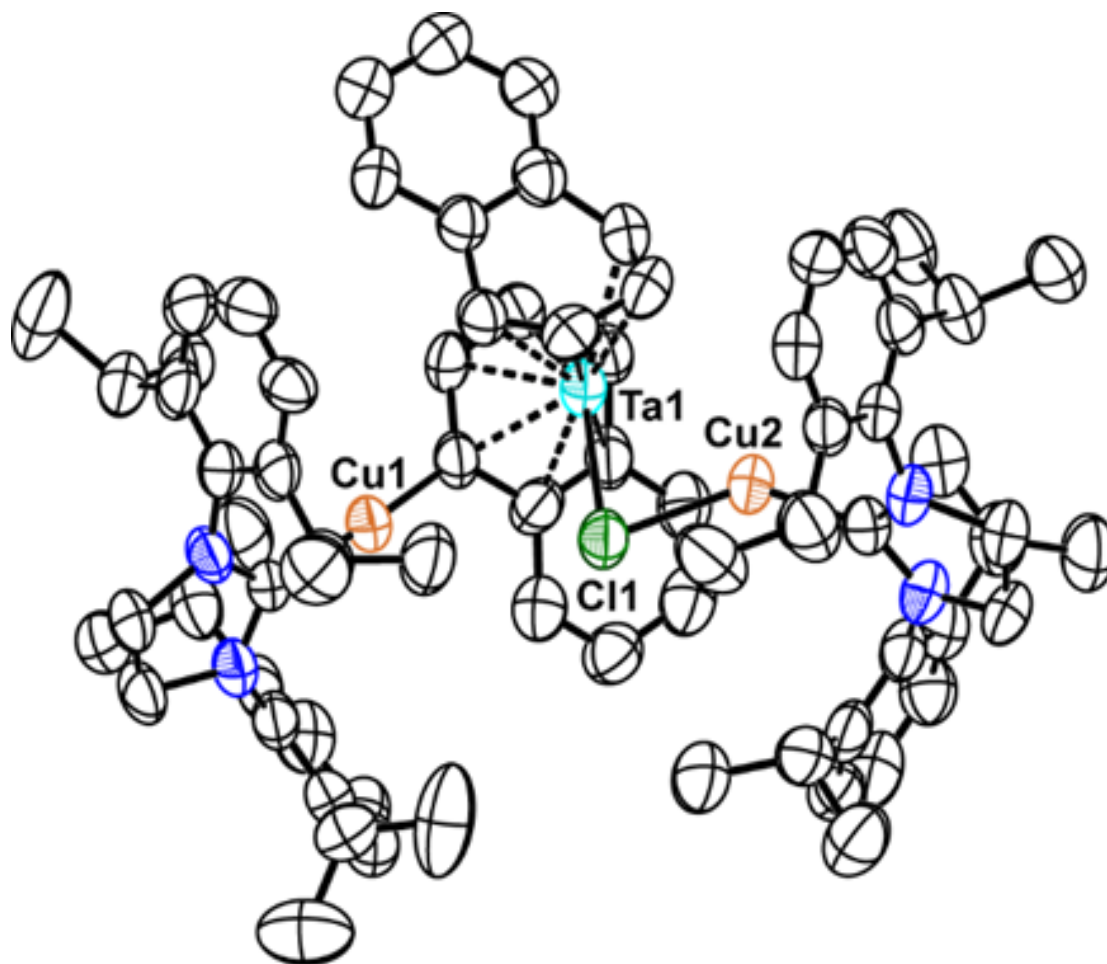


Figure S52 – Structural drawing of **2b** with 50% probability anisotropic displacement ellipsoids. H-atoms are omitted for clarity. Note that the hydride ligand was not resolved in the Fourier map and has not been included in the structural depiction.

Special Refinement Details: Whereas the quality of the structural data for **2b** are poor, this was the best sample obtained after several collections of independent crystals grown with different crystallization conditions from independent batches of sample. There are two molecules present in the asymmetric unit; one of these molecules showed no positional disorder was refined stably without restraints. The other molecule suffers from positional disorder of three isopropyl moieties on the diisopropyl phenyl rings. Two of these groups (C99 C104 C105 C106 and C 130 C131 C132 C133) were satisfactorily modeled over two discrete positions and refined with both 1,2- and 1,3-distance similarity restraints and enhanced rigid bond restraints. Even so, the minor component of the latter disorder (21%) was refined isotropically. The minor component of the third isopropyl group (C142 C146 C147 C148) did not refine stably; this positional disorder was handled

as a single component and refined with enhanced rigid bond restraints (yet still displays high ADP max/min ratios). Additionally, the significant residual electron density around the tantalum center results in prolate ellipsoids and misshapen naphthyl arene rings. Both naphthyl moieties (C75 > C94) were refined with enhanced rigid bond restraints. Finally, the large size of the primary residue generates large solvent accessible voids in the crystal lattice. These voids contained pentane and toluene solvates that were highly disordered; BYPASS was implemented to account for the residual solvent electron density. A solvent mask was calculated and 185 electrons were found in a volume of 1201 Å³ in three voids per unit cell. This is consistent with the presence of 0.5 toluene [C₇H₈] and 0.5 pentane [C₅H₁₂] molecules per asymmetric unit which account for 184 electrons per unit cell.

Structure Determination of Complex 3a

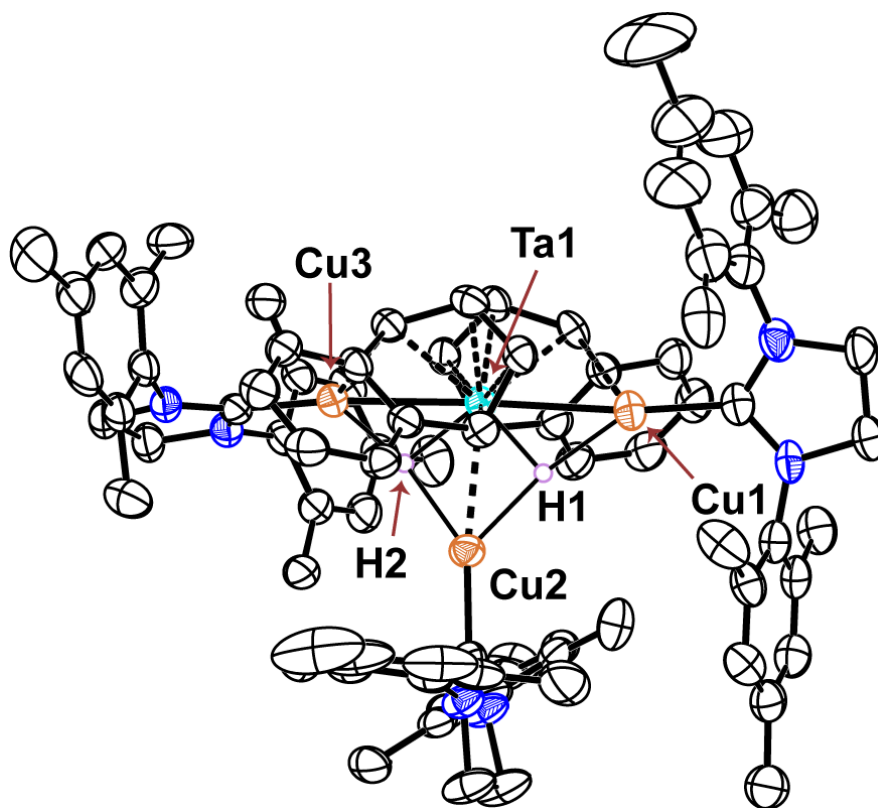


Figure S53 – Structural drawing of **3a** with 50% probability anisotropic displacement ellipsoids. The hydride hydrogens were discernable in the Fourier map and refined freely. Non-hydride H-atoms are omitted for clarity.

Special Refinement Details: The size of **3a** generates large solvent accessible voids in the crystal structure. Hexanes solvate molecules are highly disordered throughout these voids and were handled with the BYPASS feature in Olex2. A solvent mask was calculated and 356 electrons were found in a volume of 1466 Å³ in three voids per unit cell. This is consistent with the presence of 0.85 hexane [C₆H₁₄] molecule(s) (with 0.5 and 0.35 molecules in the two largest voids, respectively) per asymmetric unit and accounts for 340 electrons per unit cell. Note that fractional solvation results in a non-integer sum formula (*cf.* **Table S5**).

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