[Supporting Information to accompany *Chem. Sci.* manuscript C3SC22268C] Stabilizing unstable species through single-site isolation: A catalytically active Ta^V trialkyl in a porous organic polymer

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S1. Materials and methods.

Materials. Except for 2,3-dihydroxy-1,4-diiodobenzene (Spectra Limited Inc.), 3,6-di-*tert*-butyl catechol (SynChem), and tetrakis(4-bromophenyl)methane (Chemieliva), all other chemicals and solvents were purchased from either Sigma-Aldrich, Strem Chemicals, GFS Chemicals, Fisher Scientific, or VWR. Unless otherwise specified, all commercially supplied chemicals and solvents were used as received without further purification. 2,3-(Ethoxymethylenedioxy)-1,4-diethynylbenzene^{S1} and tetrakis(4-ethynylphenyl)methane^{S2} were synthesized using modified literature procedures. (¹BuCH₂)₃Ta=CH⁴Bu was synthesized according to a literature procedure^{S3} and purified by sublimation before use. Pentane, toluene, hexanes, and diethyl ether were dried and degassed using a Dow-Grubbs solvent purification system^{S4} installed by Vacuum Atmosphere Co. (Hawthorne, CA, USA). C₆D₆ was degassed by three freeze-pump-thaw cycles, vacuum-transferred, and dried over 4 Å molecular sieves in the glovebox. Anhydrous dodecane was sparged with N₂, and was further dried by filtration through activated alumina in the glovebox. Deionized (DI) water was provided as part of the laboratory facility at Argonne National Laboratory.

All experiments concerning tantalum compounds were conducted in an inert-atmosphere glovebox under N₂ atmosphere at ambient temperature. Elemental analysis and Ta ICP-AES analysis of the POPs was carried out by Galbraith Laboratories, Inc. (Knoxville, TN). Solution ${}^{1}\text{H}/{}^{13}\text{C}$ NMR spectra were recorded using a Bruker UltraShield 500 MHz spectrometer (${}^{1}\text{H} = 500$ MHz, ${}^{13}\text{C} = 125$ MHz) and analyzed using TopSpin (v3.1, Bruker

BioSpin, Billerica, MA) and MestReNova (v6.0.2, MestreLab Research S. L., Santiago de Compostela, Spain) softwares.

Infrared (IR) spectra were collected in a glovebox under N_2 atmosphere using a Bruker Alpha FTIR spectrometer (Bruker Optics, Billerica, MA) with a single-reflection diamond ATR setup. Spectra at 4 cm⁻¹ resolution were obtained in transmission mode over the 375-4000 cm⁻¹ range. All IR data were normalized, baseline corrected, and analyzed using OPUS (v7.0, Bruker Optics, Billerica, MA) software.

Thermal gravimetric analysis (TGA) data were obtained with a Mettler-Toledo TGA/DSC1 STARe thermal analyzer (Mettler-Toledo, Columbus. OH) at a heating rate of either 5 or 10 °C min⁻¹ under nitrogen flow.

Gas sorption measurements were performed on a Micromeritics ASAP 2020 system (Micromeritics, Norcross, GA) under N₂ at 77 K using volumetric technique. Approximately 60-90 mg of sample was used in each measurement. All samples were dried on the instrument overnight prior to analysis ((^tBuCH₂)₃Ta-A₂B₁at 25 °C, A₂B₁ and C₂B₁ at 150 °C). The data were analyzed using the Micromeritics ASAP 2020 software (v3.04, Micromeritics, Norcross, GA). Surface area measurements were determined using the Brunauer-Emmett-Teller (BET) model in the range of $0.005 < P/P_0 < 0.15$. The pore size distributions were calculated from the adsorption isotherms by density functional theory (DFT) using the slit-pore N₂ model in the range of $2.0 \times 10^{-6} < P/P_0 > 0.90$.

Solid-state ¹H and ¹³C NMR measurements were performed at Ames Laboratory (Ames, IA). Spectra were collected at 14.1 T on a Varian NMR System spectrometer (600 MHz for ¹H, 150 MHz for ¹³C) equipped with 1.6-mm and 3.2-mm magic angle spinning (MAS) probes, using direct polarization (DP) for ¹H and cross-polarization (CP) for ¹³C. Since the POP has a tendency to readily absorb water from the atmosphere, which could show up in the ¹H NMR spectrum, catPOP A_2B_1 was packed in a zirconia MAS rotor (3.2-mm) equipped with double O-ring caps in a glove box under argon atmosphere. The ¹H DPMAS spectrum of this sample was obtained with $v_R = 16$ kHz and $v_{RF}(^{1}H) = 125$ kHz for $\pi/2$ pulse. For ^{13}C analysis, catPOP $A_{2}B_{1}$ was packed in a 1.6-mm rotor under ambient air. The CPMAS spectrum used $v_R = 40$ kHz, $v_{RF}(^{1}\text{H}) = 125$, 60 and 10 kHz for $\pi/2$ pulse, cross-polarization and SPINAL-64 heteronuclear decoupling, $v_{RF}(^{13}C) = 100$ kHz for cross-polarization, $\tau_{CP} = 3.5$ ms, $\tau_{RD} = 1.5$ s, and NA = 1600. Due to sensitivity to air and moisture, the ('BuCH₂)₃Ta- A_2B_1 sample was packed in a zirconia MAS rotor (3.2-mm) equipped with double O-ring caps in a glove box under nitrogen atmosphere. To minimize the risk of chemical decomposition, the ¹H DPMAS and ¹³C $\{^{1}H\}$ CPMAS NMR measurements of this sample, which lasted <30 s and 12 min, respectively, were carried out immediately following the loading. Both measurements were repeated five times, in the same order, yielding virtually identical spectra. The reported CPMAS spectrum was obtained by co-adding the signals obtained in all experiments. The ¹H DPMAS spectrum of (¹BuCH₂)₃Ta-A₂B₁was obtained with $v_R = 23$ kHz and $v_{RF}(^1\text{H}) = 100$ kHz for $\pi/2$ pulse and its CPMAS spectrum was obtained with $v_R = 100$ kHz for $\pi/2$ pulse and its CPMAS spectrum was obtained with $v_R = 100$ kHz for $\pi/2$ pulse and its CPMAS spectrum was obtained with $v_R = 100$ kHz for $\pi/2$ pulse and its CPMAS spectrum was obtained with $v_R = 100$ kHz for $\pi/2$ pulse and its CPMAS spectrum was obtained with $v_R = 100$ kHz for $\pi/2$ pulse and its CPMAS spectrum was obtained with $v_R = 100$ kHz for $\pi/2$ pulse and its CPMAS spectrum was obtained with $v_R = 100$ kHz for $\pi/2$ pulse and its CPMAS spectrum was obtained with $v_R = 100$ kHz for $\pi/2$ pulse and its CPMAS spectrum was obtained with $v_R = 100$ kHz for $\pi/2$ pulse and its CPMAS spectrum was obtained with $v_R = 100$ kHz for $\pi/2$ pulse and its CPMAS spectrum was obtained with $v_R = 100$ kHz for $\pi/2$ pulse and its CPMAS spectrum was obtained with $v_R = 100$ kHz for $\pi/2$ pulse and its CPMAS spectrum was obtained with $v_R = 100$ kHz for $\pi/2$ pulse and its CPMAS spectrum was obtained with $v_R = 100$ kHz for $\pi/2$ pulse and its CPMAS spectrum was obtained with $v_R = 100$ kHz for $\pi/2$ pulse and its CPMAS spectrum was obtained with $v_R = 100$ kHz for $\pi/2$ pulse and its CPMAS spectrum was obtained with $v_R = 100$ kHz for $\pi/2$ pulse and its CPMAS spectrum was obtained with $v_R = 100$ kHz for $\pi/2$ pulse and $v_$ 23 kHz, $v_{RF}(^{1}H) = 100$, 73 and 100 kHz for $\pi/2$ pulse, cross-polarization, and TPPM heteronuclear decoupling, $v_{RF}(^{13}C) = 50$ kHz for cross-polarization, $\tau_{CP} = 1.5$ ms, $\tau_{RD} = 1.5$ s, and NA = 2000 (400 × 5). v_R denotes the MAS frequency, $v_{RF}(X)$ the RF magnetic field applied to X nuclei, τ_{CP} the cross-polarization time, τ_{RD} the recycle delay, and NA the number of scans. The ¹H and ¹³C NMR chemical shifts are externally referenced to TMS at $\delta_{\rm H}$ and $\delta_{\rm C}$ = 0 ppm.

Gas chromatography mass spectrometry (GC-MS) and flame ionization detection (GC-FID) were collected using a Thermo Scientific Trace GC Ultra Gas Chromograph system equipped with a Tri Plus RSH autosampler, a Thermo Scientific ISQ GC-MS detector, and a FID detector. The column used for the MS detector was an Agilent J&W DB-5 column (30 m × 0.25 mm × 0.25 µm film thickness) and the column used for the FID detector was an Agilent J&W DB-5MS column (30 m × 0.25 mm × 0.25 µm film thickness). The data was analyzed using the Themo Xcalibur 2.2 SP1.48 software.

S2. Synthesis of POPs A₂B₁ and C₂B₁

 A_2B_1 . The following protocol is a scaled-up version of a previously reported procedure.^{S5}

Inside a N₂-filled glovebox, 2,3-(ethoxymethylenedioxy)-1,4-diethynylbenzene (0.64 g, 3.0 mmol) and tetrakis(4-ethynylphenyl)methane (0.63 g, 1.5 mmol) were dissolved in dioxane (64 mL) in a 250 mL round-bottom flask equipped with a magnetic stirbar. $Co_2(CO)_8$ (0.51 g, 1.5 mmol) was subsequently added to the flask and the deep red solution was stirred at rt for 5 minutes After fitting the round-bottom flask with an N₂ adapter and a pressure-relief valve, the reaction was transferred outside the glovebox, placed in a Radley Starfish carousel that had been preheated to 100 °C, and covered with aluminum foil. The reaction was left heating in the dark for a total of 3 h and was then cooled slowly to rt. DI H₂O (100 mL) was added to the black gellike solid and the solid was filtered using a medium frit. The POP was washed with DI H₂O (120 mL) and MeOH (120 mL), air-dried for several minutes, and then transferred to a 250 mL round-bottom flask. Conc. HCl (150 mL) was added and the solid was left stirring at rt for 2 h. The resulting brown solid was collected by filtration and was washed with copious amounts of DI H₂O (6×60 mL) to remove any traces of acid and remaining cobalt catalyst. The solid was further washed with MeOH (120 mL) and CH₂Cl₂ (120 mL), subjected to Soxhlet extraction with MeOH (~150 mL) overnight (16 h), and another Soxhlet extraction with CH₂Cl₂ (2 h, ~150 mL). Drying of the remaining materials under vacuum at 105 °C afforded A_2B_1 as a dark brown solid (1 g, ~99% yield). Due to the potential oxidation sensitivity of the catechol units and the sensitivities of the Ta reagents used in future reactions, A_2B_1 was further dried overnight at 150 °C in a Schlenk tube, transferred into the glovebox, and wrapped in foil until further use. ICP-AES (wt%): Pd: 0.0037, Co: 0.253. Additional HCl washes $(3 \times 50 \text{ mL over 4 h})$ followed by additional DI H₂O washes (3 × 50 mL, 20 minutes each) did not reduce the amount of Pd and Co residues any further. ICP-AES (wt%): Pd: 0.00352, Co: 0.261. Since the amount of trace metals did not change, further metallation experiments were carried out using materials that have not been subjected to these additional washes.

 C_2B_1 . Inside a N₂-filled glovebox, 1,4-diethynylbenzene (0.18 g, 1.4 mmol) and tetrakis(4ethynylphenyl)methane (0.29 g, 0.7 mmol) were dissolved in dioxane (30 mL) in a 100 mL round-bottom flask equipped with a magnetic stirbar. $Co_2(CO)_8$ (0.24 g, 0.7 mmol) was subsequently added to the flask and the deep red solution was stirred at rt for 5 minutes. After fitting the round-bottom flask with an N₂ adapter and a pressure-relief valve, the reaction was transferred outside the glovebox, placed in a Radley Starfish carousel that had been preheated to 100 °C, and covered with aluminum foil. The reaction was left heating in the dark for a total of 3 h and was then cooled slowly to rt. DI H_2O (50 mL) was added to the black gel-like solid and the solid was filtered using a medium frit. The POP was washed with DI H₂O (60 mL) and MeOH (60 mL), air-dried for several minutes, and then transferred to a 250 mL round-bottom flask. Conc. HCl (75 mL) was added and the solid was left stirring at rt for 2 h. The resulting brown solid was collected by filtration and was washed with copious amounts of DI H₂O (2×60 mL) to remove any traces of acid and remaining cobalt catalyst. The solid was further washed with MeOH (60 mL) and CH₂Cl₂ (60 mL), subjected to Soxhlet extraction with MeOH (~150 mL) overnight (16 h), and another Soxhlet extraction with CH₂Cl₂ (2 h, ~150 mL). Drying of the remaining materials under vacuum at 105 °C afforded C_2B_1 as a brown solid (0.46 g, ~99%) yield). Due to sensitivities of the Ta reagents used in future reactions, C_2B_1 was further dried at 150 °C overnight in a Schlenk tube and transferred to the glovebox until further use.

S3. The synthesis and characterization of $({}^{t}BuCH_{2})_{3}Ta-A_{2}B_{1}$ (NMR, TGA, elemental analysis, and ICP-AES)

(^tBuCH₂)₃Ta-A₂B₁

NMR scale synthesis of $({}^{t}BuCH_{2})_{3}Ta-A_{2}B_{1}$. A 0.10 M stock solution of ferrocene (0.056 g, 0.3 mmol) and $({}^{t}BuCH_{2})_{3}Ta=CH'Bu$ (0.28 g, 0.6 mmol) was prepared in $C_{6}D_{6}$ (6 mL). $A_{2}B_{1}$ (15 mg, 0.04 mmol of catechol units) was added to a J Young NMR tube followed by the stock solution (0.6 mL). The NMR tube was sealed and inverted several times to ensure $A_{2}B_{1}$ was well immersed in the solution before being left in the glovebox at rt. After 24 h, the NMR tube was inverted several times to solubilize any neopentane in the headspace and the sample was analyzed by ${}^{1}H$ NMR spectroscopy.



Fig. S1. ¹H NMR spectra of ferrocene and (${}^{'}BuCH_{2}{}_{)_{3}}Ta=CH'Bu$ with (red) and without (black) $A_{2}B_{1}$ in $C_{6}D_{6}$ after 24 h at rt. The black circles indicate resonances due to (${}^{'}BuCH_{2}{}_{)_{3}}Ta=CH'Bu$ and the red square indicates the resonance of neopentane.



Fig. S2. ¹H NMR spectra of ferrocene and (${}^{t}BuCH_{2}{}_{3}Ta=CH'Bu$ with (red) and without (black) $C_{2}B_{1}$ in $C_{6}D_{6}$ after 24 h at rt. Black circles indicate resonances due to ${}^{t}BuCH_{2}{}_{3}Ta=CH'Bu$ and the red square indicates the resonance of neopentane.

Large-scale synthesis of (${}^{t}BuCH_{2}$)₃Ta-A₂B₁. (${}^{t}BuCH_{2}$)₃Ta=CH ${}^{t}Bu$ (0.38 g, 0.81 mmol, 1.5 equiv) was dissolved in diethyl ether (8 mL) in a 20 mL scintillation vial equipped with a magnetic stirbar. A₂B₁ (0.20 g, 0.54 mmol of catechol units) was added to the red-orange solution and was left stirring vigorously at rt. After 22 h, the POP was filtered using a medium frit, washed with diethyl ether (3 × 10 mL), and transferred to a new scintillation vial. The collected POP was re-suspended in fresh diethyl ether (10 mL) and was left stirring for an additional 24 h before being collected via filtration. The collected materials was washed with diethyl ether (3 × 10 mL) and dried under vacuum for 3 h at rt to afford an orange solid (0.45 g, 111% yield, see discussion in the main text).





 Table S1.
 Elemental and ICP-AES analysis results

Element	$(^{t}BuCH_{2})_{3}Ta-A_{2}B_{1}$ Theoretical wt%	$({}^{t}\text{BuCH}_{2})_{3}\text{Ta-}\mathbf{A}_{2}\mathbf{B}_{1}$ Experimental wt% ^{<i>a</i>}
Та	23.85	22.35
Со	<1	0.07485
С	65.69	47.48
Н	6.24	4.80
N	<1	<0.5

^{*a*}Average based on two independent samples.

S4. Synthesis and characterization of (^tBuCH₂)₃Ta(^tBu₂cat)



Initial small-scale synthesis of $({}^{t}BuCH_{2})_{3}Ta({}^{t}Bu_{2}cat)$. A solution of recrystallized 3,6-di-*tert*-butyl catechol (0.048 g, 0.2 mmol) in toluene (3 mL) was added dropwise to a stirring solution of $({}^{t}BuCH_{2})_{3}Ta=CH'Bu$ (0.1 g, 0.2 mmol) in toluene (2 mL) in a 20 mL scintillation vial over 30 seconds. The reaction was left stirring at rt for 2 h and was filtered through a filter pipet. The filtrate was evaporated to dryness to afford a crude orange precipitate (0.126 g), which was dissolved in a minimum amount of diethyl ether and placed in the drybox freezer (- 35 °C) overnight. The resulting cloudy brown diethyl ether mixture was filtered to separate out a black solid residue, reconcentrated under vacuum, and placed in the drybox freezer again overnight. The solvent was then decanted and the remaining solid was dried under vacuum to yield (${}^{t}BuCH_{2}$)_3Ta(${}^{t}Bu_{2}$ cat) as a waxy yellow solid (0.060 g, 50%). ${}^{1}H$ NMR (C₆D₆, 500 MHz): δ 1.09 (s, 27H), 1.63 (s, 18H), 1.80 (s, 6H), 6.92 (s, 2H). ${}^{13}C$ NMR (C₆D₆, 125 MHz): δ 30.56, 34.34, 34.76, 37.23, 118.30, 119.56, 134.52, 156.14. This material was used for one of the EXAFS studies, for all NMR scale reactions, and for IR analysis.

Optimized large-scale synthesis of (^{*t*}**BuCH**₂)₃**Ta**(^{*t*}**Bu**₂**cat**). A solution of recrystallized 3,6-di-*tert*-butyl catechol (0.19 mg, 0.83 mmol) in toluene (4 mL) was added drop-wise to a stirred orange solution of (^{*t*}BuCH₂)₃Ta=CH^{*t*}Bu (0.40 mg, 0.85 mmol) in toluene (6 mL). The resulting mixture was stirred for 1.5 h and then filtered to remove a dark-orange insoluble material. The solvent was removed from the filtrate under vacuum and the resulting isolated yellow solid was washed with cold pentane ($-35 \,^{\circ}$ C, 1 mL). The remaining solid was dried under vacuum, yielding (^{*t*}BuCH₂)₃Ta(^{*t*}Bu₂cat) as a bright yellow powder (0.44 g, 84%). This material was used for the second EXAFS study. (^{*t*}BuCH₂)₃Ta(^{*t*}Bu₂cat) can also be purified by recrystallization from a concentrated hexanes solution at $-35 \,^{\circ}$ C. This recrystallized material was used for EA, MW determination, and the hydrogenation experiments described in section S8 below. Elemental analysis: Calcd.: C (56.67), H (8.69); Found: C (56.86), H (8.96). Isopiestic molecular weight measurements^{S6, 7} of (^{*t*}BuCH₂)₃Ta(^{*t*}Bu₂cat) in C₆D₆ or hexanes were reproducible and consistent with a monomeric species present in solution (measured MW = 680 g/mol; calculated MW = 614.69 g/mol).



Fig. S4. ATR-IR spectra of $({}^{t}BuCH_{2})_{3}Ta-A_{2}B_{1}$ (red) and $({}^{t}BuCH_{2})_{3}Ta({}^{t}Bu_{2}cat)$ (black).

S5. Reactivity and thermal studies with (^tBuCH₂)₃Ta-A₂B₁

An internal standard stock solution was prepared using ferrocene (0.15 g, 0.8 mmol) dissolved in C_6D_6 (6 mL) and used for the following experiments:

(MeO)₃Ta-A₂B₁. (^{*i*}BuCH₂)₃Ta-A₂B₁ (15 mg, 0.02 mmol of (catecholato)Ta units) was added to a J Young NMR tube followed by the addition of a ferrocene standard (0.6 mL, 15 mg, 0.08 mmol). Degassed MeOH (8 μ L, 0.2 mmol, 10 equiv per (catecholato)Ta units) was then added to NMR tube. The NMR tube was resealed, inverted several times, and left at rt. After 24 h, the NMR tube was inverted again to solubilize any neopentane in the headspace and the sample was analyzed by ¹H NMR spectroscopy. Although an excess of MeOH was added, only ~ 73% neopentane could be detected after 24 h (Fig. S5). Subsequent heating of the NMR sample at 50 °C for 3 days resulted in an increase in the quantity of released neopentane to ~90% (Fig. S6).

[(Et₂O)Cl₂Ta-A₂B₁]Cl. (^{*I*}BuCH₂)₃Ta-A₂B₁ (15 mg, 0.02 mmol of (catecholato)Ta units) was added to a J Young NMR tube followed by the addition of a ferrocene standard (0.6 mL, 15mg, 0.08 mmol). HCl in diethyl ether (0.1 mL of a 2 M solution, 0.2 mmol, 10 equiv per (catecholato)Ta units) was then added to the NMR tube, resulting in Np₃Ta-A₂B₁ turning black. The NMR tube was resealed, inverted several times, and left at rt. After 24 h, the NMR tube was inverted again to solubilize any neopentane in the headspace and the sample was analyzed by ¹H NMR spectroscopy. Approximately 90% neopentane was observed (Fig. S7).

[$({}^{t}BuCH_{2})_{3}Ta-A_{2}B_{1} + benzaldehyde$]. (${}^{t}BuCH_{2})_{3}Ta-A_{2}B_{1}$ (15 mg, 0.02 mmol of (catecholato)Ta units) was added to a J Young NMR tube followed by the addition of a ferrocene standard (0.6 mL, 15 mg, 0.08 mmol). Benzaldehyde (2 µL, 0.02 mmol, 1 equiv per (catecholato)Ta units) was then added to the NMR tube. The NMR tube was resealed, inverted several times, and left at rt. After 24 h, the sample was analyzed by 1 H NMR spectroscopy. While approximately 60% of the benzaldehyde appeared to have been uptaken by the POP, only a small amount (<10 mol%) of (*E*/*Z*)-3,3'-dimethyl-1-phenyl-1-butene^{S8} (see control experiments in Section S6 below) was observed, consistent with the presence of a small amount of unreacted (${}^{t}BuCH_{2}$)₃Ta=CH'Bu trapped within the pores of (${}^{t}BuCH_{2}$)₃Ta-A₂B₁.

(^{*t*}**BuCH**₂)₃**Ta-A**₂**B**₁ @ **60** °C. (^{*t*}BuCH₂)₃Ta-**A**₂**B**₁ (15 mg, 0.02 mmol of (catecholato)Ta units) was added to a J Young NMR tube followed by the addition of a ferrocene standard (0.6 mL, 15 mg, 0.08 mmol). The NMR tube was sealed and inverted several times, and placed in an oil bath preheated to 60 °C. The sample was analyzed by ¹H NMR spectroscopy after 24 and 48 h of heating (Fig. S8).



Fig. S5. ¹H NMR spectra of ferrocene in C_6D_6 with (red) and without (black) (¹BuCH₂)₃Ta- A_2B_1 before MeOH is added (top) and after MeOH has been added for 24 h (bottom). Black squares indicate the resonances due to MeOH and the red square indicates the resonance of neopentane.



Fig. S6. ¹H NMR spectra of ferrocene in C_6D_6 with (¹BuCH₂)₃Ta-**A**₂**B**₁ after MeOH addition. The sample was heated for an additional 3 days at 50 °C. Black squares indicate the resonances due to MeOH and the red square indicates the resonance of neopentane.



ppm / δ

Fig. S7. ¹H NMR spectra of ferrocene in C_6D_6 with (red) and without (black) (¹BuCH₂)₃Ta-A₂B₁ before HCl is added (top) and after HCl has been added for 24 h (bottom). Black squares indicate the resonances due to diethyl ether and the red square indicates the resonance of neopentane.



Fig. S8. ¹H NMR spectra of $({}^{t}BuCH_{2})_{3}Ta-A_{2}B_{1}$ and ferrocene in C₆D₆ at rt (black), 60 °C for 24 h (red), and 60 °C for 48 h (blue). The red square indicates the resonance of neopentane.

Large-scale synthesis of (MeO)₃**Ta-A**₂**B**₁. Toluene (2 mL) was added to a 20 mL scintillation vial containing (^tBuCH₂)₃Ta-A₂**B**₁ (150 mg, 0.20 mmol of (catecholato)Ta units) and a magnetic stirbar. Degassed MeOH (40 µL, 1 mmol, 5 equiv per (catecholato)Ta units) was added and the POP was stirred for 24 h at rt. The POP was filtered using a medium frit, washed with diethyl ether (3 × 10 mL), and was suspended in fresh diethyl ether (2 mL). After stirring for 2h at rt, the POP was re-isolated and the wash/soak with diethyl ether was repeated for an additional 2 h. After collecting the POP via filtration, the material was washed with diethyl ether (3 × 10 mL), and dried under vacuum for 2 h at rt to afford an orange solid (122 mg, 96% yield). Elemental analysis: Calcd.: C (55.50), H (3.63), Ta (28.34); Found: C (51.51), H (4.15), Ta (27.06); Calcd. if one neopentyl is present: C (59.30), H (4.60), Ta (26.67).

Large-scale synthesis of $[(Et_2O)Cl_2Ta-A_2B_1]Cl$. Diethyl ether (2 mL) was added to a 20 mL scintillation vial containing (^{*i*}BuCH₂)₃Ta-A₂B₁ (150 mg, 0.20 mmol of (catecholato)Ta units) and a magnetic stirbar. HCl in diethyl ether (1 mL of a 2 M solution, 2 mmol, 10 equiv per (catecholato)Ta units) was added and the POP turned dark brown within seconds. After allowing the POP to stir for 24 h at rt, the POP was isolated by filtration using a medium frit, washed with diethyl ether (3 × 10 mL), and dried under vacuum for 2 h at rt to afford a dark brown solid (144 mg, ~100% yield). Elemental analysis: Calcd.: C (50.47), H (3.33), Ta (24.93), Cl (14.65); Found: C (51.75), H (4.22), Ta (22.36), Cl (12.66).



Fig. S9. ATR-IR comparison of $[(Et_2O)Cl_2Ta-A_2B_1]Cl$ (blue), $(^{'}BuCH_2)_3Ta-A_2B_1$ (red), and $(MeO)_3Ta-A_2B_1$ (black).

S6. Reactivity and thermal studies with (^tBuCH₂)₃Ta(^tBu₂cat)

A stock solution containing $({}^{t}BuCH_{2})_{3}Ta({}^{t}Bu_{2}cat)$ (0.057 g, 0.093 mmol) in C₆D₆ (3 mL) was prepared and used for the following experiments.



[(MeO)₂(μ-OMe)Ta(^tBu₂cat)]₂. Degassed MeOH (3.7 μL, 0.093 mmol, 5 equiv) was added to (^tBuCH₂)₃Ta(^tBu₂cat) in C₆D₆ (0.5 mL, 11.4 mg, 0.018 mmol) in a J Young NMR tube. The yellow solution immediately turned pale brown and was left at rt. After 2 h, the sample was analyzed by ¹H NMR spectroscopy to ensure the reaction went to completion. The sample was then placed under vacuum to remove C₆D₆, neopentane, and excess MeOH, yielding a crude off-white solid that was redissolved in C₆D₆ for further analysis. ¹H NMR (C₆D₆, 500 MHz, Fig. S9): δ 1.61 (s, 36H), 3.95 (s, 6H), 4.23 (s, 12H), 6.93 (s, 4H). ¹³C NMR (C₆D₆, 125 MHz): δ 30.16, 34.43, 61.55, 61.86, 117.84, 134.18, 155.83.



 $(Et_2O)Cl_3Ta(^{t}Bu_2cat)$. HCl in diethyl ether (45 µL of a 2 M solution, 0.090 mmol, 5 equiv) was added to $(^{t}BuCH_2)_3Ta(^{t}Bu_2cat)$ in C_6D_6 (0.5 mL, 11.4 mg, 0.018 mmol) in a J Young NMR tube. The yellow solution immediately turned red and was left at rt. After 2 h, the sample was analyzed by ¹H NMR spectroscopy to ensure the reaction went to completion. The sample was then placed under vacuum to remove C_6D_6 , neopentane, and

diethyl ether, yielding a crude red oil that was redissolved in C_6D_6 for further analysis. ¹H NMR (C_6D_6 , 500 MHz, Figs. S10 and S11): δ 0.75 (bs, 6H), 1.34 (s, 18H), 3.91 (bs, 4H), 6.67 (s, 2H). ¹³C NMR (C_6D_6 , 125 MHz): δ 12.74, 29.82, 34.15, 70.58, 122.37, 136.16, 155.27.

 $({}^{t}BuCH_{2})_{3}Ta({}^{t}Bu_{2}cat) @ 60 °C. ({}^{t}BuCH_{2})_{3}Ta({}^{t}Bu_{2}cat) in C_{6}D_{6} (0.25 mL, 5.7 mg, 0.0093 mmol) was diluted by C_{6}D_{6} (0.25 mL) in a J Young NMR tube. After taking a {}^{t}H NMR spectrum at rt, the sample was placed in a preheated oil bath at 60 °C. Additional {}^{t}H NMR spectra were taken after 2 and 24 h of heating (Fig. S13).$



[(^t**BuCH**₂)₃**Ta**(^t**Bu**₂**cat**) + **benzaldehyde**]. (^tBuCH₂)₃Ta(^tBu₂**cat**) in C₆D₆ (0.25 mL of the aforementioned stock solution, 5.7 mg, 0.0093 mmol) was diluted with additional C₆D₆ (0.25 mL) in a J Young NMR tube. Benzaldehyde was added (1 µL, 0.0095 mmol, 1 equiv) and the sample was left at rt. After 24 h, the crude sample was analyzed by ¹H NMR spectroscopy, which revealed ~95% amount of the alkyl addition product.^{S9} ¹H NMR (C₆D₆, 500 MHz,): δ 0.80 (s, 9H), 0.89 (s, 9H), 0.91 (s, 4H), 1.03 (s, 9H), 1.63 (s, 18H), 2.30 (dd, 1H, *J* = 10.5, 3.5 Hz), 2.58 (dd, 1H, *J* = 13.5, 3.5 Hz), 6.08 (dd, 1H, *J* = 10.5, 4 Hz), 6.91 (s, 2H), 7.10 (t, 1H, *J* = 7.5 Hz), 7.18 (t, 2H, *J* = 8 Hz), 7.48 (d, 2H, *J* = 7 Hz).



Reaction of $({}^{t}BuCH_{2})_{3}Ta=CH'Bu$ with benzaldehyde to produce (E/Z)-3,3'-dimethyl-1-phenyl-1-butene. (${}^{t}BuCH_{2})_{3}Ta=CH'Bu$ (18 mg, 0.039 mmol) was dissolved in C₆D₆ (2 mL) and an aliquot (0.5 mL, 4.5 mg, 0.0097 mmol) of this solution was transferred to a J Young NMR tube followed by the addition of benzaldehyde (1 µL, 0.0095 mmol, 1 equiv) via a gas-tight syringe. After shaking the NMR tube, the yellow solution immediately became colorless and a white precipitate (presumably (${}^{t}BuCH_{2}$)_{3}Ta=O^{S8}) crashed out. The sample was left at rt overnight and was analyzed by ${}^{1}H$ NMR spectroscopy. The production of (E/Z) 3,3'-dimethyl-1-phenyl-1-butene^{S10}, ¹¹ was observed and identified.



Fig. S10. ¹H NMR spectrum of $([(MeO)_2(\mu-OMe)Ta(^{t}Bu_2cat)]_2$ in C_6D_6 after removal of MeOH and neopentane. The blue circles indicate resonances due to the $^{t}Bu_2cat$ moieties and the black squares indicate resonances from MeO groups.

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9.0

8.5 8.0 7.5 7.0 6.5

0.



Fig. S11. ¹H NMR spectra of $[({}^{t}BuCH_{2})_{3}Ta(3,6{}^{t}Bu_{2}cat) + HCl in Et_{2}O]$ in $C_{6}D_{6}$ (A, top) and $[({}^{t}BuCH_{2})_{3}Ta-A_{2}B_{1} + HCl in Et_{2}O]$ with ferrocene in $C_{6}D_{6}$ (B, bottom) after 24 h at rt. The blue circles indicate resonances due to the ${}^{t}Bu_{2}cat$ group, the red square indicates the resonance of neopentane, and the black squares indicates resonances from Et₂O.

6.0 5.5

5.0 4.5 4.0 3.5 3.0 f1 (ppm)

2.5 2.0 1.5

1.0

0.5 0.0



Fig. S12. ¹H NMR spectrum of $(Et_2O)Cl_3Ta(^{t}Bu_2cat)$ in C_6D_6 after removal of diethyl ether and neopentane. The blue circles indicate resonances due to the $^{t}Bu_2cat$ moieties and the black squares indicate resonances from diethyl ether.





Fig. S14. ¹H NMR spectra of $({}^{'}BuCH_2)_3Ta({}^{'}Bu_2cat)$ in C_6D_6 at rt (black), 60 °C for 2 h (red), and 60 °C for 24 h (blue). The red square indicates the resonance of released neopentane. After 2 h at 60 °C, the sample became much darker in color. While precipitates could not be observed in this darkened sample, large decreases in the resonances attributed to the catechol moieties suggested the formation of insoluble materials.

S7. XAFS experiment

S7a. Experimental setup. X-ray absorption measurements were acquired on Materials Research Collaborative Access Team (MR-CAT) beam lines at the Advanced Photon Source, Argonne National Laboratory. The Ta L_{III} edge (9881 eV)^{S12} spectra were acquired on either an insertion-device beam line (10-ID) or a bending magnet beam line (10-BM). In both cases, spectra of Ta-foil were collected simultaneously with the sample measurements for energy calibration and multiple scans were taken to ensure spectrum reproducibility. Spectra for tungsten hexachloride (WCl₆) model were acquired on a bending magnet beamline (10-BM) and referenced to Zn K-edge (9660.76(3) eV).^{S13}

Insertion-device experiments utilized a cryogenically cooled double-crystal Si (111) monochromator in conjunction with an uncoated glass mirror to minimize the presence of harmonics. The monochromator was scanned continuously during the measurements with data points integrated over 0.5 eV for 0.03 s per data point. Measurements were made in transmission mode with the ionization chambers optimized for the maximum current with linear response $(2-4 \times 10^9 \text{ photons detected/s})$ using nitrogen in the incident X-ray detector and a mixture of ~50 vol% argon in nitrogen in the transmission X-ray detector. The measurements were taken with a beam size of approximately 600 μ m × 500 μ m.

Photon energies at the bending magnet were selected using a water-cooled, double-crystal Si(111) monochromator, which was detuned by approximately 50% to reduce harmonic reflections. Measurements were made in transmission mode using nitrogen in the incident ionization chamber and a mixture of ca. 50 vol% argon in nitrogen in the transmission ionization chamber. Data points were acquired in four separate regions (energies relative to the elemental Ta L_{III} edge): a pre-edge region (-250 to -30 eV, step size = 10 eV, dwell time = 0.25 s), the XANES region (-30 to +30 eV, step size = 0.5 eV, dwell time = 0.25 s), an initial EXAFS region (+30 to 7k eV, step size = 0.07 k, dwell time = 1s), and a final EXAFS region (7k to 14k eV, step size = 0.07 k, dwell time = 3 s). The detector settling time was 0.4s prior to each measurement with a beam size of 1.2 mm × 0.5 mm.

All sample manipulations were done in a nitrogen-filled glovebox. For molecular compounds, samples were prepared such that the final [Ta] = 0.05 M based on the molecular weight of the compound. This corresponds to an edge step of approximately 0.4 absorbance units, a large enough edge step to get a good signal-to-noise ratio, but small enough to avoid having the whiteline intensity of the Ta^{V} XANES region saturate the detector. For each molecular compound, a sample was prepared by dissolving the compound (~100 mg) in pre-dried and degassed toluene (4 mL). Ex-situ reaction mixtures [($^{t}BuCH_{2}$)₃Ta(3,6- $^{t}Bu_{2}$ cat) + HCl in Et₂O] and [($^{t}BuCH_{2}$)₃Ta(3,6- $^{t}Bu_{2}$ cat) + HCl in Et₂O] and [($^{t}BuCH_{2}$)₃Ta(3,6- $^{t}Bu_{2}$ cat) + HCl in Et₂O] and [($^{t}BuCH_{2}$)₃Ta(3,6- $^{t}Bu_{2}$ cat) + HCl in Et₂O] and [($^{t}BuCH_{2}$)₃Ta(3,6- $^{t}Bu_{2}$ cat) + HCl in Et₂O] and [($^{t}BuCH_{2}$)₃Ta(3,6- $^{t}Bu_{2}$ cat) + HCl in Et₂O] and [($^{t}BuCH_{2}$)₃Ta(3,6- $^{t}Bu_{2}$ cat) + HCl in Et₂O] and [($^{t}BuCH_{2}$)₃Ta(3,6- $^{t}Bu_{2}$ cat) + HCl in Et₂O] and [($^{t}BuCH_{2}$)₃Ta(3,6- $^{t}Bu_{2}$ cat) + HCl in Et₂O] and [($^{t}BuCH_{2}$)₃Ta(3,6- $^{t}Bu_{2}$ cat) + HCl in Et₂O] and [($^{t}BuCH_{2}$)₃Ta(3,6- $^{t}Bu_{2}$ cat) + HCl in Et₂O] and [($^{t}BuCH_{2}$)₃Ta(3,6- $^{t}Bu_{2}$ cat) + HCl in Et₂O] and [($^{t}BuCH_{2}$)₃Ta(3,6- $^{t}Bu_{2}$ cat) + HCl in Et₂O] and [($^{t}BuCH_{2}$)₃Ta(3,6- $^{t}Bu_{2}$ cat) + HCl in Et₂O] and [($^{t}BuCH_{2}$)₃Ta(3,6- $^{t}Bu_{2}$ cat) + HCl in Et₂O] and [($^{t}BuCH_{2}$)₃Ta(3,6- $^{t}Bu_{2}$ cat) + HCl in Et₂O] and [($^{t}BuCH_{2}$)₃Ta(3,6- $^{t}Bu_{2}$ cat) + HCl in Et₂O] and [($^{t}BuCH_{2}$)₃Ta(3,6- $^{t}Bu_{2}$ cat) + HCl in Et₂O] and [($^{t}BuCH_{2}$)₃Ta(3,6- $^{t}Bu_{2}$ cat) + HCl in Et₂O] and [($^{t}BuCH_{2}$)₃Ta(3,6- $^{t}Bu_{2}$ cat) + HCl in Et₂O] and [($^{t}BuCH_{2}$)₃Ta(3,6- $^{t}Bu_{2}$ cat) + HCl in Et₂O] and [($^{t}BuCH_{2}$)₃Ta(3,6- $^{t}Bu_{2}$ cat) + HCl in Et₂O] and [($^{t}BuCH_{2}$)₃Ta(3,6- $^{t}Bu_{2}$ cat) + HCl in Et₂O] and [($^{t}BuCH_{2}$)₃Ta(3,6- $^{t}Bu_{2}$ cat) + HCl in Et₂O] and [($^{t}BuCH_{2}$)₃Ta(3,6- $^{t}Bu_{2}$ cat) + HCl in Et₂O] and [($^{t}BuCH_{2}$)₃Ta(3,6- $^{t}Bu_{2}$ cat) + HCl in Et₂O] and [($^{t}BuCH_{2}$)₃Ta(3,6- $^{t}Bu_{2}$ cat) + HCl in Et₂O] and [($^{t}BuCH_{2}$)₃Ta(3,6- $^{t}Bu_{2}$ cat) + HCl in Et₂O] and [($^{t}BuCH_{2}$)₃Ta(3,6- $^{t}Bu_{2}$ cat) + HCl in Et₂O] and [($^{t}BuCH_{2}$)₃Ta(3,6- $^{t}Bu_{2}$ Cat) + HCl in Et₂O] and [($^{t}BuCH_{2}$)₃Ta(3,6- $^{t}BuCH_{2}$ Cat) + HCl i ¹Bu₂cat) + MeOH] were prepared on a smaller scale (10 mg / 0.6 mL) directly in J-Young NMR tubes as per their descriptions above. A 0.5 mL aliquot was then loaded into a PEEK or Meldin sample cup modified slightly from the design shown in Nelson and Miller^{S14} to have a path length of 3.5 mm. The sample was isolated from air and moisture by sealing the sample cup using a Meldin or stainless steel Swagelok VCO fitting. Additional reagents were added by syringe. MeOH was added neat and HCl was added as a 2.0 M solution in Et₂O. Solid POP samples were prepared by weighing the POP (~ 5 mg) directly into the same PEEK or Meldin sample holders described above^{\$14} and suspending the solid in dodecane (0.5 mL). The samples were then removed from the glovebox and placed in the beamline in a temperature-controlled sample holder mounted on a Parker X,Y,Z stage with µm directional resolution. An X,Y positional scan at a single energy was used to optimize the sample position, particularly for the POPs, which tended to disperse towards the bottom of the sample holder.

S7b. XAFS Data Analysis Background and normalization procedures were carried out using the Athena^{S15} software package using standard methods. Edge energies were taken as the initial maximum of the first derivative of the edge, after each of the scans had been calibrated and aligned to the foil reference (Zn foil for both tungsten hexachloride and the Ta foil, and Ta foil for tantalum complexes).

Standard procedures based on WINXAS 3.1 software^{S16} were used to fit the Ta–N/O/C and Ta–Cl first shell coordination XAS data. Phase shifts and backscattering amplitudes for Ta–N and Ta–O were obtained from experimental standards using a 0.05 M solution of Ta(NMe₂)₅ in toluene (5 Ta–N at 2.03 Å)^{S17} and a 0.05 M solution of Ta(OEt)₅ in diethyl ether (5 Ta–O at 1.94 Å).^{S18, 19} A 0.05 M solution of WCl₆ in toluene (6 W-Cl at 2.28 Å)^{S20} was used as an experimental standard for Ta-Cl scattering pathways (Table S2). Fits with both Ta–O and Ta–N phases and amplitudes were carried out for each sample, and found to be self-consistent. Debye-Waller factors (DWFs) were calibrated using the (catecholato)Ta amide complexes Ta(NMe₂)₃(HNMe₂)(catecholate) and

 $Ta(NMe_2)(HNMe_2)(^{t}Bu_2cat)$ (Table S3) with known crystal structures^{S21} and then assumed to be the same for all the molecular and POP-supported complexes.

The EXAFS coordination parameters were obtained by a simultaneous least-square fit in k-space of the first shell $M-C k^2$ and k-weighted Fourier-transformed data (for samples containing only Ta-C/N/O, $\Delta k = 2.4-9.0 \text{ Å}^{-1}$ and $\Delta R = 1.0-2.2 \text{ Å}$; for samples containing Ta-Cl, $\Delta k = 2.4-11.1 \text{ Å}^{-1}$ and $\Delta R = 0.8-2.5 \text{ Å}$). The fits were equally good with k^1 and k^3 weightings as well as in k-space for the first shell isolated inverse Fourier transform data. The fits and relative errors in coordination fit parameters are given in Tables S3 and S4. The Fourier magnitude and imaginary parts of the Ta L_{III} EXAFS data and fits of the Ta-N and Ta-O and Ta-Cl first shell fits, respectively, are show in Figs. S14, and S18-23. Experimental reproducibility was confirmed across several batches of the POP-supported Ta complexes, as well as with replicates amongst the batches. The average, taken across all the variations, is shown in Table S4. Higher-shell and multiple-scatterer scattering paths consistent with the longer range Ta-C distances seen in the crystal structures are observed for both the metallated POPs as well as the fully soluble tantalum complexes, but have not been quantitatively fit.

S7c. XAFS Tables

Sample	XANES Edge (KeV)	Ox. State	Scatter Pair	Ν	R (Å)	DWF	E ₀ (eV)	Note
	± 0.0004			± 0.10%	± 0.02	± 0.0005	±0.2	
$Ta(NMe_2)_5$	9.8823	Ta ^V	Ta–N	5	2.03	_	_	Ref ^{S17}
Ta(OEt) ₅	9.8831	Ta ^V	Та-О	5	1.95	_	—	Ref ^{,S18}
WCl ₆	10.2055	W^{VI}	W-Cl	6	2.28	_	—	Ref ^{S20}

Table S2. XANES and EXAFS fitting results for the experimental standards at the Ta L_{III} edge.

Sample	XANES Edge (KeV)	Ox. State	Scatter Pair	N	R (Å)	DWF	E ₀ (eV)	Note
	± 0.0004			± 0.10%	± 0.02	± 0.0005	± 0.2	
Me ₂ N,,,,, Me ₂ N,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,	9.8825	Ta ^v	Ta-N/O	5.7	2.01	0.003	-2.3	1,2
° 🚽		Ta ^V	Ta-N/O	6.2	2.01	0.002	1.9	1,3
	9.8825	Ta ^v	Ta-N/O	5.7	2.02	0.003	-1.8	1,2
t t		Ta ^v	Ta-N/O	6.3	2.02	0.002	2.4	1,3
LXX	9.8820	Ta ^v	Ta-N/O	5.1	2.01	0.003	-1.2	2,4
		Ta ^v	Ta-N/O	5.3	2.01	0.002	2.5	3,4
	9.8831	Ta ^v	Ta-N/O	5.6	2.00	0.003	-2.3	2
		Ta ^v	Ta-N/O	5.9	1.99	0.002	1.0	3
	9 8829	Ta ^v	Ta-N/O	3.5	1.94	0.001	0.4	3,5
	2.0022	Ta ^v	Ta-Cl	2.5	2.35	0.001	-0.45	5

Table S3: XANES and EXAFS Fitting Results for molecular model compounds at the Ta L_{III} edge.

(1) EXAFS model compounds used to optimize Debye-Waller factors. Coordination numbers and distances were based on known crystal structure data.^{S21} (2) Fit results using single-shell Ta–N standard. (3) Fit results using single-shell Ta–O standard. (4) Fitted with fixed Debye-Waller factors determined from EXAFS model compounds $Ta(NMe_2)_3(HNMe_2)(catecholate)$ and $Ta(NMe_2)(HNMe_2)(^Bu_2cat)$. (5) Double shell fit: Ta–Cl and Ta–O single shells fitted simultaneously.

Sample	XANES Edge (KeV)	Ox. State	Scatter Pair	N	R (Å)	DWF	E ₀ (eV)	Note
	±0.0004			±0.10%	±0.02	± 0.0005	±0.2	
$(^{t}BuCH_{2})_{3}Ta-A_{2}B_{1}$			•					
Batch 1	9.8822	Ta ^v	Ta-N/O	5.1	1.97	0.003	-2.5	1,3
		Ta ^V	Ta-N/O	4.9	1.96	0.002	0.8	2,3
Batch 2	9.8820	Ta ^V	Ta-N/O	4.8	1.98	0.003	-2.7	1,3
		Ta ^v	Ta-N/O	5.4	1.97	0.002	1.0	2,3
Batch 3	9.8821	Ta ^v	Ta-N/O	4.9	1.98	0.003	-2.6	1,3
		Ta ^v	Ta-N/O	5.1	1.97	0.002	1.3	2,3
Batch 4	9.8826	Ta ^v	Ta-N/O	4.8	1.98	0.003	-2.1	1,3
		Ta ^v	Ta-N/O	5.0	1.98	0.002	1.6	2,3
Batch 5 replicate 1	9.8823	Ta ^v	Ta-N/O	4.5	2.00	0.003	-1.8	1,3
		Ta ^v	Ta-N/O	4.7	1.99	0.002	1.8	2,3
Batch 5 replicate 2	9.8823	Ta ^v	Ta-N/O	4.7	1.97	0.003	-2.5	1,3
		Ta ^v	Ta-N/O	4.9	1.97	0.002	1.6	2,3
Batch 5 replicate 3	9.8820	Ta ^v	Ta-N/O	4.5	2.01	0.003	-0.9	1,3
		Ta ^v	Ta-N/O	4.7	2.00	0.002	2.6	2,3
Batch 6		Ta ^v	Ta-N/O	4.7	2.00	0.005	-0.6	1,3,5
		Ta ^v	Ta-N/O	4.7	2.00	0.003	2.8	2,3,5
			Avg (all)	$4.8 \pm$	1.98 ±			
			Avg (all)	0.2	0.15			
$[(^{t}BuCH_{2})_{3}Ta-\mathbf{A}_{2}B_{1}+H0]$	Cl in Et ₂ O]							
Batch 5 replicate 2	9.8827	Ta ^v	Ta-Cl	2.0	2.35	0.002	-2.2	4
			Та-О	4.0	1.95	0.002	1.9	2,4
Batch 6	9.8828	Ta ^v	Ta-Cl	1.7	2.38	0.001	-0.4	4,6
			Та-О	4.3	1.95	0.001	1.7	4,6
$[(^{t}BuCH_{2})_{3}Ta-A_{2}B_{1}+MeOH]$								
Batch 6	9.8822	Ta ^v	Та-О	4.7	1.97	0.005	-1.5	1,5
			Та-О	4.7	1.96	0.003	1.8	2,5

Table S4: XANES and EXAFS fitting results for POP samples at the Ta L_{III} edge.

(1) Fit results using single-shell Ta–N standard. (2) Fit results using single-shell Ta–O standard. (3) Fitted with fixed Debye-Waller factors determined from EXAFS model compounds $Ta(NMe_2)_3(HNMe_2)(catecholate)$ and $Ta(NMe_2)(HNMe_2)(Bu_2cat)$. (4) Double shell fit: Ta–Cl and Ta–O single shells fitted simultaneously. (5) DWF are higher in these because of decreased signal to noise in the data, and consequently, a shorter Fourier transform range $\Delta k = 2.4$ -7.7 Å⁻¹. (6) This sample was heated to 45 °C under dynamic vacuum



Fig. S15. The Ta L_{III} -edge normalized XANES spectra for Ta(NMe₂)₅ (black solid) and Ta(OEt)₅ (red).



Fig. S16. The Ta L_{III} -edge normalized XANES spectra for WCl₆.



Fig. S17a. The Ta L_{III} -edge, k^2 -weighted Fourier-transformed EXAFS spectra for Ta(NMe₂)₅ (black), Ta(OEt)₅ (red), and WCl₆ (blue). The magnitude components of the spectra are shown together.

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|_X (R)|(Å⁻³)

|χ (R)|(Å⁻³)





Fig. S17b. The Ta L_{III} -edge, k^2 -weighted Fourier-transformed EXAFS spectra for Ta(NMe₂)₅ (black), Ta(OEt)₅ (red), and WCl₆ (blue). The magnitude component (solid line) of each spectrum is shown together with its imaginary component (dashed line).

R (Å)





The Ta L_{III}-edge, normalized XANES spectrum for (^tBuCH₂)₃Ta=CH^tBu.



Fig. S19. The Ta L_{III} -edge, k^2 -weighted Fourier-transformed EXAFS spectrum for $({}^{t}BuCH_2)_3Ta=CH'Bu$. The magnitude component is shown as a solid line and imaginary component is shown as a dashed line.



Fig. S20. The Ta L_{III} -edge normalized XANES (solid lines) and 1st derivative (dashed lines) spectra for (^{*t*}BuCH₂)₃Ta(^{*t*}Bu₂cat) (black), (Et₂O)Cl₃Ta(^{*t*}Bu₂cat) (red), and ([(MeO)₂(μ -OMe)Ta(^{*t*}Bu₂cat)]₂.



Fig. S21. The Ta L_{III} -edge, k²-weighted Fourier-transformed EXAFS spectrum and a first-shell fit using the Ta–N reference for ('BuCH₂)₃Ta('Bu₂cat). Both the magnitude (solid lines) and imaginary (dashed lines) experimental data (black) and theoretical fits (red) are shown.



Fig. S22. The Ta L_{III} -edge, k²-weighted Fourier-transformed EXAFS spectrum and a first-shell fit using the Ta—N reference for the [('BuCH₂)₃Ta('Bu₂cat) + HCl in Et₂O] reaction. Both the magnitude (solid lines) and imaginary (dashed lines) experimental data (black) and theoretical fits (red) are shown.



Fig. S23. The Ta L_{III} -edge, k²-weighted Fourier-transformed EXAFS spectrum and a first-shell fit using the Ta–N reference for [(¹BuCH₂)₃Ta(¹Bu₂cat) + MeOH]. Both the magnitude (solid lines) and imaginary (dashed lines) experimental data (black) and theoretical fits (red) are shown.



Fig. S24. The Ta L_{III} -edge, k^2 -weighted Fourier-transformed EXAFS spectrum and a first-shell fit using the Ta—O reference for (^tBuCH₂)₃Ta-A₂B₁. Both the magnitude (solid lines) and imaginary (dashed lines) experimental data (black) and theoretical fits (red) are shown.



Fig. S25. The Ta L_{III} -edge, k^2 -weighted Fourier-transformed EXAFS spectrum and a first-shell fit with Ta-Cl and Ta-O references for the product of the $[({}^{t}BuCH_{2})_{3}Ta-A_{2}B_{1} + HCl in Et_{2}O]$ reaction. Both the magnitude (solid lines) and imaginary (dashed lines) experimental data (black) and theoretical fits (red) are shown.



Fig. S26. The Ta L_{III} -edge, k^2 -weighted Fourier-transformed EXAFS spectrum and a first-shell fit with Ta–O references for the product of the $[(^{t}BuCH_{2})_{3}Ta-A_{2}B_{1} + MeOH]$ reaction. Both the magnitude (solid lines) and imaginary (dashed lines) experimental data (black) and theoretical fits (red) are shown.

S7e. DFT Table

Table S5.	Atomic Cartesian coordinates in Å for energy-minimized structure (DFT: B3LYP 6-31G*) of
	$Ta(OEt)_5(OEt_2)$. ^{S19}	

Atom	x/Å	y/Å	z/Å
Та	0.073818	0.556072	0.075684
0	-0.58728	0.670116	-1.75366
0	-1.76214	0.837628	0.65129
0	0.717364	2.343013	0.184279
0	1.666562	-0.29385	-0.68122
0	0.675914	0.154015	1.875252
0	-0.69922	-1.73975	0.094289
С	-1.52109	-2.19072	1.194084
Н	-0.89271	-2.72387	1.916176
Н	-1.8672	-1.26986	1.661304
С	-0.03454	-2.77108	-0.66936
Н	0.490501	-2.22811	-1.45351
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С	-2.70464	-3.04113	0.748665
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Н	-3.35441	-3.22797	1.611606

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С	0.954977	-3.59324	0.146254
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С	3.896844	-1.0772	-1.19195
Н	4.93938	-1.06468	-0.85076
Н	3.858248	-0.64985	-2.20012
Н	3.567021	-2.12059	-1.25188

S31

S8. Catalytic hydrogenation studies with (^tBuCH₂)₃Ta-A₂B₁ and (^tBuCH₂)₃Ta(^tBu₂cat)

Hydrogenation experiments were carried out in a home-built pressurized batch reactor with a PEEK or Meldin sample holder.^{S14} The reactor was modified from the literature to connect to a pressurizable reactor head made from standard SwagelokTM components. The reactor head contains a gas inlet valve, a pressure readout, and a pressure relief valve (225 psi). The gas inlet valve is a two-way and three-way valve in series to allow for complete purging of the gas lines without exposure of interior of the loaded cell to air. As a safety precaution, all hydrogenation addition and heating setups were conducted in a fume hood behind a blast shield. Prior to use, the burst pressure of the PEEK or Medlin components were calculated to ensure an appropriate wall thickness was chosen based on the operating pressure. The entire setup was also pressure and leak tested with nitrogen.

In a typical experiment, catalyst (0.5 wt% Ta) was added to a sample holder equipped with a stir bar. POP catalysts were added directly to the sample holder followed by the addition of dodecane. Molecular catalysts were prepared as 0.03 M stock solutions in dodecane and an aliquot was added to the sample holder. Cyclohexene (0.6 M solution in dodecane) was then added to either setup (2.0 mL total reaction volume, 0.3 M cyclohexene concentration overall). The pressure reactor was assembled, removed from the glove box, and was purged three times with 200 psi of H_2 to completely remove any trace of air from the hydrogen addition lines and the nitrogen from the reactor headspace. The setup was pressurized one more time to 200 psi, sealed, and transferred to a preheated oil bath at 60 °C. After being heated for the appropriate amount of time, the setup was removed from the oil bath and left to cool to rt before being depressurized. The entire reaction mixture was then passed through a filter pipet to remove any insoluble species and was immediately analyzed by GC-FID. Gas chromatography was carried out using the following method: a 1 µL split injection with a split ratio of 200 run under a constant gas flow of 1 mL/min. The oven temperature profile is as follows: initial temperature = 33 °C, hold for 2:20 minutes, ramp at 7.5 $^{\circ}$ C/min, final temperature = 150 $^{\circ}$ C, total run time = 17.80 min. Under these conditions cyclohexane has a retention time of 4.43 min, cyclohexene has a retention time of 4.70 min, and dodecane has a retention time of 16.06 min based on the injection of pure compounds. Conversions were determined by taking the area of each peak and dividing by the overall summation. The data points at 15, 30, 60, and 120 min were collected from a series of samples that was prepared at the same time and run consecutively. The data points at 7.5 min and 20 h data points were collected from samples that were prepared at the same time and ran separately.

 $({}^{t}BuCH_{2})_{3}Ta-A_{2}B_{1}$ hydrogenation setup. $({}^{t}BuCH_{2})_{3}Ta-A_{2}B_{1}$ (2.5 mg, 0.5 wt% Ta) was weighed out into the sample holder. A stir bar was added, followed by the addition of dodecane (1.0 mL) and 0.6 M cyclohexene in dodecane (1.0 mL).

 $({}^{t}BuCH_{2})_{3}Ta({}^{t}Bu_{2}cat)$ hydrogenation setup. For accuracy, stock solutions of $({}^{t}BuCH_{2})_{3}Ta({}^{t}Bu_{2}cat)$ were prepared from recrystallized $({}^{t}BuCH_{2})_{3}Ta({}^{t}Bu_{2}cat)$ (see Section S4) and used immediately. A typical 0.030 M stock solution used in these experiments was prepared by dissolving $({}^{t}BuCH_{2})_{3}Ta({}^{t}Bu_{2}cat)$ (37 mg, 0.060 mmol) in dodecane (2.0 mL). The reactions containing 0.5 mol% of this precatalyst were then prepared by combining the stock solution (0.1 mL), dodecane (0.9 mL), and 0.60 M cyclohexene in dodecane (1.0 mL) to the sample holders (0.3 M in cyclohexene, 0.0015 M in $({}^{t}BuCH_{2})_{3}Ta({}^{t}Bu_{2}cat)$).

(^{*t*}BuCH₂)₃Ta=CH^{*t*}Bu hydrogenation setup. Since (^{*t*}BuCH₂)₃Ta-A₂B₁ may have about 10 mol% unreacted Ta alkylidene, additional cyclohexene hydrogenation experiments were conducted to determine whether this trace species could be kinetically competent to explain our observed hydrogenation reactivity. A 0.003 M stock solution of (^{*t*}BuCH₂)₃Ta=CH^{*t*}Bu was prepared by dissolving (^{*t*}BuCH₂)₃Ta=CH^{*t*}Bu (2.8 mg, 0.0060 mmol) in dodecane (2.0 mL). This stock solution (0.1 mL) was added to the sample holder along with dodecane (0.9 mL), and 0.60 M cyclohexene in dodecane (1.0 mL). After 2 h at 60 °C and 200 psi H₂, less than 4% cyclohexane was present. This indicates that the amount of unreacted ^{*t*}BuCH₂)₃Ta=CH^{*t*}Bu present in (^{*t*}BuCH₂)₃Ta-A₂B₁ is not kinetically competent to be our primary active catalyst.

 A_2B_1 and ${}^{t}Bu_2cat$ hydrogenation setups. To rule out catalysis by trace metals and Brønsted-acid, cyclohexene hydrogenation was attempted with A_2B_1 (triple-washed, see Section S2) and recrystallized ${}^{t}Bu_2cat$ at 0.5 and 5 mol% catechol. A_2B_1 was set up under identical conditions as $({}^{t}BuCH_2)_3Ta-A_2B_1$ with either 0.5 mol% (1.2 mg) or 5 mol% (12 mg) catechol. A 0.03 M stock solution of ${}^{t}Bu_2cat$ (0.0133 g) in dodecane (2.0 mL) was prepared and diluted accordingly. For a 0.5 mol% reaction, the ${}^{t}Bu_2cat$ stock solution (0.1 mL) were added to the sample holder along with dodecane (0.9 mL), and 0.60 M cyclohexene in dodecane (1.0 mL). For a 5 mol% reaction, 1.0 mL of each stock solution were used. Less than 1% cyclohexane was detected by GC for both A_2B_1 and ${}^{t}Bu_2cat$ after 20 h, suggesting that no Brønsted-acid catalysis is occurring.

 $({}^{t}BuCH_{2})_{3}Ta-A_{2}B_{1}$ hydrogenation setup with toluene. $({}^{t}BuCH_{2})_{3}Ta-A_{2}B_{1}$ was also tested as a catalyst for the hydrogenation of toluene (0.60 M in dodecane) under similar reaction conditions (0.5 mol% catalyst, 60 °C, 200 psi of H₂). Approximately ~12% of toluene was converted to methylcyclohexane (average based on two trials).

Catalyst	7.5 min	15 min	30 min	60 min	120 min	$1200 \min^a$	1200 min ^b
	< 1% ^c	< 1% ^c	< 1% ^c	< 1% ^c	< 1% ^c	$8.3 \pm 3.4\%^d$	~99 % ^d
	$10.0 \pm 2.5\%$ ^c	23.6 ± 2.6% ^d	48.5 ± 7.7% ^d	79.7± 10.3% ^d	91.5 ± 12.1% ^d	~99% ^d	~99% ^d
H H H H H H H H H H H H H H H H H H H	N/A	N/A	N/A	N/A	N/A	< 0.1% ^e	<0.1% ^e
С С С С С С С С С С С С С С С С С С С	N/A	N/A	N/A	N/A	N/A	< 0.1% ^c	<0.1% ^c

Table S6. Percent (%) conversion of cyclohexene to cyclohexane at 60 $^{\circ}$ C at 200 psi H₂.





Fig. S27. GC trace of cyclohexane (black, bottom), cyclohexene (red, middle), and the 30 min. reaction solution with $({}^{BuCH_2})_{3}Ta-A_2B_1$ as the catalyst (blue, top). Cyclohexene and cyclohexane are the only products observed with $({}^{BuCH_2})_{3}Ta-A_2B_1$ as the catalyst.

Author contribution audit. MJAJ and STN conceived the initial experiments. KKT, EMB, and NAS carried out the synthetic and characterization experiments. MHW synthesized the initial sample of POP A_2B_1 . KKT and MHW carried out the gas sorption and TGA experiments. EAM conceived and designed the catalysis experiments in the pressurized batch reactor. KKT and NAS performed the catalysis experiments. EAM led the EXAFS effort and carried out the data analysis. TK and JFG carried out the SS NMR experiments. MP supervised the part of the project carried out at Ames lab and Iowa State University. OKF, JTH, and STN supervised the part of project from Northwestern. EAM, MJAJ, and STN supervised the part of project from ANL. KKT wrote the initial drafts of the paper and the ESI with inputs from the coauthors. KKT and STN finalized the manuscript.

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- S19. An optimized structure was computed for $Ta(OEt)_5(OEt_2)$ without any symmetry constraints at the level of DFT using the B3LYP exchange-and-correlation functional and the 6-31G* basis set using the Spartan '08 code (Wavefunction, Inc., Irvine, CA). The electronic structure of Ta was treated using a pseudopotential as described in the Spartan '08 user documentation. The final structure displayed no imaginary frequencies in its vibrational spectrum, confirming that it is a local minimum on the potential energy surface. Cartesian coordinates (in Å) for the positions of all atoms in the optimized structure are collected in Table S5.
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