Preparation of Cyclohexene Isotopologues
and Stereoisotopomers from Benzene

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A. Synthetic methods. NMR spectra were obtained on 500, 600 or 800 MHz spectrometers. Chemical shifts are referenced to tertramethylsilane (TMS) utilizing residual $^1$H signals of the deuterated solvents as internal standards. Chemical shifts are reported in ppm and coupling constants ($J$) are reported in hertz (Hz). Infrared Spectra (IR) were recorded on a spectrometer as a glaze on a Horizontal Attenuated Total Reflectance (HATR) accessory, with peaks reported in $\text{cm}^{-1}$. Electrochemical experiments were performed under a nitrogen atmosphere. Most cyclic voltammetric data were recorded at ambient temperature at 100 mV/s, unless otherwise noted, with a standard three electrode cell from +1.8 V to -1.8 V with a platinum working electrode, acetonitrile (MeCN) solvent, and tetrabutylammonium (TBAH) electrolyte (~1.0 M). All potentials are reported versus the normal hydrogen electrode (NHE) using cobaltocenium hexafluorophosphate ($E_{1/2} = -0.78 \text{ V}, -1.75 \text{ V}$) or ferrocene ($E_{1/2} = 0.55 \text{ V}$) as an internal standard. Peak separation of all reversible couples was less than 100 mV. All synthetic reactions were performed in a glovebox under a dry nitrogen atmosphere unless otherwise noted. All solvents were purged with nitrogen prior to use. Deuterated solvents were used as received from Cambridge Isotopes. When possible, pyrazole (Pz) protons of the (trispyrazolyl) borate (Tp) ligand were uniquely assigned (e.g., “Pz3B”) using two-dimensional NMR data (see Fig. S1). If unambiguous assignments were not possible, Tp protons were labeled as “Pz3/5 or Pz4”. All $J$ values for Pz protons are 2 (±0.4) Hz.
B. Synthesis of compounds

Synthesis of WTp(NO)(PMe$_3$)(η$^2$-d$_6$-benzene) (17)

In an oven-dried 50 mL round bottom flask 25.0 g (297 mmol) of freshly degassed benzene-$d_6$ was added with a Teflon-coated magnetic stir bar. This solution was stirred and 1 (0.404 g, 1.44 mmol) was added resulting in a homogeneous yellow reaction mixture which was allowed to stir for 18 h. The reaction mixture was then added to 100 mL of pentane and the solvent volume was reduced in vacuo until half of the original solvent volume had been evaporated. Upon the evaporation of solvent, a golden-yellow colored solid precipitated out of solution. This yellow solid was collected on a fine 15 mL fitted disc and washed with 2 x 15 mL of pentane to yield a yellow solid that was allowed to desiccate for six h. A yellow solid was recovered (0.241 g, 59%). $^1$H NMR features matched those reported previously for 1 with the absence of protons on the benzene ring.

Synthesis of WTp(NO)(PMe$_3$)(η$^2$-2,3-benzenium) (2) and WTp(NO)(PMe$_3$)(η$^2$-1,2-benzenium) (3)

A 4-dram vial was charged with 5 mL of DCM and chilled to -30°C for 15 min. 1 (1.52 g, 2.61 mmol) was then added, resulting in a heterogeneous yellow reaction mixture. Diphenylammonium triflate (DPhAT) (0.909 g, 2.84 mmol) was added to the reaction mixture at -30°C resulting in the formation of a homogenous red solution. This solution was allowed to stand at -30°C for 20 min. This reaction solution was then added to stirring Et$_2$O that had been chilled to -30°C (60 mL) to yield a dull yellow precipitate. The yellow solid was collected on a 30 mL fine porosity fritted disc and washed with chilled Et$_2$O (2 x 20 mL). The isolated yellow solid was then desiccated for 2 h yielding 2 and 3 (1.63 g, 2.24 mmol, 86% yield) in a 10:1 ratio.

CV (MeCN at -6 °C) $E_{p,a} = +0.70$ V (NHE). IR: $\nu$(BH) = 2520 cm$^{-1}$, $\nu$(NO) = 1637 cm$^{-1}$. Complex 2 (major): $^{31}$P NMR (CD$_3$CN, δ): -7.44 ($J_{WP} = 274$). $^1$H NMR (CD$_3$CN, δ, 0°C): 8.33 (1H, d, Pz3B/5B), 8.02 (1H, d, Pz5C), 7.97 (1H, d, Pz3C), 7.94 (1H, d, Pz3B/5B), 7.80 (1H, d, Pz5A), 6.93 (1H, broad singlet, H1), 6.54 (1H, t, Pz4C), 6.49 (1H, t, Pz4B), 6.31 (1H, t, Pz4A) 6.17 (1H, m, H4), 5.04 (1H, m, H5), 4.91 (1H, t, $J = 7.2$, H2), 4.24 (1H, m, H3), 4.16 (1H,
d, $J = 28.3$, H6-\textit{exo}), 4.00 (1H, d, $J = 28.3$, H6-\textit{endo}), 1.18 ((H, d, $J_{PH} = 9.9$, PMe$_3$). $^{13}$C NMR (CD$_3$CN, $\delta$, 0°C): 147.9 (Pz3A), 146.7 (Pz5C), 145.7 (C1), 143.0 (Pz3/5), 139.4 (Pz3/5), 139.3 (2C, Pz3/5), 126.1 (C4), 119.5 (C5), 109.2 (Pz4B), 108.7 (Pz4C), 107.8 (Pz4A), 95.1 (C2), 64.5 (C3), 30.7 (C6), 13.1 (PMe$_3$, d, $J_{PC} = 34.2$). Complex 3 (minor): $^1$H NMR (CD$_3$CN, $\delta$, 0°C): 8.31 (1H, d, Pz3/5), 8.11 (1H, d, Pz3/5), 8.01 (1H, d, Pz3/5), 7.92 (1H, d, Pz3C), 7.81 (1H, d, Pz3/5), 6.55 (1H, buried, H4), 6.52 (1H, t, Pz4), 6.49 (1H, buried, Pz4), 6.34 (2H, overlapping, Pz4 & H3), 5.89 (1H, m, H5), 4.71 (1H, t, $J = 7.5$, H2), 4.65 (1H, m, H1), 4.34 (1H, d, $J = 25.8$, H6-\textit{exo}), 3.36 (d, $J = 25.8$, 1H, H6-\textit{endo}), 1.11 (9H, buried, PMe$_3$). Attempts at elemental analysis were not successful due to the unstable nature of the complex at ambient temperatures.

**Synthesis of WTp(NO)(PMe$_3$)(\eta$^2$-1,3-cyclohexadiene) (4)**

To a 4-dram vial was added 2 mL of MeCN and 1 (0.200 g, 0.344 mmol) to generate a heterogeneous yellow reaction mixture. This solution was then cooled to -30°C. DPhAT was added to this reaction mixture and the solution was allowed to stand at -30°C. Over 15 min a homogeneous red reaction mixture develops indicating the formation of 2 in solution. Separately a solution of 2 mL of MeOH was chilled to -30°C and to this solution NaBH$_4$ (0.030g, 0.79 mmol) was added. The NaBH$_4$/MeOH solution was then added to a dewar of liquid nitrogen and the solution was frozen. The homogenous red reaction mixture of 2 was then added to this frozen solution of MeOH and NaBH$_4$ and the reaction mixture was allowed to thaw while sitting at -30°C. After one hour the reaction mixture had turned to a homogenous orange color. A 60 mL coarse fritted porosity disc was filled with ~ 5 cm of neutral alumina and set in Et$_2$O. The homogeneous orange solution was then filtered through the neutral alumina column and a light yellow band was eluted with 100 mL of Et$_2$O. The solvent was removed in vacuo until a pale yellow solid remained. This was re-dissolved in 2 mL of DCM and added to a 4-dram vial that contained 15 mL of sitting hexanes. This homogeneous yellow solution was subsequently allowed to cool at -30°C for 16 h. After being allowed to cool a light green crystalline product had developed on the sides of the vial. The organic layer was decanted and the product was then dried with N$_2$ (g) and allowed to desiccate for 8 h before a mass was taken of the resultant light yellow crystalline product (0.162 g, 81%). Characterization has been reported previously.$^1$
Synthesis of WTp(NO)(PMe₃)(η²-1,3-cyclohexadiene) (5)

A mixture of complexes 4 and 5 (0.298 g, 0.511 mmol) were dissolved in 2 mL of DME and allowed to cool to -30 °C over a period of 15 min. To this homogeneous light yellow solution was added HOTf (0.198 g, 1.311 mmol) and the reaction mixture turned to a homogeneous orange color. This reaction mixture was allowed to sit at -30 °C for 5 min and then subsequently added to 15 mL of standing ether at room temperature. A dark brown solid congregated on the bottom of the flask, and the organic layer was decanted before the solid was re-dissolved in 2 mL of DCM and again precipitated into 50 mL of stirring ether to generate a light yellow heterogeneous mixture. This solid was then dried under dynamic vacuum in a desiccator for 2 h and its identity as 6 was confirmed by NMR. This solid was then dissolved in DCM (2 mL) and allowed to sit at -30 °C. In a separate 4 dram vial was added DBU (0.582 g, 3.82 mmol) along with DCM (1 mL) and this solution was also cooled to -30 °C over a course of 15 min. The DBU/DCM solution was then added to the DCM solution of 6 and upon addition a homogeneous pink reaction mixture develops. This reaction mixture was allowed to stand for 5 min at room temperature and then loaded onto a coarse 60 mL fritted disc that had been filled with ~ 3 cm of basic alumina and set in ether. The pink band was eluted with 60 mL of ether and the solvent was then removed in vacuo. A light yellow film coats the bottom of the filter flask, this was re-dissolved in DCM (2 mL) and added to standing pentane (15 mL) and was allowed to sit at -30 °C for 16 hr. The next day a yellow crystalline material had formed at the sides of the vial. The organic layer was then decanted and the vial was dried under dynamic vacuum for 6 h to yield a fine yellow powder (0.102 g, 34%). Characterization has been reported previously.¹

Synthesis of WTp(NO)(PMe₃)(η²-cyclohexene) (7)

A 4 dram vial was charged with 1 mL of DME, complex 1 (0.200 g, 0.344 mmol) and cyclohexene (2.00 g, 24.3 mmol) and this heterogeneous yellow reaction mixture was allowed to stir. After 27 h the now homogenous purple reaction mixture was added to a 250 mL filter flask and the solvent was removed in vacuo. The resulting pink solid was re-dissolved in 2 mL of DCM and slowly added to 30 mL of stirring pentanes that had been chilled to -30 °C. Upon addition a light pink solid precipitated out of solution. This light pink solid was collected on a 30 mL fine porosity fritted disc and subsequently washed with 3 x 5 mL of chilled pentane. The collected product was then desiccated for 2 h to yield a fine light pink powder (0.083 g, 41%).
Alternative Synthesis of WTP(NO)(PMe₃)(η²-cyclohexene) (7)

To a 4-dram vial 6 (0.107 g, 0.136 mmol) was dissolved in 1 mL of MeOH and chilled to -30°C. To this was added NaBH₄ that had been dissolved and chilled in a -30°C MeOH solution. The solution of 6 was then added to the NaBH₄/MeOH solution and the resulting reaction mixture was allowed to sit at -30°C for 16 h. The reaction mixture was then eluted through a silica column on a fine 15 mL fritted disc and a light yellow band was eluted with ether. The solvent was then removed in vacuo and the resulting reaction mixture was allowed to sit at 25°C for 2 h during which a light yellow solid had precipitated from solution. This solid was then isolated on a fine 15 mL fritted disc, washed with 2x5 mL of hexanes to yield an off-white solid (0.058 g, 67%).

CV (MeCN) $E_{p,a} = +0.28$ V (NHE). IR: $ν(BH) = 2482$ cm⁻¹, $ν(NO) = 1554$ cm⁻¹. ¹H-NMR (CDCl₃, δ, 25 °C): 8.28 (1H, d, Pz3A), 8.08 (1H, d, Pz3B), 7.69 (1H, d, Pz5B), 7.64 (1H, d, Pz5C), 7.60 (1H, d, Pz5A), 7.24 (1H, d, Pz3C), 6.28 (1H, t, PzB), 6.20 (1H, t, Pz4A), 6.13 (1H, t, Pz4C), 3.00 (1H, m, H6exo) 2.92 (2H, overlap, m, H4-endo/exo), 2.71 (1H, m, H1), 2.64 (1H, m, H6-endo), 1.75 (2H, overlap, m, H6-endo/exo), 1.46 (2H, overlap, m, H5-endo/exo), 1.38 (1H, m, H2), 1.21 (9H, d, $J_{PH} = 8.1$, PMe₃). ¹³C-NMR (CDCl₃, δ, 25 °C). 143.4 (Pz3B), 142.9 (Pz3A), 140.1 (Pz3C), 136.2 (Pz5), 135.6 (Pz5). ¹³C-NMR (MeCN, δ, 25 °C): -9.1 ($J_{WP} = 291$, PMe₃). Anal. Calcd for $C_{20}H_{29}BN₇OPW$: C, 36.79; H, 4.98; N, 16.76. Found: C, 37.35; H, 4.58; N, 16.69.

Characterization in MeCN-$d₃$

¹H-NMR (MeCN-$d₃$, δ, 25 °C): 8.21 (1H, d, Pz3A), 8.03 (1H, d, Pz3B), 7.85 (1H, d, Pz5B), 7.78 (1H, d, Pz5C), 7.75 (1H, d, Pz5A), 7.35 (1H, d, Pz3C), 6.36 (1H, t, Pz4B), 6.27 (1H, t, Pz4A), 6.21 (1H, t, Pz4C), 3.04 (1H, m, H6exo) 2.93 (1H, m, H3-endo), 2.72 (1H, m, H3-endo), 2.63 (1H, m, H6-endo), 1.69 (1H, m, H4-endo), 1.66 (1H, m, H5-endo). ¹³C-NMR (MeCN-$d₃$, δ, 25 °C). 144.2 (Pz3B), 143.3 (Pz3A), 141.7 (Pz3C), 137.6 (Pz5), 136.9 (2C, overlapping Pz5), 107.4 (Pz4B), 106.9 (Pz4A), 106.6 (Pz4C), 53.5 (2C, overlapping C1 and C2), 30.7 (C6), 30.2 (C3), 25.6 (2C, overlapping C4/C5), 25.4 (2C, overlapping C4/C5). 13.8 (PMe₃, d, $J_{PC} = 27.5$).

Synthesis of WTP(NO)(PMe₃)(η²-1,4-cyclohexadiene) (8)

A 4-dram vial was charged with 1 mL of DME, complex 1 (0.301 g, 0.518 mmol) and 1,4-cyclohexadiene (2.00g, 24.9 mmol) and this heterogeneous yellow reaction mixture was allowed to stir. After 50 h the homogeneous purple reaction mixture was slowly added to 30 mL of stirring pentanes that had been chilled to -30°C. Upon addition a light pink solid precipitated out of solution. This light pink solid was collected on a 30 mL fine porosity fritted disc and subsequently
washed with 3 x 5 mL of chilled pentane. The collected product was then desiccated for 2 h to yield a fine pink powder (0.191 g, 63%).

CV (MeCN) $E_{p,a} = +0.27$ V (NHE). IR: ν(BH) = 2481 cm$^{-1}$, ν(NO) = 1553 cm$^{-1}$. $^1$H-NMR (acetone-$d_6$, δ, 25 ºC): 8.25 (1H, d, Pz3A), 8.08 (1H, d, Pz3B), 7.92 (1H, d, Pz5B), 7.88 (1H, d, Pz5C), 7.80 (1H, d, Pz5A), 7.49 (1H, d, Pz3C), 6.38 (1H, t, Pz4B), 6.28 (1H, t, Pz4A), 6.27 (1H, t, Pz4C), 5.83 (1H, m, H4) 5.78 (1H, m, H5), 3.55 (1H, m, H6-exo), 3.45 (2H, overlap, H3-exo and H3-endo), 3.10 (1H, d, $J=17.8$ Hz, H6-endo), 2.83 (1H, m, H1), 1.34 (1H, m, H2), 1.21 (9H, d, $J_{PH}=8.2$, PMe3).

$^{13}$C-NMR (acetone-$d_6$, δ, 25 ºC). 144.0 (Pz3/5), 142.8 (Pz3/5), 141.5 (Pz3/5), 137.3 (Pz3/5), 136.7 (Pz3/5), 136.6 (Pz3/5), 127.7 (C4/5), 127.6 (C4/5), 107.1 (Pz4), 106.7 (Pz4), 106.2 (Pz4), 51.7 (C1, d, $J_{PC}=11.9$), 51.4 (C2), 30.1 (C3, buried under acetone, connected by HSQC), 13.6 (PMe3, d, $J_{PC}=27.4$).

$^{31}$P-NMR (CDCl3, δ, 25 ºC): -8.9 (J$_{WP}$ = 292, PMe3). Anal. Calcd for C$_{18}$H$_{27}$BN$_7$OPW: C, 37.08; H, 4.67; N, 16.82. Found: C, 37.35; H, 4.58; N, 16.69.

Synthesis of WTp(NOMe)(PMe3)(η²-cyclohexene)(OTf-) (9)

A 4-dram vial was charged with MeCN followed by 7 (0.203 g, 0.35 mmol). This heterogeneous yellow reaction mixture was cooled to -30°C. After 20 min methyl triflate (0.252 g, 1.54 mmol) that had been cooled to -30°C was added and the reaction mixture was allowed to warm to room temperature over a period of 5 min. During this time the reaction mixture changed to a homogeneous green solution. After the reaction mixture turned to the homogeneous solution, 12 mL of Et$_2$O were added and the reaction mixture was allowed to sit at -30°C for 30 minutes. The organic layer was decanted to reveal a crystalline yellow material sticking to the bottom of the vial. This was then washed with 2 x 5 mL of Et$_2$O and then dried under an N$_2$ (g) stream and subsequently desiccated over 4 h. A yellow material was collected. (0.116 g, 45%).

CV (MeCN) $E_{p,a} = +1.2$, $E_{p,c} = -1.6$ V (NHE). IR: ν(BH) = 2511 cm$^{-1}$, ν(NO) = NA. $^1$H-NMR (MeCN-$d_3$, δ, 25 ºC): 8.51 (1H, d, Pz3A), 8.11 (1H, d, Pz3B), 8.02 (1H, d, Pz5B), 7.93 (2H, d, overlapping Pz5B/C), 7.47 (1H, d, Pz3C), 6.55 (1H, t, Pz4B), 6.48 (1H, t, Pz4A), 6.33 (1H, t, Pz4B), 4.03 (3H, s, NOMe), 3.97 (1H, m, H1), 3.57 (1H, m, H6-exo), 3.39 (1H, m, H3-exo), 3.14 (1H, m, H3-endo), 2.88 (1H, m, H6-endo), 2.34 (1H, m, H2), 1.65 (1H, m, H4-exo), 1.60 (1H, m, H5-exo), 1.51 (1H, m, H5-endo), 1.48 (1H, m, H4-exo), 1.30 (9H, d, $J_{PH}=9.4$, PMe3).

$^{13}$C-NMR (MeCN-$d_3$, δ, 25 ºC). 145.6 (Pz3B), 144.8 (Pz3A), 142.8 (Pz3C), 139.7 (Pz5A/C), 138.8 (Pz5A/C), 138.5 (Pz5B), 108.9 (Pz4B), 108.3 (Pz4C), 107.9 (Pz4A), 66.5 (NOMe), 64.5 (C1, $J_{PC}=8.2$), 63.2 (C2), 31.8 (C3), 31.4 (C6), 24.6 (C4), 23.9 (C5), 13.9 (PMe3, d, $J_{PC}=31.5$). $^{31}$P-NMR (MeCN, δ, 25 ºC): -10.76 ($J_{WP} = 268$, PMe3). Anal. Calcd for C$_{20}$H$_{32}$BN$_7$O$_4$F$_3$PSW: C, 32.06; H, 4.31; N, 13.09. Found: C, 32.00; H, 4.37; N, 12.92. ESI-MS : obsd (%), calcd (%): 598.1984 (83.66)
Synthesis of Diphenylammonium-\(d_2\) Triflate (DPhAT- \(d_2\))

Generation of an acidic deuterium source relied on stirring diphenyl ammonium triflate (DPhAT) (2.00 g, 6.25 mmol) in an excess of MeOD (50.0 g, 152 mmol). The mixture was allowed to stir for 16 h and the solvent was removed in vacuo to yield \(d_2\)-DPhAT. Typical yields 90%.

Representative Synthesis for the Generation of a Tungsten-Cyclohexene Isotopologue Complex

Synthesis of 12

Prepared a solution of 1 (0.510 g, 0.878 mmol) in 2 mL of MeOD and 1 mL of MeCN-\(d_3\) in a 4-dram vial and chilled the reaction to -30°C. Separately chilled a solution of HOTF (0.151 g, 1.00 mmol) in MeOD (5.01 g, 151 mmol) in a 4-dram vial as an acidic deuterium source and separately chilled to -30°C over the course of 30 minutes. In a separate, oven-dried test tube chilled in MeOD (3 mL) to -60°C in a chilled toluene bath. To this test tube added NaBD\(_4\) (0.205 g, 4.90 mmol) and let this heterogeneous white reaction mixture stir over the course of 15 min. While this was stirring added the acidic solution of MeOH to the homogeneous yellow solution of 1. Upon addition the reaction mixture turns to a homogeneous red color, indicative of the formation of 2 in solution. The solution of 2 was then allowed to sit for 15 min at -60°C during which time it retained its red, homogeneous composition. After 15 min this reaction mixture was then added dropwise to the stirring test tube with NaBD\(_4\) and MeOD, upon whose addition vigorously bubbling started to commence (CAUTION! Evolution of H\(_2\)(g)). After all of 2 had been added to the test tube with the solution of NaBD\(_4\) and MeOD, the reaction mixture was allowed to stir for 1.5 h before it was determined to be completed by \(^{31}\)P NMR. The reaction mixture was then removed from the -60°C bath and the cap was loosened and the reaction mixture was allowed to warm to room temperature over the course of 15 min. During this time the reaction mixture turns from a light yellow to a light lime green color and vigorous bubbling starts to occur. After the bubbling has been judged to stop, the reaction mixture was eluted through a coarse 60 mL fritted disc filled with ~3 cm of basic alumina that had been set in diethyl ether. A lime green band was then eluted with ether (100 mL) and the solvent was then removed in vacuo. Once a lime green solid film coats the bottom of the
filter flask, the product was re-dissolved in a minimal amount of DCM (~ 3 mL) and added to 15 mL of standing hexanes in a 4-dram vial. This was then allowed to sit at -30°C over the course of 16 h, during which time a fine, lime green crystalline product has developed on the sides of the vial. The organic layer was then decanted and the product was dried with a N<sub>2</sub>(g) stream and allowed to desiccate for six hours before a mass was collected of the lime green crystalline solid (0.365 g, 71%).

**Synthesis of 13**

\[
\begin{array}{c}
\text{PMe}_3 \\
\text{Tp} \quad \text{W} \quad \text{NO} \quad 4 \quad 5 \\
2 \quad 1 \quad 6 \\
\end{array}
\]

**12** (0.365 g, 0.624 mmol) was dissolved in DME (3 mL) and cooled to -30 °C to generate a homogeneous yellow mixture in a 4-dram vial. Separately **HOTf** (0.215 g, 1.42 mmol) was dissolved in 2 mL of DME and also allowed to cool to -30°C over a course of 15 min in a separate 4-dram vial. The acidic DME solution was then added dropwise to the standing solution of **3**. This solution was allowed to stand at room temperature for 1 min and then was added dropwise to a solution of stirring ether (250 mL). Upon addition a fine, light yellow solid precipitated from solution. The solution was allowed to triturate for 10 min before the reaction mixture was filtered through a fine 15 mL porosity frit to yield a fine, yellow powder. This solid was then washed with ether (3 x 10 mL) and allowed to desiccate for six hours under dynamic vacuum before a mass was taken (0.365 g, 79%).

**Synthesis of 14**

\[
\begin{array}{c}
\text{PMe}_3 \\
\text{Tp} \quad \text{W} \quad \text{NO} \quad 4 \quad 5 \\
2 \quad 1 \quad 3 \\
\end{array}
\]

A 4-dram vial was charged with **13** (0.114 g, 0.155 mmol) and dissolved in MeOH (3 mL) to generate a homogeneous orange solution. This solution was chilled to -30°C over a course of 15 min and to this solution was added NaBH<sub>4</sub> (0.040 g, 1.06 mmol). Upon addition to the solution some bubbling occurs. This solution was allowed to stand at -30°C for one hour and turns from a homogeneous orange to a homogeneous yellow color. The solution was then allowed to stand at room temperature for 10 min before being diluted with ether (10 mL). Separately a 30 mL medium porosity frit was filled with ~ 3 cm of silica and set in ether. The reaction mixture was then loaded onto this silica column and was filtered through by elution with ~ 100 mL of ether total to elute a light yellow band. The solvent was then removed in vacuo and the product was re-dissolved in DCM (2 mL) and added to a 4-dram vial of standing pentane (15 mL). This solution was allowed to stand at -30°C for 16 h before the solvent was again stripped to dryness to yield a fine off-white solid (0.061 g, 65%).
Synthesis and characterization of 47

To a 4-dram vial were added WTp(NO)(PMe₃)(η²-1-(trifluoromethyl)cyclohexa-1,3-diene)² (50 mg, 0.077 mmol) followed by acetone (1.3 mL, -30°C), resulting in a heterogeneous mixture. A 1M solution of HOTf in acetonitrile (0.1 mL, 0.1 mmol, -30°C) was then added, resulting in a homogeneous yellow solution, which was allowed to stir for 19 h at room temperature. This orange solution was then cooled to -30°C for 30 min. In a separate 4-dram vial, NaBH₄ (10 mg, 0.26 mmol) and MeOH (0.2 mL, -30°C) were combined. The reaction solution was then added to the NaBH₄ mixture with stirring, and this solution was left at -30°C for 1 h. The reaction solution was allowed to warm to room temperature for 30 min, before precipitation was induced by adding H₂O (3 mL). The resulting tan solid was collected on a 15 mL fine porosity fritted disc, washed with H₂O (2 x 5 mL), and pentane (2 x 3 mL, -30°C) and desiccated, yielding 47 (40 mg, 0.061 mmol, 79% yield).

1H NMR (acetone-d₆, δ): 8.24 (d, 1H, PzA₃), 8.15 (d, 1H, PzB₃), 7.96 (d, 1H, PzB₅), 7.93 (d, 1H, PzA₅), 7.50 (d, 1H, PzC₃), 6.42 (t, 1H, PzB₄), 6.31 (t, 1H, PzC₄), 6.28 (t, 1H, PzA₄), 3.49 (m, 1H, H1), 3.17 (m, 1H, H4-endo), 2.98 (m, 1H, H4-exo), 2.55 (d, J = 10.8, 1H, H6-exo), 2.07 (buried, 1H, H6-exo), 1.76 (dm, J = 14.1, 1H, H6-endo), 1.59 (m, 1H, H5-exo), 1.57 (m, 1H, H5-endo), 1.43 (m, 1H, H3), 1.18 (d, J = 8.3, 9H, PMe₃).

13C NMR (acetone-d₆, δ): 144.2 (PzB₃), 143.0 (PzA₃), 141.7 (PzC₃), 137.7 (Pz₅), 137.0 (Pz₅), 136.8 (Pz₅), 133.2 (q, JₐCF = 282.3, CF₃), 107.3 (PzB₄), 106.9 (PzC₄), 106.3 (PzA₄), 52.0 (C₃), 47.9 (d, JₚC = 13.0, C₂), 43.9 (m, C₁), 29.1 (C₄), 22.6 (C₆), 20.9 (C₅), 13.0 (d, JₚC = 27.8, PMe₃).

ESI-MS: obsd (%), calcd (%): 652.1702 (84.59), 652.1702 (85.97), 653.1727 (76.24), 653.1728 (79.46), 654.1724 (100), 654.1726 (100), 655.1770 (36.53), 655.1769 (40.83), 656.1757 (80.76), 656.1758 (84.86).

Characterization for 48

CV (MeCN) Eₚ,a = 0.61 V (NHE). IR: ν(BH) = 2513 cm⁻¹, ν(CN) = 2228 cm⁻¹, ν(NO) = 1558 cm⁻¹. 1H-NMR (CDCl₃, δ, 25°C): 8.05 (2H, overlapping d, Pz₃A and Pz₃B), 7.71 (1H, d, Pz₅A), 7.69 (1H, d, Pz₅C), 7.64 (1H, d, Pz₅B), 7.24 (1H, d, Pz₃C), 6.31 (1H, t, Pz₄A), 6.26 (1H, t, Pz₄B), 6.19 (1H, t, Pz₄C), 3.99 (1H, broad s, H₃), 3.12 (1H, m, H6-exo), 2.72 (1H, m, H5-exo), 2.68 (1H, m, H₁), 2.07 (1H, m, H₄-exo), 1.77 (1H, m, H₄-endo), 1.70 (2H, overlapping, H₅-exo and H₅-endo), 1.38 (1H, m, J = 11.1, H₂), 1.18 (9H, d, JₚH = 8.3, PMe₃). 31P-NMR (CDCl₃, δ, 25°C): -10.55 (Jₚ₉ = 285) 13C-NMR (CDCl₃, δ, 25°C): 143.3 (Tp₃/₅), 142.4 (Tp₃/₅), 140.1 (Tp₃/₅), 136.6 (Tp₅/₃), 136.1 (Tp₅/₃), 128.1 (CN), 106.6 (Tp₄), 106.1 (Tp₄), 106.0 (Tp₄), 52.3 (C₂), 49.7 (C₁, JₚC = 11.6), 31.0 (C₃), 28.7 (C₆, d, JₚC = 3.5), 27.5 (C₄), 22.0 (C₅), 13.8 (PMe₃, JₚC = 27.9).

Synthesis was analogous to 48-4-exo,5-endo-d₂ (vida infra) but utilized only the proteated versions of the sodium borohydride and methanol.
Synthesis of 52

![Diagram of 52](image)

To a 4-dram vial were added WTp(NO)(PMe$_3$)(η$_2$-1-(trifluoromethyl)cyclohexa-1,3-diene)$_{28}$ (50 mg, 0.077 mmol) followed by acetone (1.3 mL, -30°C), resulting in a heterogeneous mixture. A 1M solution of HOTf in acetonitrile (0.1 mL, 0.1 mmol, -30°C) was then added, resulting in a homogeneous yellow solution, which was allowed to stir for 19 h at room temperature. This orange solution was then cooled to -30°C for 30 min. In a separate 4-dram vial, NaBD$_4$ (11 mg, 0.26 mmol) and MeOD (0.2 mL, -30°C) were combined. The reaction solution was then added to the NaBD$_4$ mixture with stirring, and this solution was left at -30°C for 1 h. The reaction solution was allowed to warm to room temperature for 30 min, before precipitation was induced by adding H$_2$O (3 mL). The resulting tan solid was collected on a 15 mL fine porosity fritted disc, washed with H$_2$O (2 x 5 mL), and pentane (2 x 3 mL, -30°C) and desiccated, yielding 52 (48 mg, 0.073 mmol, 95% yield). 94% deuterium incorporation of C4. Deuterium incorporation determined by integration of $^1$H NMR signal at 2.98 ppm.

Synthesis of WTp(NO)(PMe$_3$)(η$_2$-1-trifluoromethyl-5-deutero-1,3-cyclohexadiene)

![Diagram of WTp(NO)(PMe$_3$)(η$_2$-1-trifluoromethyl-5-deutero-1,3-cyclohexadiene)](image)

To a 4-dram vial charged with a stir pea were added WTp(NO)(PMe$_3$)(η$_2$-2,3-α,α,α-trifluorotoluene) (200 mg, 0.308 mmol) followed by MeCN (1.8 mL, -30°C), resulting in a heterogeneous mixture. A 1M solution of HOTf in MeCN (0.32 mL, 0.32 mmol, -30°C) was immediately added with stirring, resulting in a homogeneous orange solution, which was allowed to sit for 20 min at -30°C. In a separate 4-dram vial, NaBD$_4$ (39 mg, 0.93 mmol) was dissolved in MeOH (1 mL, -30°C). This chilled hydride solution was then added to the orange reaction solution dropwise with vigorous stirring. The reaction was allowed to sit at -30°C for 10 h, at which point a solid had precipitated out of solution. The reaction solution was stirred at room temperature for 5 min, before further precipitation was induced by adding H$_2$O (5 mL). The resulting solid was collected on a 15 mL fine porosity fritted disc, washed with H$_2$O (2 x 5 mL), and pentane (2 x 4 mL, -30°C) and desiccated (179 mg, 0.275 mmol, 89% yield). Greater than 95% deuterium incorporation at C5.

Synthesis of 53
NaBH$_4$ (14 mg, 0.37 mmol) was dissolved in d$_4$-methanol (0.4 mL, -30°C) in a 4-dram vial charged with a stir pea. WTP(NO)(PMe$_3$)(η$^2$-1-(trifluoromethyl)cyclohexa-1,3-diene-5-d) (50 mg, 0.077 mmol) was added to another 4-dram vial charged with a stir pea. In a separate 4-dram vial, CD$_3$CN (0.8 mL, -30°C) and a 1M solution of HOTf in MeCN (0.16 mL, 0.16 mmol, -30°C) were combined and cooled to -40°C for 20 min. The acid solution was added to the vial with tungsten complex, with stirring, resulting in a homogeneous yellow solution, which was allowed to sit for 2 min at -40°C. The yellow reaction solution was then added to the chilled hydride mixture with stirring. The pale yellow reaction was left at -40°C for 8 min then moved to the freezer at -30°C for 40 min, during which time solid precipitated out of solution. The heterogeneous reaction mixture was removed from the freezer and further precipitation was induced by adding H$_2$O (2 mL). The pale yellow solid was collected on a 15 mL fine porosity fritted disc, washed with H$_2$O (5 mL), and pentane (2 x 3 mL, -30°C) and desiccated, yielding 53 (35 mg, 0.054 mmol, 70% yield). 95% deuterium incorporation at C5. Deuterium incorporation determined by integration of $^1$H NMR signal at 1.60 ppm.

Synthesis of 54

NaBD$_4$ (14 mg, 0.33 mmol) was dissolved in d$_4$-methanol (0.4 mL, -30°C) in a 4-dram vial charged with a stir pea. WTP(NO)(PMe$_3$)(η$^2$-1-(trifluoromethyl)cyclohexa-1,3-diene-5-d) (50 mg, 0.077 mmol) was added to another 4-dram vial charged with a stir pea. In a separate 4-dram vial, CD$_3$CN (0.8 mL, -30°C) and a 1M solution of HOTf in MeCN (0.16 mL, 0.16 mmol, -30°C) were combined and cooled to -40°C. The acid solution was added to the vial with tungsten complex, with stirring, resulting in a homogeneous yellow solution, which was allowed to sit for 2 min at -40°C. The yellow reaction solution was then added to the chilled hydride mixture with stirring. The pale yellow reaction was left at -40°C for 8 min then moved to the freezer at -30°C for 40 min, during which time solid precipitated out of solution. The heterogeneous reaction mixture was removed from the freezer and further precipitation was induced by adding H$_2$O (2 mL). The pale yellow solid was collected on a 15 mL fine porosity fritted disc, washed with H$_2$O (5 mL), and pentane (2 x 3 mL, -30°C) and desiccated, yielding 53 (36 mg, 0.055 mmol, 71% yield). 95% deuterium incorporation at C4 and 95% deuterium incorporation at C5. Deuterium incorporation determined by integration of $^1$H NMR signals at 2.98 and 1.60 ppm.

Synthesis of 55
To a 4-dram vial charged with a stir pea were added WTP(NO)(PMe₃)(η²-2,3-α,α,α-trifluorotoluene) (100 mg, 0.154 mmol) followed by MeCN (0.45 mL, -30°C), resulting in a heterogeneous mixture. A 1M solution of HOTf in MeCN (0.3 mL, 0.3 mmol, -30°C) was immediately added with stirring, resulting in a homogeneous orange solution, which was allowed to sit for 20 min at -30°C. In a separate 4-dram vial, NaCNBH₃ (29 mg, 0.46 mmol) was dissolved in MeOH (0.45 mL, -30°C). This chilled hydride solution was then added to the orange reaction solution dropwise with vigorous stirring. After addition of the hydride solution a solid precipitated out of the reaction mixture. The reaction was allowed to sit at -30°C for 1.5 h, then the pale yellow solid was collected on a 15 mL fine porosity fritted disc, washed with H₂O (2 x 5 mL), and pentane (2 x 5 mL, -30°C) and desiccated, yielding 55 (81 mg, 0.12 mmol, 78% yield). 

$E_{p,a} = +0.49$ V (NHE). IR: $\nu$(BH) = 2487 cm⁻¹, $\nu$(NO) = 1548 cm⁻¹. Anal. Calc’d for C₁₉H₂₆BF₃N₇OPW·2CH₂Cl₂: C, 30.65; H, 3.92; N, 11.91. Found: C, 31.08; H, 4.10; N, 12.21. $^{31}$P NMR (acetone-d₆, δ): -13.84 ($J_{WP}$ = 272). $^1$H NMR (acetone-d₆, δ): 8.18 (d, 1H, PzB3), 7.97 (d, 1H, PzB5), 7.96 (d, 1H, PzC5), 7.80 (d, 1H, PzA5), 7.73 (d, 1H, PzA3), 7.40 (d, 1H, PzC3), 6.43 (t, 1H, PzB4), 6.33 (t, 1H, PzC4), 6.28 (t, 1H, PzA4), 4.01 (m, 1H, H1), 3.18 (m, 1H, H4-exo), 2.96 (t, J = 12.1, 1H, H2), 2.17 (d of m, J = 14.4, 1H, H4-endo), 1.93 (m, 1H, H6-endo), 1.81 (m, 1H, H5-endo), 1.63 (m, 1H, H6-exo), 1.57 (m, 1H, H5-exo), 1.29 (d, J = 12.1, 1H, H3), 1.04 (d, $J_{PH}$ = 8.3, 9H, PMe₃). $^{13}$C NMR (acetone-d₆, δ): 144.0 (PzA3), 143.1 (PzB3), 141.1 (PzC3), 137.5 (PzC5), 137.2 (PzB5), 136.7 (PzA5), 131.1 (q, $J_{CF}$ = 278.4, CF₃), 107.5 (PzB4), 107.1 (PzC4), 106.6 (PzA4), 58.1 (C3), 46.7 (d, J = 14.6, C2), 45.0 (q, $J_{CF}$ = 24.7, C1), 25.3 (C4), 20.4 (C6), 19.8 (C5), 13.3 (d, $J_{PC}$ = 29.1, PMe₃).

**Synthesis of 56**

To a 4-dram vial charged with a stir pea were added WTP(NO)(PMe₃)(η²-2,3-α,α,α-trifluorotoluene) (100 mg, 0.154 mmol) followed by CD₃CN (0.35 mL, -30°C), resulting in a heterogeneous mixture. A 1M solution of HOTf in MeCN (0.39 mL, 0.39 mmol, -30°C) was immediately added with stirring, resulting in a homogeneous orange solution, which was allowed to sit for 20 min at -30°C. In a separate 4-dram vial, NaCNBD₃ (30 mg, 0.46 mmol) was dissolved in 1:1 methanol:δ₄-methanol (0.8 mL, -30°C). This chilled hydride solution was then added to the orange reaction solution dropwise with vigorous stirring. The reaction was allowed to sit at -30°C for 3 h, at which point a solid had precipitated out of solution. The pale yellow solid was collected on a 15 mL fine porosity fritted disc, washed with H₂O (5 mL), and pentane (2 x 5 mL, -30°C) and desiccated, yielding 56 (75 mg, 0.11 mmol, 71% yield). 10% deuterium incorporation at C1, 81% deuterium incorporation at C5, and 60% deuterium incorporation at C4. Deuterium incorporation determined by integration of $^1$H NMR signals at 4.01, 3.18, and 1.57 ppm.
Synthesis of 57

To a 4-dram vial charged with a stir pea were added WTp(NO)(PMe₃)(η²-2,3-α,α,α trifluorotoluene) (100 mg, 0.154 mmol) followed by CD₃CN (0.35 mL, -30°C), resulting in a heterogeneous mixture. A 1M solution of HOTf in MeCN (0.39 mL, 0.39 mmol, -30°C) was immediately added with stirring, resulting in a homogeneous orange solution, which was allowed to sit for 20 min at -30°C. In a separate 4-dram vial, NaCNBD₃ (30 mg, 0.46 mmol) was dissolved in d₄-methanol (0.8 mL, -30°C). This chilled hydride solution was then added to the orange reaction solution dropwise with vigorous stirring. The reaction was allowed to sit at -30°C for 4 h, at which point a solid had precipitated out of solution. The pale yellow solid was collected on a 15 mL fine porosity fritted disc, washed with H₂O (2 x 5 mL), and pentane (2 x 5 mL, -30°C) and desiccated, yielding 57 (75 mg, 0.11 mmol, 71% yield). 77% deuterium incorporation at C1, 84% deuterium incorporation at C5, and 93% deuterium incorporation at C4. Deuterium incorporation determined by integration of ¹H NMR signals at 4.01, 3.18, and 1.57 ppm.

Synthesis of 58

¹H NMR Characterization of 58-4-exo,5-endo-d₂ matches that of 48 but with an 90% loss of ¹H signal intensity at 2.07 ppm and a 93% loss of ¹H signal intensity at 1.77 (isotopic purity estimated by ¹H NMR). There is an unintended 15% underintegration at 3.12 representing scrambling of deuterium in the H6-exo position.

A test tube was charged with NaCN (0.235 g, 4.80 mmol) and MeOD (2 mL) along with a small stir bar and was allowed to stir at room temperature for 2 h to dissolve. This reaction mixture was then transferred to a -60°C toluene bath and to this solution was added HOTf (3 drops). Separately a solution of 13 (0.200 g, 0.272 mmol) was dissolved in a solution of MeOD (2 mL) and propionitrile (1mL). This homogeneous yellow reaction mixture was then transferred to the a -60°C toluene bath. After sitting in the reduced temperature toluene bath for 30 min the solution of 13 was added dropwise to the stirring solution of NaCN/MeOD at -60° and this light yellow solution was allowed to stir at -60°. After 2 h of stirring the reaction was determined to be completed by a ³¹P NMR experiment and the reaction vessel was removed from the box and diluted with 50 mL of DCM. The reaction mixture was then added to a 100 mL solution of DI H₂O saturated with NaCl (brine solution) in a 250 mL separatory funnel and the mixture was extracted with 3 x 50 mL DCM. The organic layers were then collected and dried over anhydrous MgSO₄ for 15 min. The DCM mixture was then eluted through a medium 60 mL medium porosity frit and the MgSO₄ on the frit was washed with DCM (50 mL total) to dissolve any remaining product. The DCM was then removed under reduced pressure until a light brown film remained. The film
was re-dissolved in 3 mL of DCM and added to 100 mL of stirring pentane. Upon addition a light pink solid precipitated from solution. This heterogeneous solution was allowed to triturate for 10 min before the reaction mixture was filtered through a fine 15 mL frit. The isolate light pink solid was then washed with 2 x 10mL pentane and allowed to desiccate under dynamic vacuum for 3 h. A mass was taken of the fine light pink solid (0.095 g, 57 %).

**Synthesis of 59**

\[ \text{PMe}_2 \]
\[ \text{NO} \]
\[ \text{TP} \]
\[ \text{D} \]
\[ \text{CN} \]

\(^1\text{H} \) NMR Characterization of 59-4-exo-d\(_1\) matches that of 48 but with an 87\% loss of \(^1\text{H} \) signal intensity at 1.77 ppm (isotopic purity estimated by \(^1\text{H} \) NMR).

To a 4-dram vial was added 2 mL of propionitrile and 1 (0.252 g, 0.434 mmol) to generate a heterogeneous yellow reaction mixture. This solution was then cooled to -30\(^\circ\)C. DPhAT was added to this reaction mixture and the solution was allowed to stand at -30\(^\circ\)C. Over 15 min a homogeneous red reaction mixture develops indicating the formation of 2 in solution. Separately a solution of 2 mL of MeOH was chilled to -60 °C in a toluene bath and to this solution NaBD\(_4\) (0.078 g, 1.86 mmol) was added. The NaBD\(_4\)/MeOH solution was then allowed to stir in a -60 °C. The homogenous red reaction mixture of 2 was then added to this -60 °C cooled solution of MeOH and NaBD\(_4\). After seven hours the reaction mixture had turned to a homogenous orange color and was removed from the -60 °C toluene bath and diluted with 40 mL of Et\(_2\)O and allowed to stir for 10 min at room temperature. A 60 mL medium fritted porosity disc was filled with ~ 5 cm of silica and set in Et\(_2\)O. The homogeneous orange solution was then filtered through the silica column and a light yellow band was eluted with ~100 mL of Et\(_2\)O. The solvent was removed in vacuo until a pale yellow solid remained. This was re-dissolved in 1 mL of DCM and added to a 4-dram vial that contained 15 mL of sitting hexanes. This homogeneous yellow solution was subsequently allowed to cool at -30\(^\circ\)C for 16 h. After being allowed to cool a light green crystalline product had developed on the sides of the vial. The organic layer was decanted and the product was then dried with N\(_2\) (g) and allowed to desiccate for 16 h under static vacuum before its identity was confirmed by \(^1\text{H} \) NMR. The resulting lime green solid was subsequently dissolved in 2 mL of MeOH and cooled to -30 °C. Separately, a 4-dram vial was charged with NaCN (0.250 g, 5.1 mmol) along with MeOH and allowed to stir for 15 min at room temperature. This reaction mixture was then transferred to a -60 °C toluene bath and allowed to stir. To the -30\(^\circ\)C MeOH solution of 4-6,exo-d\(_1\) added HOTf (0.102 g, 0.680 mmol). Upon addition the reaction mixture goes from a heterogeneous green to a homogeneous yellow solution. This solution of 4-6,exo-d\(_1\) was then cooled in the -60 °C toluene bath over a course of 10 minutes before it was added dropwise to the stirring solution of NaCN/MeOH that had been stirring in the -60\(^\circ\)C toluene bath. This solution was allowed to stir for 5 h at -60\(^\circ\)C before it was removed from the toluene bath. The reaction mixture was diluted with ~ 50 mL of Et\(_2\)O and loaded onto a 30 mL medium fritted porosity disc that was filled with ~ 5 cm of silica and set in Et\(_2\)O. A lime green band was collected upon elution with 100 mL of Et\(_2\)O and the solvent was removed in vacuo to reveal a lime green solid. This solid
was then dissolved in 2 mL of DCM and added to 15 mL of standing pentane in a 4-dram vial and allowed to sit at -30°C for 16 hr during which time a white solid precipitated out of solution. The next day the white solid was allowed to triturate in a minimal amount of MeCN given that the desired product was marginally soluble in MeCN. The organic layer was then decanted and the reaction mixture was dried with N₂(g) and allowed to desiccate for 3 h under active vacuum before a mass was taken (0.048 g, 18% overall yield).

**Synthesis of 60**

![Diagram](image)

¹H NMR Characterization of 48-5-endo-d₁ matches that of 48 but with an 85% loss of ¹H signal intensity at 1.70 ppm (isotopic purity estimated by ¹H NMR). Although overlap is present with the H5-endo proton, the precursor compound shows suppression of the expected endo-proton.

To a 4-dram vial added 1 (0.264 g, 0.454 mmol) along with propionitrile (2 mL) and this was allowed to sit at -30°C. Separately a solution of NaBH₄ (0.111 g, 2.92 mmol) was added to a -60 °C solution of MeOD (2 mL) in a test tube. In another 4-dram vial diphenylammonium triflate (DPhAT, 0.175 g, 0.546 mmol) was dissolved in MeOD (2.78 g, 83.9 mmol) and allowed to sit at -30°C for 10 min before it was added to the solution of 1 in propionitrile. This reaction mixture was then transferred to a -60 °C toluene bath in a 4-dram vial and allowed to cool over a period of 10 min. This reaction mixture, now a homogeneous red coloration, was then added to the -60 °C cooled solution of stirring NaBH₄/MeOD. Upon addition some bubbling occurs and this reaction mixture was allowed to stir for 5 h at -60 °C. After 5 h the reaction mixture was removed from the -60 °C toluene bath and diluted with 40 mL of Et₂O and allowed to stir for 10 min at room temperature. A 60 mL medium fritted porosity disc was filled with ~5 cm of silica and set in Et₂O. The homogeneous orange solution was then filtered through the silica column and a light yellow band was eluted with ~100 mL of Et₂O. The solvent was removed in vacuo until a pale yellow solid remained. This was re-dissolved in 2 mL of DCM and added to a 4-dram vial that contained 15 mL of sitting hexanes. This homogeneous yellow solution was subsequently allowed to cool at -30°C for 16 h. After being allowed to cool a light green crystalline product had developed on the sides of the vial. The organic layer was decanted and the product was then dried with N₂(g) and allowed to desiccate for 16 h under static vacuum before its identity was confirmed by ¹H NMR as 2-5-endo-d₁. This solid was then combined with MeOH (2 mL) in a 4-dram vial and allowed to cool to -30 °C over a course of 15 min. Separately a large test tube vial was charged with MeOH (2 mL), NaCN (0.240 g, 4.90 mmol) and this heterogeneous solution was allowed to stir at room temperature for 15 min. This solution was then transferred to a -60 °C toluene bath and allowed to stir for 10 min. To the -30 °C MeOH solution of 2-5-endo-d₁ added HOTf (0.102 g, 0.680 mmol) that had also been cooled to -30 °C. This solution, a light homogeneous yellow solution was transferred to the -60 °C toluene bath and allowed to stir for 5 min. This homogeneous yellow solution was then added dropwise to the -60 °C solution of NaCN/MeOH and allowed to stir for 5 h. This solution was allowed to stir for 5 h at -60°C before it was removed from the toluene bath. The reaction mixture was diluted with ~50 mL of Et₂O and loaded onto a 30 mL medium fritted
porosity disc that was filled with ~ 3 cm of silica and set in Et₂O. A lime green band was collected upon elution with 100 mL of Et₂O and the solvent was removed in vacuo to reveal a lime green solid. The next day the white solid was allowed to tritrate in a minimal amount of MeCN given that the desired product was marginally soluble in MeCN. The organic layer was then decanted and the reaction mixture was dried with N₂ (g) and allowed to desiccate for 3 h under active vacuum before a mass was taken (0.048 g, 17% overall yield).

**Synthesis of 61**

\[
\begin{align*}
\text{WTp(NO)(PMe₃)(η²-1,2-6-cyano-cyclohexadiene) (prepared by a previously reported method)²⁸ (0.088g, 0.145 mmol) was dissolved in DME (1 mL) and allowed to cool to -30°C. Separately a test tube vial was charged with MeOD (1 mL) and cooled to -60 °C in a toluene bath over a course of 15 min and to this solution was added NaBD₄ (0.050 g, 1.21 mmol) and allowed to stir at -60 °C. Next HOTf (0.041 g, 0.273 mmol) was then added at -30 °C to the solution of tungsten in DME and upon addition the reaction mixture turns to a homogeneous yellow color. This solution was allowed to cool to -60 °C over a course of 10 min after being transferred to the -60 °C toluene bath. This yellow reaction mixture was then added dropwise to the solution of NaBD₄/MeOD. This solution was allowed to stir for 16 h at -60°C before it was removed from the toluene bath. The reaction mixture was diluted with ~ 50 mL of Et₂O and loaded onto a 15 mL medium fritted porosity disc that was filled with ~ 2 cm of silica and set in Et₂O. The column was then eluted with 100 mL of Et₂O and the solvent was removed in vacuo to reveal a white solid This solid was then dissolved in 2 mL of DCM and added to 15 mL of standing pentane in a 4-dram vial and allowed to sit at -30°C for 16 hr during which time a white solid precipitated out of solution. The next day the white solid was allowed to triturate in a minimal amount of MeCN given that the desired product was marginally soluble in MeCN. The organic layer was then decanted and the reaction mixture was dried with N₂ (g) and allowed to desiccate for 3 h under active vacuum before a mass was taken (0.038 g, 43% yield).}
\end{align*}
\]
Synthesis of 62

![Compound Image]

$^1$H NMR Characterization of 62-4-endo-$d_1$ matches that of 48 but with a 99% loss of $^1$H signal intensity at 2.07 ppm (isotopic purity estimated by $^1$H NMR, in this case proton impurity is beyond $^1$H NMR detection limit).

To a 4-dram vial added 1 (0.257 g, 0.442 mmol) along with MeCN (2 mL) and this was allowed to sit at -30°C. Separately a solution of NaCN (0.197 g, 4.02 mmol) in MeOD (2 mL) was prepared in a separate 4-dram vial and allowed to stir for 15 min at room temperature before it was transferred to a toluene bath that had been chilled to -40 °C. In another 4-dram vial diphenylammonium triflate (DPhAT, 0.168 g, 0.525 mmol) was dissolved in MeOD (2.38 g, 71.9 mmol) to generate an in situ source of acidic deuterium and allowed to sit at -30°C for 10 min. This acidic deuterium source was then added to the solution of 1 in MeCN at -30 °C and upon addition the reaction mixture turns from a heterogeneous yellow solution to a homogeneous red/orange solution. This reaction mixture was then allowed to sit in the -40 °C toluene bath for 5 min before it was added dropwise to the -40°C solution of stirring NaCN/MeOD. Upon addition the reaction mixture turns from a homogeneous red solution to a homogeneous yellow solution and this reaction mixture was allowed to stir for 16 h. After 16 h an off-white solid had precipitated out of solution. The solution was filtered through a fine 15 mL fritted porosity disc to yield an off-white solid. This solid was then washed with DI H$_2$O (3 x 5 mL) and then pentane (3 x 5 mL) and allowed to desiccate under active vacuum for 4 h and its identity confirmed by $^1$H NMR and a mass was taken (0.112g, 0.18 mmol). The resulting off white solid was subsequently dissolved in 2 mL of MeOH and cooled to -30 °C over the course of 10 min. Separately a test tube of MeOH was cooled in a -50°C toluene bath before NaBH$_4$ (0.117 g, 3.09 mmol) was added to the chilled solution. To the solution of 4-6,endo-$d_1$ was added a -30°C solution of HOTf(0.061 g, 0.41 mmol) and this reaction mixture was transferred and cooled for 15 min in the – 50 °C toluene bath before the reaction mixture was added dropwise to the -50°C NaBH$_4$/MeOH solution. This solution was allowed to stir for 16 h at -50°C before it was removed from the toluene bath. The reaction mixture was diluted with ~ 50 mL of Et$_2$O and loaded onto a 15 mL medium fritted porosity disc that was filled with ~ 2 cm of silica and set in Et$_2$O. A lime green band was collected upon elution with 100 mL of Et$_2$O and the solvent was removed in vacuo to reveal a lime green solid. This solid was then dissolved in 2 mL of DCM and added to 15 mL of standing pentane in a 4-dram vial and allowed to sit at -30°C for 16 hr during which time a white solid precipitated out of solution. The next day the white solid was allowed to triturate in a minimal amount of MeCN given that the desired product was marginally soluble in MeCN. The organic layer was then decanted and the reaction mixture was dried with N$_2$(g) and allowed to desiccate for 3 h under active vacuum before a mass was taken (0.038 g, 14% overall yield).
Synthesis of 63

1H NMR Characterization of 63-5-exo-d1 matches that of 48 but with an 91% loss of 1H signal intensity at 1.70 ppm (isotopic purity estimated by 1H NMR). Although overlap is present with the H5-endo proton, the precursor compound shows suppression of the expected exo-proton.

To a 4-dram vial added 1 (0.250 g, 0.430 mmol) along with MeCN (2 mL) and this was allowed to sit at -30°C. Separately a solution of NaN (0.200 g, 4.08 mmol) in MeOH (2 mL) was prepared in a separate 4-dram vial and allowed to stir for 15 min at room temperature before it was transferred to a toluene bath that had been chilled to -40 °C. In another 4-dram vial diphenylammonium triflate (DPhAT, 0.150 g, 0.469 mmol) was dissolved in MeOH (1 mL) and allowed to sit at -30°C for 10 min. This acidic solution was added to the solution of 1 in MeCN at -30 °C and upon addition the reaction mixture turns from a heterogeneous yellow solution to a homogeneous red/orange solution. This reaction mixture was then allowed to sit in the -40 °C toluene bath for 5 min before it was added dropwise to the -40°C solution of stirring NaCN/MeOD. Upon addition the reaction mixture turns from a homogeneous red solution to a homogeneous yellow solution and this reaction mixture was allowed to stir for 16 h. After 16 h an off-white solid had precipitated out of solution. This solution was filtered through a fine 15 mL fritted porosity disc to yield an off-white solid. This solid was then washed with DI H2O (3 x 5 mL) and then pentane (3 x 5 mL) and allowed to desiccate under active vacuum for 4 h and its identity confirmed by 1H NMR and a mass was taken (0.177 g, 0.291 mmol). This solid was then added to a 4-dram vial with MeOD (3.17 g, 95.9 mmol) to generate a heterogeneous white solution and allowed to cool to -30°C. Separately a 4-dram vial was charged with HOTf (0.088 g, 0.587 mmol) followed by MeOD (0.792 g, 24.0 mmol) and allowed to cool to -30°C. Separately a test tube vial was charged with MeOD (1 mL) and cooled to -50 °C in a toluene bath over a course of 15 min and to this solution was added NaBH4 (0.130 g, 3.43 mmol) and allowed to stir at -50 °C. The 4-dram solution of HOTf/MeOD was then added at -30 °C to the solution of tungsten in MeOD and upon addition the reaction mixture turns to a homogeneous color. This solution was then allowed to cool to -50 °C over a course of 10 min and then added dropwise to the solution of NaBH4/MeOD. This solution was then allowed to stir for 16 h at -50°C before it was removed from the toluene bath. The reaction mixture was diluted with ~ 50 mL of Et2O and loaded onto a 15 mL medium fritted porosity disc that was filled with ~ 2 cm of silica and set in Et2O. A lime green band was collected upon elution with 100 mL of Et2O and the solvent was removed in vacuo to reveal a lime green solid. This solid was then dissolved in 2 mL of DCM and added to 15 mL of standing pentane in a 4-dram vial and allowed to sit at -30°C for 16 hr during which time a white solid precipitated out of solution. The next day the white solid was allowed to triturate in a minimal amount of MeCN given that the desired product was marginally soluble in MeCN. The organic layer was then decanted and the reaction mixture was dried with N2 (g) and allowed to desicate for 3 h under active vacuum before a mass was taken (0.042 g, 16% overall yield).
C. Figures

**Fig. S1.** $^1$HNMR spectrum (0 °C) of the tungsten $\eta^2$-benzenium complex 2, and NOE (red arrows) and chemical exchange correlations (colored protons) for $\eta^2$-benzenium complex 2 and 3.

**Fig. S2.** Relative energies (calculated) of $\eta^3$-benzenium isomers.
Fig. S3. DFT calculations for η²-benzenium complexes 2 and 3 and a comparison to the π-allyl (6) and cyclohexene (7) analogs (all distances reported in Å). Note in 2 the shortened C1-C2 bond (1.38 Å) (cf. cyclohexene 7, 1.53 Å) indicating a significant π interaction. A WII resonance contributor is shown for comparison.
Fig. S4. Molecular structure determinations and relevant NOE interactions for 4, 6, and 7.
Fig. S5. Direct protonation of 1,4-diene complex (8) with purported nitrosyl assist and $^1$HNMR spectrum of 25.
W isotopes: $^{184}$W: 183.95 (100.0%), $^{186}$W: 185.95 (92.8%), $^{182}$W: 181.95 (86.5%), $^{183}$W: 182.95 (46.7%)

B isotopes: $^{11}$B: 11.01 (100.0%), $^{10}$B: 10.01 (24.8%)

**Figure S6.** Composite of HRMS data showing parent ion envelope of complexes $9-d_6$
Figure S7. $^{13}$C NMRs of Cyclohexene-$d_1$ (derived from Complexes 42 and 32) and $d_2$ (derived from Complexes 45 and 46) Isotopologues Compared to $d_0$-Cyclohexene
Fig. S8. Several mechanisms which could result in the formation of 2, proposed nitrosyl-assisted transition state, and observed chemical exchange.
Figure S9. Chemical exchange between 2 and 3 along with chemical exchange due to ring isomerization in 2.
Figure S10. Illustrative $^1$H NMR comparison between 7 and $7-3,4,6$-exo-d$_3$ (49; 6X = H$_{6,exo}$; 3X = H$_{3,exo}$; 4X = H$_{4,exo}$)
Common features include a simplification in splitting pattern of remaining $^1$H signals along with isotopic shifts.

Fig. S11. The potential of (R)-WTp(NO)(PMe$_3$) to determine absolute configurations of enantiotopomers.
The figure above (S11) illustrates the ability of a resolved form of {WTp(NO)(PMe$_3$)(benzene)} to differentiate between various cyclohexene isotopologues. For example, when the benzene complex (R)-1 is combined with (R)-3-deuterocyclohexene, two isotopomers of the resulting cyclohexene complex will be formed (This is a result of the tungsten complex’s inability to chemically differentiate between the two faces of the 3-deuterocyclohexene). A $^1$H NMR spectrum will show the 3-exo and the 6-endo positions each at half intensity. In contrast, if 5-3-deuterocyclohexene is complexed, then only the 3-endo and 6-exo signals will be diminished. The ee of the 3-deuterocyclohexene can easily be determined from the relative ratios of the 3-endo and 3-exo signals. In a similar manner (R,R)-trans-3,6-dideuterocyclohexene and its enantiomer can be easily differentiated, both from each other and from the cis isomer. Finally, the (R,R,R,R)-3,4,5,6-tetradideuterocyclohexene stereoisomer shown above can be differentiated from its enantiomer and from the all-cis diastereomers. We note that there is virtually no other practical method to differentiate these cyclohexene stereoisotopomers.
Note on DFT Calculations. Optimized geometries and intermediates were calculated using B3LYP and the associated basis functions for tungsten and the 6-31G(d) basis for all other atoms. This combination has proved to be reliable for Os, Mo, Re, and W systems for relative (binding) energies, charge transfer, and preferred structures, especially in similar systems. Transition state modeling utilized unrestricted B3LYP and the SDD basis set.

Fig. S12. Distortions in the benzene ring as a result of dihapto-coordination.

Fig. S13. DFT calculations show enhanced stabilization of conjugated \( \eta^2 \)-diene complexes relative to \( \eta^2 \)-arene and unconjugated \( \eta^2 \)-diene counterparts.
Fig. S14. Synthetic Pathways to isotopologues of a 3-(trifluoromethyl)cyclohex-1-ene tungsten complex
Fig. S15. Synthetic pathways to isotopologues of a 3-cyanocyclohex-1-ene tungsten complex.

Available substitution patterns

Realized Isotopologues
D. Tables.

**Table S1.** The sequential reduction of benzene to cyclohexene bound to tungsten: Possible isotopomers.

The sequential reduction of benzene to cyclohexene bound to tungsten: Possible isotopomers.

![Diagram of the reduction process](image)

Red indicates prepared complex. IP = isotopic purity as determined by HRMS.

**Table S2.** Isotopologues and isotopomers of cyclohexene complex 7 and cyclohexene.

| Isotopologue | Complex 7-d₅ | Cyclohexene-d₅ | Cyclohexene-d₅ Possible |
|--------------|--------------|----------------|------------------------|
| d₀           | 1            | 1              | 1                      |
| d₁           | 10           | 4              | 5                      |
| d₂           | 14           | 11             | 25                     |
| d₃           | 8            | 8              | 60                     |
| d₄           | 2            | 2              | 110                    |
| d₅           | 0            | 0              | 126                    |
| d₆           | 2            | 2              | 110                    |
| d₇           | 8            | 8              | 60                     |
| d₈           | 14           | 11             | 25                     |
| d₉           | 10           | 4              | 5                      |
| d₁₀          | 2            | 1              | 1                      |
| Total        | 72           | 52             | 528                    |
Table S3. Table of select cyclohexene isotopologue complexes with isolated yields and estimates of purity and selectivity (determination by 1H NMR).

| Percent Yield | Selectivity estimated by 1H NMR | Purity estimated by 1H NMR | Percent Yield | Selectivity estimated by 1H NMR | Purity estimated by 1H NMR |
|---------------|---------------------------------|-----------------------------|---------------|---------------------------------|-----------------------------|
| 42            | 63%                             | 99%                         | 35            | 37%                             | 90%                         | 77%                        |
| 32            | 70%                             | 99%                         | 33            | 52%                             | 90%                         | 95%                        |
| 39            | 59%                             | 93%                         | 49            | 56%                             | 91%                         | 87%                        |
| 41            | 50%                             | 92%                         | 51            | 53%                             | 93%                         | 92%                        |
| 40            | 55%                             | 99%                         | 50            | 36%                             | 93%                         | 98%                        |
| 14            | 66%                             | 91%                         | 16            | 39%                             | 94%                         | 73%                        |
| 45            | 59%                             | 95%                         | 38            | 52%                             | 78%                         | 99%                        |
| 43            | 39%                             | 95%                         | 36            | 27%                             | 85%                         | 99%                        |
| 44            | 44%                             | 95%                         | 37            | 63%                             | 67%                         | 90%                        |
| 46            | 48%                             | 90%                         |               |                                 |                             |                            |

Table S4. Determination of enhanced KIE in deuteriation of complex 4

| Theoretical $^1$H Impurity | Observed $^1$H Impurity | KIE Determination |
|-----------------------------|--------------------------|-------------------|
| 3%                          | 49%                      | 31                |
| 5%                          | 57%                      | 40                |
| 10%                         | 82%                      | 41                |

(see section K for detailed explanation)
E) HRMS determinations
Theoretical values were calculated from https://www.envipat.eawag.ch/index.php

HRMS Spectra for 9-dn Complexes

Figure SE1. HRMS data for Compound 9-dn

ESI-MS : obsd (%), calc (%),

598.1984 (83.66), 598.1985 (85.93), 599.2010 (79.46), 600.2007 (100), 600.2009 (100), 601.2051 (37.70), 601.2052 (40.85), 602.2039 (83.65), 602.4041 (84.87).
Figure SE2. HRMS data for Compound 9-3-d₃

ESI-MS: obsd (%), calcd (%),
599.2045 (62.97), 599.2048 (85.94), 600.2078 (88.55), 600.2074 (79.46), 601.2083 (100), 601.2071 (100), 602.2117 (70.63), 602.2115 (40.85), 603.2106 (70.21), 603.2104 (84.88).

99% deuterium incorporation.

Figure SE3. HRMS data for Compound 9-3,5-d₂
ESI-MS: obsd (%), calcd (%),
600.2099 (88.06), 600.2111 (85.94), 601.2124 (85.46), 601.2136 (79.46), 602.2129 (100), 602.2134 (100), 603.2162 (48.65), 603.2178 (40.84), 604.2165 (76.72), 604.2167 (84.88).

86% deuterium incorporation for 7-3exo,5exo-d₂

![Figure SE4. HRMS data for Compound 9-3,4,5-d₃](image)

ESI-MS: obsd (%), calcd (%),
601.2175 (82.27), 601.2173 (85.95), 602.2209 (93.57), 602.2199 (79.46), 603.2221 (100), 603.2197 (100), 604.2248 (73.32), 604.2240 (40.84), 605.2248 (81.91), 605.2229 (84.88).

96% deuterium incorporation for 9-3exo,4exo,5endo-d₃
Figure SE5. HRMS data for Compound 9-3,4,5,6-d₄

ESI-MS : obsd (%), calcd (%),

602.2228 (93.37), 602.2242 (85.95), 603.2254 (100), 603.2267 (79.45), 604.2269 (100), 604.2265 (100), 605.2289 (69.22), 605.2309 (40.82), 606.2298 (75.93), 606.2298 (84.88).

79% deuterium incorporation for 9-3exo,4exo,5endo,6exo-d₄
Figure SE6. HRMS data for Compound 9-1,2,3,4,5,6-d₆

ESI-MS : obsd (%), calcd (%),

604.2356 (84.02), 604.2362 (85.94), 605.2382 (77.11), 605.2387 (79.46), 606.2383 (100), 606.2385 (100), 607.2422 (39.32), 607.2429 (40.81), 608.2415 (81.77), 608.2418 (84.89).

98% deuterium incorporation for 9-1,2,3endo,4endo,5exo,6endo-d₆
Figure SE7. HRMS data for Compound $9-1,2,3,3,4,5,6-d_7$

ESI-MS: obsd (%), calcd (%),

605.2452 (96.99), 605.2424 (85.97), 606.2473 (95.24), 606.2450 (79.44), 607.2484 (100), 607.2448 (100), 608.2495 (48.65), 608.2495 (70.86), 609.2509 (94.74), 609.2481 (84.89).

96% deuterium incorporation for $9-1,2,3,3\text{,}endo,5\text{,}exo,6\text{-}d_7$
Figure SE8. HRMS data for Compound \textit{9-1,2,3,4,4,5,6-d}_8

ESI-MS: obsd (%), calcd (%),

606.2480 (91.56), 606.2487 (85.97), 607.2504 (86.25), 608.2511 (100), 608.2511 (100), 609.2560 (47.46), 609.2554 (40.79), 610.2551 (81.53), 610.2543 (84.89).

\textit{99\% deuterium incorporation for 9-1,2,3,4,4,5exo,6endo-d}_8
F) $^1$H and $^{13}$C {$^1$H} Spectra of compounds.

Figure SF1. 1H NMR Spectrum of 2 and 3
Figure SF2. 13C{1H} NMR Spectrum of 2 and 3
Figure SF3. 1H NMR Spectrum of 8
Figure SF4. $^{13}$C{1H} NMR Spectrum of 8
Figure SF5. 1H NMR Spectrum of 7
Figure SF6. 13C{1H} NMR Spectrum of 7
Figure SF7. 1H NMR Spectrum of 9
Figure SF8. 13C {1H} NMR Spectrum of 9
Supporting Data for Isotopologues:
d₁-Isotopologues

Figure SF9. 1H NMR Spectrum of 42
Figure SF10. 1H NMR Spectrum of 7
Figure SF11. 1H NMR Spectrum of 32
Figure SF12. $^{13}$C{1H} NMR Spectrum of 32
d$_2$-Isotopolouges:

Figure SF13. 1H NMR Spectrum of 45
Figure SF14. 1H NMR Spectrum of 43
Figure SF15. 1H NMR Spectrum of 44
Figure SF16. 1H NMR Spectrum of 14
Figure SF17. 13C NMR Spectrum of Compound 14
Figure SF18. 1H NMR Spectrum of Compound 46
Figure SF19. 1H NMR Spectrum of Compound 35
Figure SF20. 1H NMR Spectrum of Compound 33
Figure SF21. 1H NMR Spectrum of Compound 50
Figure SF22. 1H NMR Spectrum of Compound 49
D4-Isotopolouges

Figure SF23. 1H NMR Spectrum of Compound 16
D6-Isotopolouges

Figure SF24. 1H NMR Spectrum of Compound 37
Figure SF25. 1H NMR Spectrum of Compound 37

Note: Resonances from 7.00 to 7.30 are those of free diphenylammonium triflate salt. The resonances at 2.64 and 3.10 show the loss in stereofidelity at carbon position C6.
Note: Resonances from 7.00 to 7.30 are those of free diphenylammonium triflate salt. The resonances at 2.64 and 3.10 show the loss in stereofidelity at carbon position C6.
Figure SF27. 1H NMR Spectrum of Compound 39 and 40
Figure SF28. 1H NMR Spectrum of Compound 41 and 50
Figure SF29. 1H NMR Spectrum of Compound 51
NMR Spectra for Representative Intermediates in converting 1 to 11 to 12 to 13 to 50.

Figure SF30. 1H NMR Spectrum of (11)
Figure SF31. 1H NMR Spectrum of (12)
Figure SF32. 1H NMR Spectrum of (13)
Figure SF33. 1H NMR Spectrum of (50)
Figure SF34. 1H NMR Spectrum of 18
Figure SF35. 1H NMR Spectrum of Compound 47
Figure SF36. 13C {1H} NMR Spectrum
Figure SF37. $^1$H NMR Data of Compound 58
Figure SF38. $^{13}$C \{1H\} NMR Data of Compound 58
Figure SF39. $^1$H NMR Data of Compound 59
Figure SF40. 1H NMR. 1H NMR Data of Compound 62
Figure SF41. $^1$H NMR Data of Compound 60
Figure SF42. \(^1\)H NMR Data of Compound 63
Figure SF43. $^1$H NMR Data of Compound 61
Figure SF44. Comparison of 1H NMR Spectra for 48 and 58
Figure SF45. Comparison of 3-cyanocyclohex-1-ene d1 Isotopologues as their Tungsten Complexes.
(D indicates suppressed proton signal owing to deuterium incorporation)
Figure SF46. Compound 47 $^1$H NMR
Figure SF47. Compound 47 $^{13}$C {$^1$H}
Figure SF48. Compound 53 $^1$H NMR
Figure SF49. Compound 52 $^1$H NMR
Figure SF50. Compound 54 $^1$H NMR
Figure SF51. Comparison of exo-3-(trifluoromethyl)cyclohexene isotopologues as their tungsten complexes (47, 52-54; arrows indicate signal suppression owing to deuterium incorporation)
Figure SF52. Compound 55 $^1$H NMR
Figure SF53. Compound 55 \(^{13}\text{C}\) \{\(1\)H\} NMR
Figure SF54. Compound 56 $^1$H NMR
Figure SF55. Compound 57 $^1$H NMR
Figure SF56. Comparison of endo-3-(trifluoromethyl)cyclohexene isotopologues as their tungsten complexes (55-57; arrows indicate signal suppression owing to deuterium incorporation)
G. Stereochemical Determination of Complexes 6, 7, and 9 via 2D NMR Data

1. Description of data supporting the regiochemical assignments of protons for cyclohexene ligand of Complex 9

   a. Assignment of H₁ and H₂:
   PMe₃ resonance at 1.29 ppm shows NOE correlations to Pz₃B resonance at 8.11 and Pz₃C resonance at 7.47. Additionally, the PMe₃ ligand shows an NOE interaction to a signal at 3.96 ppm. A ¹H {³¹P} NMR spectrum results in a simplification of multiplicity of H₁ due to large splitting with the ³¹P nucleus (I = ½; JHP is typically 10-12 Hz for WTP(NO)(PMe₃)(alkene) complexes). The Pz₃C resonance at 7.47 ppm shows a strong NOE correlation with H₁ resonance at 3.96 ppm and Pz₃A shows an NOE interaction with H₂ that resonates at 2.34 ppm.

   b. Assignment of C₁ and C₂:
   The H₁ resonance at 3.96 and shows a strong HSQC correlation 64.2 ppm, assigned as C₁. Additionally this signal is split by the ³¹P nucleus with a JPC = 8.2 Hz. The H₂ signal (2.34 ppm) shows an HSQC interaction with the 63.2 ppm resonance assigned as C₂.

   c. Assignment of H₆exo and H₆endo:
   These protons resonating at 3.56 and 2.87 show an HSQC correlation with C₆ (31.3 ppm), implying that they are a diastereotopic methylene group. The resonance at 3.96 ppm (H₁) shows a strong COSY interaction with a signal at 3.56 ppm. Further, C₁ (64.2 ppm) shows HMBC interactions to proton resonances at 3.56(H₆exo) and 2.87(H₆endo) ppm. These H₆ resonances show NOE interactions with the PMe₃ ligand with the 2.87 ppm (H₆endo) showing a more intense NOE interaction. The 2.87 resonance also shows an NOE interaction with the methyl group on the nitrosyl, supporting its assignment as the "endo" proton. An NOE resonance between the methyl group and the resonance at 3.56 is not observed.
d. Assignment of H₅ protons:
These resonances show an HSQC interaction to the same carbon at 23.8 ppm implying that they are a diastereotopic methylene group. The H₆ protons both display COSY interactions with resonances at 1.59 and 1.51 ppm.

e. Assignment of the H₃ protons
The resonance for the H₂ proton at 2.34 ppm shows a strong COSY and NOESY interaction with a resonance at 3.38 ppm, assigned as H₃. This H₃ resonance, along with a second at 3.13 ppm show HSQC correlations with a carbon at 31.8 ppm. Therefore, these resonances are a diastereotopic methylene group.

f. Assignment of the H₄ protons:
The 1.48 and 1.64 protons show HSQC interactions with a carbon resonance at 24.6 ppm implying that they are part of a diastereotopic methylene group. H₃ resonances at 3.13 and 3.38 ppm show strong COSY and NOESY Interactions to proton resonances at 1.48 and 1.64 ppm which are assigned as the H₄ protons.

g. Internal check: Although the similarity in resonances precludes unambiguous determination of interacting protons, there are COSY and NOSY interactions between all of the H₅ and H₄ protons the there is an HMBC interaction from C₄ (24.6 ppm) to the H₅ resonances and likewise HMBC interactions from C₅ (23.8) to the H₄ resonances. Note: There is no stereochemistry implied for H₄ or H₅ pairs. This is only an assignment of regiochemistry.
The analysis described above for 9 was used to assign the regiochemical positions for other fully proteated complexes (namely complex 6 and 7) and elucidation of the stereochemical assignments for complex 6, 7, and 9 is highlighted below.

2. **Assignments for [WTp(PMe$_3$)(NO)(η$^2$-cyclohexadienium)](OTf) (6)**

![Diagram of complex 6](image)

**Figure SG1.** Tp Doublets for 6

**Figure SG2.** Tp Triplets (and H$_3$) for 6
a. **Tp Assignments for Compound 6:**

**NOESY**

*From NOESY data:*
- The signal at 6.32 ppm correlates to 8.01 & 7.71 ppm  
  *Tp group 1*
- The signal at 6.51 ppm correlates to 8.34 & 7.88 ppm  
  *Tp group 2*
- The signal at 6.60 ppm correlates to 8.12 & 7.91 ppm  
  *Tp group 3*

*Also from NOESY data:*
- The signal at **8.01** correlates to 3.45 (cyclohexene) & 6.45 (cyclohexene)  
  *Tp group 1 = PzA*
- The signal at **8.12** correlates to 1.26 ppm (PMe₃), 4.62 (cyclohexene), 5.19 (cyclohexene)  
  *Tp group 3 = PzC*
- The signal at **8.34** correlates to 1.26 ppm signal (PMe₃)  
  *Tp group 2 = PzB*

|          | TpH₃ (ppm) | TpH₄ (ppm) | TpH₅ (ppm) |
|----------|------------|------------|------------|
| PzA      | 8.01       | 6.32       | 7.71       |
| PzB      | 8.34       | 6.51       | 7.88       |
| PzC      | 8.12       | 6.60       | 7.91       |

Summary: Both TpH₃ and TpH₃ protons (doublets) interact with TpH₄ (NOESY), but TpH₃ protons have interactions with other ligands whereas TpH₅ protons do not.)
b. Cyclohexadienium ligand Assignments (Compound 6)

![Cyclohexadienium ligand diagram](image)

c. Figure SG3. $^1$H NMR of 3.1-5.3 ppm range (ligand protons)

![Figure SG3 NMR](image)

Figure SG4. $^1$H NMR of 1.0-2.5 ppm range (ligand protons)

![Figure SG4 NMR](image)
Identification of diastereotopic methylene groups and bound protons (carbon shifts in parentheses) by HSQC data:

**HSQC**

**Allyl Protons (H₁, H₂, & H₃)**

4.62 (70.5), 5.18 (105.2), 6.41 (134.2)

**Diastereotopic methylene groups:**

Pair A: 1.38 & 1.63 (19.5)

Pair B: **

Pair C: **

**Four protons at 2.48, 3.30 (2), and 3.43 ppm correlate to two carbons at 26.3 & 26.4 ppm. Cannot be distinguished by HSQC.**

**Figure SG5:** NOESY: 4.62 ppm correlates to 1.26 (PMe₃) and 5.18 (allyl) ppm. 5.18 ppm correlates to 4.62 (allyl) and 6.41 (allyl) ppm. 6.41ppm correlates to 5.18 (allyl) and 8.01 ppm (PzA H₃).

*These data support 4.62 ppm as H₁, 5.18 ppm as H₂, and 6.41 ppm as H₃*

d. Diastereotopic methylene group assignments (Compound 6 continued)

**NOESY (detail)**

Both 3.43ppm and 3.30ppm correlate to 6.41 ppm (allyl peak, H₃).

*This suggests these signals correspond to H₄ protons.*

Both 3.30–ppm (the right side of the 3.30 peak) and 2.48 ppm (not shown) correlate to 4.62 (H₁).

*This suggests these signals correspond to H₆ protons.*

*By elimination, pair A (1.38 & 1.63 ppm) is assigned to correspond to H₅.*

**Figure SG6.** Endo/Exo assignments by NOESY (Compound 6 continued)
**Figure SG7. NOESY Correlations:** The signal at 2.48 (H₆) correlates to: 1.27 (PMe₃), 1.63 (H₅), 3.30 (H₆/H₄ strong), 3.44 (H₄ weak), 4.63 (H₁ weak)

*These NOE correlations suggest that 2.48 ppm corresponds to H₆ exo.*

The signal at 3.30 (H₆) correlates to: 1.27 (PMe₃ weak), 4.63 ppm (H₁)

*These NOE correlations further support that 2.48 ppm corresponds to H₆ exo.*

The signal at 3.30 (H₄) correlates to: 6.42 ppm (H₃)

*Note that NOESY correlations between 3.30 ppm protons and peaks between 1.3 and 3.5 ppm cannot be assigned definitively to one of the two protons. Definitively assigned peaks are the only ones listed.*

The signal at 3.43 (H₄) correlates to: 1.63 (H₅), 2.48 (H₆ weak), 6.42 (H₃ weak), 8.02 (PzA H₃)

*These NOE correlations suggest that 3.43 ppm is H₄ endo.*

The signal at 1.38 (H₅) correlates to: 1.63 (H₅ strong), 2.48 (H₆ very weak), 3.30 (H₄/H₆ strong)
The signal at 1.63 (H₅) correlates to: 1.38 (H₅ strong), 2.48 (H₆), 3.30 (H₄/H₆), 3.44 (H₄)

*These NOE correlations suggest that the proton corresponding to 1.63 ppm is on same side of the cyclohexene ring as that for 2.48 ppm. Therefore, the proton represented by 1.63 ppm is H₅ endo.*
e. Final $^1$H NMR Assignments for Complex 6

Cyclohexadienium Ligand

|          | $H_1$ (ppm) | $H_2$ (ppm) | $H_3$ (ppm) | $H_4$ (ppm) | $H_5$ (ppm) | $H_6$ (ppm) |
|----------|-------------|-------------|-------------|-------------|-------------|-------------|
| exo      | 4.62        | 5.18        | 6.41        | 3.43        | 1.63        | 2.48        |
| endo     |             |             |             | 3.30        | 1.38        | 3.30        |

Tp Ligand

|          | $H_3$ (ppm) | $H_4$ (ppm) | $H_5$ (ppm) |
|----------|-------------|-------------|-------------|
| PzA      | 8.01        | 6.32        | 7.71        |
| PzB      | 8.34        | 6.51        | 7.88        |
| PzC      | 8.12        | 6.60        | 7.91        |

PMe$_3$: 1.27 ppm

3. Assignments for WTp(PMe$_3$)(NO)(η$^2$-cyclohexene) (7)

Figure SG8. $^1$H NMR of Tp Doublets (compound 7)
Figure SG9. $^1$H NMR of Tp Triplets (compound 7)

![NMR spectrum showing Tp triplets at 6.5, 6.2, and 6.1 ppm.]

a. Tp Assignments (compound 7)

Figure SG10. COSY (compound 7)

![COSY spectrum showing correlations between hydrogen atoms.]

complex 7
Figure SG11. NOESY (compound 7)

From COSY data:
The signal at 6.21 ppm correlates to 7.35 & 7.78 ppm  \textit{Tp group 1}
The signal at 6.27 ppm correlates to 7.75 & 8.21 ppm  \textit{Tp group 2}
The signal at 6.36 ppm correlates to 7.85 & 8.03 ppm  \textit{Tp group 3}

From NOESY data:
The signal at 7.35 ppm correlates to 1.16 (PMe$_3$) & 2.72 ppm (cyclohexene)  \textit{Tp group 1 = PzC}
The signal at 8.03 ppm correlates to 1.16 ppm (PMe$_3$)  \textit{Tp group 3 = PzB}
The signal at 8.21 ppm correlates to 2.86 ppm (cyclohexene)  \textit{Tp group 2 = PzA}

|       | H$_3$ (ppm) | H$_4$ (ppm) | H$_5$ (ppm) |
|-------|-------------|-------------|-------------|
| PzA   | 8.21        | 6.27        | 7.75        |
| PzB   | 8.03        | 6.36        | 7.85        |
| PzC   | 7.35        | 6.21        | 7.78        |

Summary: Both TpH$_5$ and TpH$_3$ protons (doublets) interact with TpH$_4$ (NOESY, COSY), but TpH$_3$ protons have interactions with other ligands whereas TpH$_5$ protons do not.)
(Continued Analysis of Complex 7)

**Figure SG12.** 1.3-3.15 ppm Range (Cyclohexene protons)
b. **Cyclohexene Ligand Assignments**

Identification of diastereotopic methylene groups and bound protons (carbon shifts in parentheses) by HSQC data

**Figure SG13. HSQC data for compound 7**

| Tungsten-bound methane groups:                        |
|-------------------------------------------------------|
| H₁: 2.72 ppm (53.6 ppm)                               |
| H₂: 1.18 ppm (53.6 ppm)                               |

Diastereotopic methylene groups:

- **Pair A:** **(25.4 ppm)**
- **Pair B:** **(25.5 ppm)**
- **Pair C:** 2.63 & 3.04 ppm (**30.7 ppm**)
- **Pair D:** 2.86 & 2.93 ppm (**30.2 ppm**)

**Two protons at 1.41 ppm and protons resonating at 1.66 and 1.70 ppm could not be specifically assigned due to close proximity of the carbon signals.**
Continued Analysis of Complex 7

c. Pair assignment by COSY data.

**Figure SG14. COSY data for complex 7**

2.72 ppm (H1) correlates to 1.18 ppm (H2) and 3.04 ppm, which is part of CH2 “Pair C”

“Pair C” → H6 protons
1.18 ppm signal (H2) correlates to 2.72 ppm (H1) and 2.93 ppm, which is part of CH2 “Pair D”

“Pair D” → H3 protons
2.63 ppm and 3.05 ppm (“Pair C”) both correlate with 1.66 ppm and 1.41 ppm signals

1.66, 1.41 ppm → H5 protons
2.93 ppm (part of “Pair D”) correlates with 1.70 ppm signal.

1.70 ppm → H4 proton
2.03 ppm (part of “Pair D”) correlates with 1.41 ppm

1.41 ppm → H4 proton

d. endo/exo assignments by NOESY

**Figure SG15. NOESY (complex 7)**

The peak at 2.72 ppm (H1) correlates with one at 1.16 ppm (either PMe3 or H2), 3.04 ppm (H6)
This indicates that the proton resonating at 3.04 ppm is H6exo and therefore 2.63 ppm is H6endo
The peak at 1.18 ppm (H₂) correlates with one at 2.86 ppm (weak, H₃), 2.93 ppm (H₃)
This indicates that the proton resonating at 2.93 ppm is H₃exo since 2.86 ppm is much weaker, so the resonance at 2.86 ppm corresponds to H₃endo.

The peak at 2.86 (H₃) correlates with 1.18 (weak, H₂), 1.41– (weak, H₄), 1.70 (strong, H₄), 8.21 (PzA H₃)
This indicates that 2.86 ppm is H₃endo, due to Tp NOE interaction; this suggests that 1.70 ppm is H₄endo and the signal at 1.41 ppm is H₄exo.
The peak at 2.93 (H₃) correlates with 1.18 (H₂), 1.41– (strong, H₄), 1.70 (weak, H₄)
This further supports that 1.41 ppm is H₄exo and 1.70 ppm is H₄endo.

The peak at 2.63 (H₆) correlates with peaks at 1.16 ppm (PMe₃), 1.66 ppm (H₃), 3.04 ppm (H₆)
This supports that 2.63 ppm is H₆endo, due to the PMe₃ NOE interaction
This suggests that 1.66 ppm is H₆endo and 1.41 ppm is H₆exo.
The peak at 3.04 ppm (H₆) correlates with peaks at 1.16 ppm (PMe₃), 1.41 ppm (H₃), 2.63 ppm (H₆), and 2.72 ppm (H₁); This confirms that 1.41 ppm is H₆exo and 1.66 ppm is H₆endo.

e. Final ¹H NMR Assignments for Complex 7

| Cyclohexene Ligand |
|--------------------|
| H₁ (ppm) | H₂ (ppm) | H₃ (ppm) | H₄ (ppm) | H₅ (ppm) | H₆ (ppm) |
| 2.72 | 1.18 | endo | 2.86 | 1.70 | 1.66 | 2.63 |
| | exo | 2.93 | 1.41 | 1.41 | 3.04 |

| Tp Ligand |
|----------|
| H₃ (ppm) | H₄ (ppm) | H₅ (ppm) |
| PzA | 8.21 | 6.27 | 7.75 |
| PzB | 8.03 | 6.36 | 7.85 |
| PzC | 7.35 | 6.21 | 7.78 |

PMe₃: 1.16 ppm
4. Stereochemical Assignments for WTp(PMe)$_3$(NOMe)(η$^2$-cyclohexene) [OTf$^-$] (9)

Figure SG16. Tp Doublets

Figure SG17. Tp Triplets
a. **Tp Assignments Analysis of Complex 9**

**Figure SG18. COSY data of Complex 9**

**Figure SG19. NOESY data of Complex 9**

*From COSY data:*
- The peak at 6.33 ppm correlates to 7.47 & 7.92 ppm  
  \( Tp \) \textit{group 1}  
- The peak at 6.48 ppm correlates to 7.92 & 8.51 ppm  
  \( Tp \) \textit{group 2}  
- The peak at 6.55 ppm correlates to 8.01 & 8.11 ppm  
  \( Tp \) \textit{group 3}  

*From NOESY:*
- The peak at 7.47 ppm correlates to 1.29 (PMe3) & 3.97 ppm (cyclohexene)  
  \( Tp \) \textit{group 1}  
- The peak at 8.11 ppm correlates to 1.29 (PMe3) & 4.03 ppm (NOMe)  
  \( Tp \) \textit{group 3}  

\( PzC \)  
\( PzB \)
The peak at 8.51 ppm correlates to 2.34, 3.13, 3.38 (cyclohexene) & 4.03 ppm (NOMe) $Tp$

**group 2 = PzA**

|      | H$_3$ (ppm) | H$_4$ (ppm) | H$_5$ (ppm) |
|------|-------------|-------------|-------------|
| PzA  | 8.51        | 6.48        | 7.92        |
| PzB  | 8.11        | 6.55        | 8.01        |
| PzC  | 7.47        | 6.33        | 7.92        |

Summary: Both TpH$_3$ and TpH$_5$ protons (doublets) interact with TpH$_4$ (NOESY, COSY), but TpH$_3$ protons have interactions with other ligands, whereas TpH$_5$ protons do not.
(Continued Analysis of Complex 9)

**Figure SG20.** 2.7-4.1 ppm range Complex 9

![NMR spectrum of Complex 9 in the 2.7-4.1 ppm range](image)

**Figure SG21.** 1.3-2.5 ppm Complex 9

![NMR spectrum of Complex 9 in the 1.3-2.5 ppm range](image)
b. Cyclohexene Ligand Assignments
Identification of diastereotopic methylene groups and tungsten-bound methine groups (carbon shifts in parentheses) by HSQC data

Figure SG22. Complex 9 HSQC

|        | Bound methine protons:     |
|--------|----------------------------|
|        | H₁ 3.97 ppm (63.6 ppm)     |
|        | H₂ 2.34 ppm (62.3 ppm)     |
|        | Diastereotopic methylene groups: |
|        | Pair A: 1.59 & 1.50 ppm (22.9ppm) |
|        | Pair B: 1.64 & 1.50 ppm (23.7ppm) |
|        | Pair C: **                  |
|        | Pair D: **                  |

** data suggests that 3.13 & 3.38 (30.7) and 3.56 & 2.87 (30.4) are pairs, but difficult to confirm from HSQC data alone.
(Continued Analysis of Complex 9)

c. Methylene assignments by COSY data

**Figure SG23. Complex 9 COSY**

COSY correlations are present between:
- 2.87 & 3.56 ppm (Pair C)
- 3.13 & 3.38 ppm (Pair D)

*Pairs confirmed*

H$_1$ (3.97) correlates to 2.34 ppm (H$_2$) and 3.56 ppm (Pair C): “Pair C” $\to$ H$_6$ protons

H$_2$ (2.34 ppm) correlates to 3.97 (H1) and 3.38 ppm (Pair D): “Pair D” $\to$ H$_3$ protons

1.59 (Pair A) correlates with 2.87 & 3.56 (Pair C)

“Pair A” $\to$ H$_5$ protons

1.64 (Pair B) correlates with 3.38 (Pair D)

“Pair B” $\to$ H$_4$ protons

Endo/Exo assignments by NOESY

**Figure SG24. Complex 9. NOESY**

Signals present in both quadrants:

Peaks at 3.13 & 3.38 ppm (H$_3$ protons) correlate with 8.51 ppm (PzA H$_3$)

3.13ppm has a stronger signal: this indicates that 3.13ppm is H$_3$endo and 3.38 is H$_3$exo

Peak at 1.64 (H$_4$) correlates weakly with 8.51ppm (PzA H$_3$)
This suggests that 1.64ppm signal is $H_{4\text{endo}}$
(Continued Analysis of Complex 9)

**Figure SG25.** Complex 9 NOESY (upper right quadrant)

The H₁ signal (3.97 ppm) correlates with: 3.56 (strong, H₆), 2.87 (weak, H₆), 2.34 ppm (strong, H₂)

→ This indicates 3.56 ppm is H₆exo, and 2.87ppm is H₆endo

The H₂ signal (2.34 ppm) correlates with: 3.97 (strong, H₁), 3.38 (strong, H₃), 3.13 (weak H₃)

→ This indicates that 3.38 ppm is H₃exo, and 3.13ppm is H₃endo

Note: this assignment also agrees with Tp NOE interaction data

**Correlations of H6 protons**

H₆exo (3.56ppm) correlates with 3.97, 2.87, and 1.59 ppm (strong, H₃), 1.50ppm (weak, H₃)

H₆endo (2.87ppm) correlates with 3.97, 3.56, and 1.59 ppm (weak, H₃), 1.50ppm (strong, H₃)

This suggests that hydrogens corresponding to 3.56, 1.59ppm are on same side of the cyclohexene ring (exo), and that hydrogens corresponding to 2.87, 1.50ppm are on the same side of this ring (endo).

**Correlations of H3 protons**
H$_{3\text{exo}}$ (3.38ppm) correlates with signals at 3.13, 2.34, and 1.64 ppm (weak, H$_4$), 1.50 (strong, H$_4$)

H$_{3\text{endo}}$ (3.13ppm) correlates with signals at 3.38, 2.34, and 1.64 ppm (strong, H$_4$), 1.50 (weak, H$_4$)

This suggests that protons corresponding to 3.38, 1.50ppm are on same side of the ring (exo) and that protons corresponding to 3.13, 1.64 ppm are on same side (endo)

**Correlations of PMe$_3$**
The signal for PMe$_3$ (1.29 ppm) correlates with those at 3.97 ppm (strong, H$_1$), 3.56 (weak, H$_6$), and 2.87 (strong, H$_6$).

These data indicate that the signal at 2.87ppm corresponds to H$_{6\text{endo}}$

**Correlations of NOMe**
NOMe (4.03 ppm) correlates with 3.13 (H$_3$), 1.64 (H$_4$), 1.50 (H$_5$), 1.29 ppm (PMe$_3$)

These data indicate that the three ring protons 3.13 (H$_3$), 1.64 (H$_4$), and 1.50 ppm (H$_5$) are endo

d. **Final $^1$H NMR Assignments for Complex 9**

| H$_1$ (ppm) | H$_2$ (ppm) | H$_3$ (ppm) | H$_4$ (ppm) | H$_5$ (ppm) | H$_6$ (ppm) |
|------------|------------|------------|------------|------------|------------|
| 3.97       | 2.34       | endo       | 3.13       | 1.64       | 1.50       | 2.87       |
|            | exo        | 3.38       | 1.50       | 1.59       | 3.56       |

**Tp Ligand**

|          | H$_3$ (ppm) | H$_4$ (ppm) | H$_5$ (ppm) |
|----------|------------|------------|------------|
| PzA      | 8.51       | 6.48       | 7.92       |
| PzB      | 8.11       | 6.55       | 8.01       |
| PzC      | 7.47       | 6.33       | 7.92       |

**PMe$_3$:** 1.29 ppm

**NOMe:** 4.03 ppm

Stereochemical assignments are further corroborated by quantitative NOE data, XRD and neutron diffraction crystal structure data (see below).
5. 1D NOESY Spectra analysis of Complex 9

Technical: Data were collected on a 600 MHz Varian NMR and experiments were conducted in CDCl₃. Each spectral run utilized a 500 ms mixing time. The irradiated resonance integration was set to 1000. Inverted spectral signals indicated through space NOE interactions between the irradiated peak and protons at the indicated positions. Larger integrations for the inverted proton signals indicated stronger NOE interactions (and therefore closer H-H distances).

Figure SG26. Irradiation of Tp₃A Resonance

Figure SG27. Spectra of Protons that Display NOE Interactions with the Tp₃A Resonance
Figure SG28. Irradiation of H_{endo} Resonance

Figure SG29. Spectra of Protons that Display NOE Interactions with the H_{endo} Resonance

H_{endo} shows stronger correlations to PMe₃ and NOMe resonances via NOE interactions than when H_{exo} is irradiated.

H_{endo} shows decreased NOE interaction with H₁ resonance (compared to NOE between H₁ and H_{exo} resonance when the latter is irradiated.)
Figure SG30. Irradiation of H_{exo} Resonance

Figure SG31. Spectra of Protons that Display NOE Interactions with the H_{exo} Resonance

H_{exo} resonance shows enhanced NOE to H_{endo} resonance compared to spectra resulting from H_{endo} irradiation spectra. H_{exo} also shows less NOE interaction to PMe$_3$ resonance compared to H_{endo} irradiated spectra.

These data support original assignment of H_{endo} vs. H_{exo} assignments.

S123
Figure SG32. Irradiation of H$_{\text{exo}}$ Resonance

Figure SG33. Spectra of Protons that Display NOE Interactions with the H$_{\text{exo}}$ Resonance
Figure SG34. Irradiation of H$_{\text{endo}}$ Resonance

Figure SG35. Spectra of Protons that Display NOE Interactions with the H$_{\text{endo}}$ Resonance
Figure SG36. Irradiation of H₁ Resonance

Figure SG37. Spectra of Protons that Display NOE Interactions with the H₁ Resonance
H. Confirmation of Stereochemical Assignment of Complex 9 from One-Dimensional NOE Data

Quantitative NOE determinations for compound 9

Estimates for the interproton distances for the cyclohexene ligand of 9, [WTP(NOMe)(PMMe)(η²-1,2-cyclohexene)](OTf), were estimated via quantitative NOE experiments so as to confirm the assigned resonances of protons on the cyclohexene ligand (i.e. protons on sp3 carbons that are exo or endo, relative to the metal). Quantitative NOE data was combined with bond lengths experimentally determined from single crystal X-ray diffraction data for 9, using the dominant conformation of the cyclohexene ring. Mixing time was set at 500 ms.

Only H1, H2, H3exo, H3endo and H6exo, H6endo gave isolated resonances in CDCl3 (no overlap with signals).3

Experimental proton-proton distances from crystallographic data are compared with estimated distances derived from 1D NOE data in the table below. This comparison provides additional evidence supporting the proton NMR assignments for the ligand of 9. Error in the distance determination ranged from 0-19%, with most values being under 10%, in strong support of the original assignments. Average error: 8.7% (conformation A; major conformer)

For comparison, we also did this analysis using contra-indicated assignments of stereochemistry (reversing endo and exo assignments) to determine the significance of the error analysis. Here, errors ranged from 11-44%, with 7 out of 9 values being 20% or greater. Average error: 28.3% (conformation A; major conformer)

Note on conformational disorder:

The crystal structure determination of 9 by X-ray diffraction shows significant disorder around the C4, C5 and C6 carbons indicating that the cyclohexene ligand exists as two different conformers in the crystal. DFT calculations suggest a minimal energy difference between the two conformers. Therefore, the solution NMR spectra may reflect an average of more than one conformer in solution.

Proton distances estimated by the 1D NOESY experiments are in closer agreement with the distances obtained from the major conformer in the X-ray structure than they are from those of the minor conformer, and the former are the values reported in the table below. We note that minor conformers of small organic compounds have been demonstrated to significantly alter calculated interproton distances. We propose that the existence of a minor conformation is partly responsible for the errors observed between calculated and observed proton distances. See reference 4 for the impact of minor amounts of conformational isomers on the estimation of interproton distances.
## Table SH1. NOE analysis for conformer A

### For Conformer A

| atom 1 atom 2 | Crystal Structure Distance (Å) | NOE Predicted Distance (Å) | % Error |
|---------------|-------------------------------|---------------------------|---------|
| Tp3A Tp4A     | 2.52                          | NA                        | NA      |
| Tp3A H₃exo    | 3.20                          | 2.60                      | 10%     |
| Tp3A H₃endo   | 1.91                          | 2.11                      | 19%     |

| atom 1 atom 2 | Crystal Structure Distance (Å) | NOE Predicted Distance (Å) | % Error |
|---------------|-------------------------------|---------------------------|---------|
| H₃exo H₃endo  | 1.60                          | NA                        | NA      |
| H₃ H₃endo     | 2.79                          | 2.49                      | 11%     |

| atom 1 atom 2 | Crystal Structure Distance (Å) | NOE Predicted Distance (Å) | % Error |
|---------------|-------------------------------|---------------------------|---------|
| H₃exo H₃endo  | 1.60                          | NA                        | NA      |
| H₃ H₃exo      | 2.25                          | 2.11                      | 6%      |

| atom 1 atom 2 | Crystal Structure Distance (Å) | NOE Predicted Distance (Å) | % Error |
|---------------|-------------------------------|---------------------------|---------|
| H₃exo H₃endo  | 1.60                          | NA                        | NA      |
| H₃ H₂         | 2.21                          | 1.97                      | 11%     |

| atom 1 atom 2 | Crystal Structure Distance (Å) | NOE Predicted Distance (Å) | % Error |
|---------------|-------------------------------|---------------------------|---------|
| H₃exo H₃endo  | 1.60                          | NA                        | NA      |
| H₃endo Tp3A   | 1.91                          | 1.79                      | 6%      |

| atom 1 atom 2 | Crystal Structure Distance (Å) | NOE Predicted Distance (Å) | % Error |
|---------------|-------------------------------|---------------------------|---------|
| H₂ H₁         | 2.20                          | NA                        | NA      |
| H₃exo H₂      | 2.21                          | 2.21                      | 0%      |

| atom 1 atom 2 | Crystal Structure Distance (Å) | NOE Predicted Distance (Å) | % Error |
|---------------|-------------------------------|---------------------------|---------|
| H₂ H₁         | 2.20                          | NA                        | NA      |
| H₃exo H₁      | 2.26                          | 2.33                      | 4%      |
| Tp3C H₁       | 2.2                           | 1.87                      | 15%     |

### For Conformer B

| atom 1 atom 2 | Crystal Structure Distance (Å) | NOE Predicted Distance (Å) | % Error |
|---------------|-------------------------------|---------------------------|---------|
| H₃exo H₃endo  | 1.59                          | NA                        | NA      |
| H₁ H₃endo     | 2.58                          | 2.47                      | 3%      |

| atom 1 atom 2 | Crystal Structure Distance (Å) | NOE Predicted Distance (Å) | % Error |
|---------------|-------------------------------|---------------------------|---------|
| H₃exo H₃endo  | 1.59                          | NA                        | NA      |
| H₁ H₃exo      | 2.27                          | 2.09                      | 8%      |
Contra-indicated Assignments for Complex 9: analysis using quantitative NOE data

NOTE: The data summarized below represent INVERTED stereochemical assignments, used for comparison with what we believe to be the correct assignments (see previous page). HSQC data confirms the carbon associations (vide infra) of all ring protons for 9, but exo/endo assignments rely on NOE data. If the assignment of endo/exo protons for the diastereotopic methylene protons on a given carbon of the cyclohexene ring is inverted, there is an increase in the observed % error between each predicted proton-proton distance and its agreement with crystal structure data.

The only value that stays the same between both the Correct and Inverted Assignment Distances is the distance approximated between H_{exo} and H1 (both measurements give ~11% error between observed proton-proton distance in the crystal structure).
Table SH.2 NOE analysis for conformer A, inverted assignments.

### For Conformer A (Inverted Assignments)

| Atom 1  | Atom 2  | Crystal Structure Distance (Å) | NOE Predicted Distance (Å) | % Error |
|---------|---------|--------------------------------|---------------------------|---------|
| Tp3A    | Tp4A    | 2.52                           | NA                        | NA      |
| Tp3A    | Hexo    | 3.20                           | 2.60                      | 36%     |
| Tp3A    | Hbendo  | 1.91                           | 2.11                      | 34%     |
| Hexo    | Hbendo  | 1.60                           | NA                        | NA      |
| H1      | Hbendo  | 2.79                           | 2.49                      | 11%     |
| Hexo    | H3      | 1.60                           | NA                        | NA      |
| H1      | Hexo    | 2.25                           | 2.11                      | 25%     |
| H3      | H2      | 2.61                           | 1.97                      | 25%     |
| Hbendo  | H3      | 1.60                           | NA                        | NA      |
| Hbendo  | H2      | 2.61                           | 2.74                      | 24%     |
| Hbendo  | Tp3A    | 1.91                           | 1.79                      | 44%     |
| H2      | H1      | 2.20                           | NA                        | NA      |
| H3      | H2      | 2.61                           | 2.21                      | 40%     |

### For Conformer B (Inverted Assignments)

| Atom 1  | Atom 2  | Crystal Structure Distance (Å) | NOE Predicted Distance (Å) | % Error |
|---------|---------|--------------------------------|---------------------------|---------|
| Hexo    | Hbendo  | 1.59                           | NA                        | NA      |
| H1      | Hbendo  | 2.27                           | 2.47                      | 9%      |
| Hexo    | Hexo    | 1.59                           | NA                        | NA      |
| H1      | Hexo    | 2.56                           | 2.09                      | 18%     |
I. Structural Determination by Single Crystal X-Ray and Neutron Diffraction

Single crystal X-ray diffraction

Single crystals of 4, 7 and 9 were coated with Paratone oil and mounted on a MiTeGen MicroLoop. The X-ray intensity data were measured on a Bruker Kappa APEXII Duo system. A graphite monochromator and a Mo Kα fine-focus sealed tube ($\lambda = 0.71073$ Å) were used for 4 and 7. An Incoatec Microfocus IµS (Cu Kα, $\lambda = 1.54178$ Å) and a multilayer mirror monochromator were used for 9. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. Data were corrected for absorption effects using the Multi-Scan method (SADABS). The structures were solved and refined using the Bruker SHELXTL Software Package within APEX3 and OLEX2. Non-hydrogen atoms were refined anisotropically. The B-H hydrogen atom in 4 and 7 were located in the diffraction map and refined isotropically. All other hydrogen atoms were placed in geometrically calculated positions with $U_{iso} = 1.2U_{eq}$ of the parent atom ($U_{iso} = 1.5U_{eq}$ for methyl). In 7, the cyclohexene ring was disordered over two positions. The relative occupancy of the disordered atoms was freely refined. Constraints were used on the anisotropic displacement parameters of the disordered atoms, and restraints were used on the disordered bonds. In 9, one carbon atom in the ring was found to be disordered over two positions. The relative occupancies were freely refined and constraints were used on the anisotropic displacement parameters of the disordered atoms. Disorder modeling of the triflate CF$_3$ group was attempted, but nothing was found to improve it significantly so it was left as is.

Report on the disorder in the molecular structure determination of Complex 9

A yellow rod-like specimen of C$_{20}$H$_{12}$BF$_3$N$_7$O$_4$PSW, approximate dimensions 0.082 mm x 0.092 mm x 0.135 mm, was coated with Paratone oil and mounted on a MiTeGen MicroLoop. The X-ray intensity data were measured on a Bruker Kappa APEXII Duo system equipped with an Incoatec Microfocus IµS (Cu Kα, $\lambda = 1.54178$ Å) and a multilayer mirror monochromator.

The total exposure time was 17.66 hours. The frames were integrated with the Bruker SAINT software package (Bruker (2012). *Saint; SADABS; APEX3*. Bruker AXS Inc.) using a narrow-frame algorithm. The integration of the data using a triclinic unit cell yielded a total of 13453 reflections to a maximum $\theta$ angle of 68.85° (0.83 Å resolution), of which 5018 were independent (average redundancy 2.681, completeness = 97.4%, $R_{int} = 9.76\%$, $R_{merge} = 10.23\%$) and 3778 (75.2%) were greater than 2$\sigma$(F$^2$). The final cell constants of $a = 10.2029(10)$ Å, $b = 11.9606(15)$ Å, $c = 13.3666(14)$ Å, $\alpha = 65.417(9)^\circ$, $\beta = 82.701(8)^\circ$, $\gamma = 69.064(8)^\circ$, volume = 1385.1(3) Å$^3$, are based upon the refinement of the XYZ-centroids of 6197 reflections above 20 $\sigma$(I) with 7.271° < $\theta$ < 136.1°. Data were corrected for absorption effects using the numerical method (SADABS). The ratio of minimum to maximum apparent transmission was 0.589. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.4666 and 0.7921.

The structure was solved and refined using the Bruker SHELXTL Software Package within APEX3 and OLEX2, using the space group P -1, with Z = 2 for the formula unit, C$_{20}$H$_{12}$BF$_3$N$_7$O$_4$PSW. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in geometrically calculated positions with $U_{iso} = 1.2U_{eq}$ of the parent atom ($U_{iso} = 1.5U_{eq}$ for methyl). One carbon atom in the ring was found to be disordered over two positions. The relative occupancies were freely refined and constraints were used on the anisotropic displacement parameters of the disordered atoms. Disorder modeling of the triflate CF$_3$ group was attempted, but nothing was found to improve it significantly so it was left as is. The final anisotropic full-matrix least-squares refinement on F$^2$ with 351 variables converged at R1 = 7.36%, for the observed data and wR2 = 21.70% for all data. The goodness-of-fit was 1.077. The largest peak in the final difference electron density synthesis was 2.100 e/Å$^3$ and the largest hole was -2.904 e/Å$^3$ with an RMS deviation of 0.223 e/Å$^3$. On the basis of the final model, the calculated density was 1.796 g/cm$^3$ and F(000), 740 e$^-$. 

Single crystal neutron diffraction.
Neutron diffraction data for W(Tp)(NO)(PMe$_3$)(η$_2$-cis-3,4-dideutero-cyclohexene), 45-d$_2$, were measured on the TOPAZ single-crystal time-of-flight Laue diffractometer at the Spallation Neutron Source (SNS), Oak Ridge National Laboratory. A block-shaped crystal of 45-d$_2$, with dimensions of 0.30 × 0.35 × 0.50 mm was mounted on the tip of a MiTeGen loop using fluorinated grease and transferred to the TOPAZ goniometer for data collection at 100 K. To ensure good coverage and redundancy, data were collected using crystal orientations optimized with CrystalPlan software for optimal coverage of symmetry-equivalent reflections of the monoclinic cell. The integrated raw Bragg intensities were obtained using the 3-D ellipsoidal Q-space integration in accordance with previously reported methods. Data reduction, including neutron TOF spectrum, Lorentz, and detector efficiency corrections, was carried out with the ANVRED3 program. Spherical absorption correction was applied with $\mu = 0.1433 + 0.1805 l$ mm$^{-1}$.

The reduced data were saved as SHELX HKLF2 format, in which the wavelength is recorded separately for each reflection, and data were not merged. Starting with the X-ray structure at 100 K as an input model, the neutron crystal structure was refined using the SHELXL-2018/3 program.

**Table SI.1 Crystal Data for the X-ray diffraction structures 4, 7 and 9, and the neutron diffraction structure 45.**

|                  | 4   | 7   | 9   | 45             |
|------------------|-----|-----|-----|----------------|
| **CCDC**         | 1885723 | 1885724 | 1885725 | 1972890        |
| **Chemical formula** | C$_{21}$H$_{33}$BN$_7$O$_2$PW | C$_{18}$H$_{29}$BN$_7$OPW | C$_{20}$H$_{32}$BF$_3$N$_7$O$_4$PSW | C$_{18}$H$_{27.16}$BD$_{1.84}$N$_7$OPW |
| **FW (g/mol)**   | 641.17 | 585.11 | 749.21 | 586.96         |
| **T (K)**        | 150(2) | 100(2) | 100(2) | 100(2)         |
| **Crystal size (mm)** | 0.71073 | 0.71073 | 1.54178 | 0.40 – 3.46 |
| **Crystal habit** | yellow block | yellow block | yellow rod | yellow block |
| **Crystal system** | monoclinic | monoclinic | triclinic | monoclinic |
| **Space group**  | P 2$_1$/c | P 2$_1$/n | P -1 | P 2$_1$/n |
| **a (Å)**        | 11.5210(7) | 8.6369(10) | 10.2029(10) | 8.6247(6)   |
| **b (Å)**        | 15.1962(10) | 15.2743(17) | 11.9605(15) | 15.2535(10) |
| **c (Å)**        | 15.1514(10) | 17.0360(19) | 13.3686(14) | 17.0072(12) |
| **α (°)**        | 90 | 90 | 65.417(9) | 90 |
| **β (°)**        | 153.9590(10) | 97.190(2) | 82.701(8) | 97.164(7) |
| **γ (°)**        | 90 | 90 | 69.064(8) | 90 |
| **V (Å$^3$)**    | 2574.3(3) | 2229.8(4) | 1385.1(3) | 2219.9(3) |
| **Z**            | 4 | 4 | 2 | 4 |
| **ρcalc (g/cm$^3$)** | 1.654 | 1.743 | 1.796 | 1.756 |
| **μ (mm$^{-1}$)** | 4.581 | 5.276 | 9.520 | 0.1433 + 0.1805 × $\lambda$. |
| $\theta$ range ($^\circ$) | 1.93 to 29.59 | 1.80 to 36.34 | 3.64 to 68.85 | 7.687 to 78.007 |
|--------------------------|----------------|----------------|----------------|-----------------|
| Index ranges             | -16 $\leq h \leq$ 15 | -14 $\leq h \leq$ 14 | -12 $\leq h \leq$ 12 | -12 $\leq h \leq$ 12 |
|                          | -21 $\leq k \leq$ 17 | -25 $\leq k \leq$ 25 | -12 $\leq k \leq$ 14 | -21 $\leq k \leq$ 21 |
|                          | -20 $\leq h \leq$ 21 | -28 $\leq h \leq$ 28 | -16 $\leq h \leq$ 16 | -23 $\leq h \leq$ 24 |
| Reflns coll.             | 30092           | 75222          | 13453          | 12475           |
| Ind. reflns              | 7224 [R(int) = 0.0254] | 10831 [R(int) = 0.0255] | 5018 [R(int) = 0.0976] | 3653 [R(int) = 0.1099] |
| Data / restraints /     | 7224 / 0 / 307   | 10831 / 3 / 276 | 5018 / 0 / 351 | 3653 / 17 / 518 |
| parameters              |                |                |                |                  |
| Goodness-of-fit on F$^2$ | 1.047          | 1.054          | 1.077          | 1.290           |
| $R_1$ [F>2$\sigma$(F)]  | 0.0171          | 0.0153         | 0.0736         | 0.0959          |
| wR$_2$ [all data]       | 0.0392          | 0.0344         | 0.2170         | 0.1330          |

**Figure S11.** ORTEP drawing of the molecule of 45-$d_2$. Carbon atoms C12, C13, C14, C15 / C12B, C13B, C14B, C15B of the cyclohexene ring with attached hydrogen/deuterium atoms are disordered over two positions; the site occupancy factors refined to 0.885 (2) and 0.115 (2) for the disordered carbon atoms on the two conformers. Atom displacement ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.
Figure SI2. Omit map showing the nuclear scattering density of the missing deuterium D14, D15 (positive: yellow) and H14A, H15B hydrogen (negative: cyan) atoms in cis configuration of the neutron structure of 45-d2. Site occupancies from neutron diffraction: \{0.812(3) / 0.073(3)\} for \{D14 / H14B\} on C14, \{0.817(3) / 0.068(3)\} for \{D15 / H15A\} on C15 in the major component of the cyclohexene-d2 ring. Atom displacement ellipsoids are drawn at the 50% probability level. Hydrogen atoms except those on the cyclohexene-d2 group are shown as sticks for clarity.

**Conclusion:** deuterium positions are consistent with assignments determined from NMR data.

**J. Estimates of Isotopic Purity Using Various Techniques**

Detailed estimates of deuterium integration utilizing high resolution mass spectrometry (HRMS) are provided in **Figure S6**. Deuterium occupancy at stereospecific sites on the cyclohexene ring is determined primarily from 1H NMR data (relying on the suppression of proton resonances that have been substituted for a deuterium in complex 9: **Table S3**). As a confirmation of the stereochemical analysis in S3, several isotopomers of 9 (derived from complexes 42, 45, 14, 50 and 16), were also analyzed by Molecular Rotation Resonance (MRR) spectroscopy through the analysis of their deuterated cyclohexene ligand. Compounds of the form 9 – d_n were heated at 200 °C, which caused a portion of the cyclohexene ligand to be liberated. The free cyclohexene was then analyzed by MRR spectroscopy. Details on the MRR technique and analysis are described in a separate document (MRR Supporting Materials). It’s important to note that while the major observed cyclohexene species in all MRR measurements corresponds to the stereoisotopomer predicted by NMR data, some isotopic scrambling was observed during the heating process used to liberate the cyclohexene ligand. The major mechanisms that accounts for the rearrangement appears to be a shift of the alkene bond. The amount of scrambling was affected by the temperature used to release the cyclohexene ligand, the amount of oxygen exposure of the metal complex before MRR analysis, and potentially to solvent impurities. Thus, % composition presented in Table SJ1 should be considered a lower limit for the anticipated stereoisotopomer.

In the case of the sample 45-d2, crystals were grown which were subjected to neutron diffraction. The same material used in the diffraction study was then dissolved and treated with methyl triflate to give the methylated nitrosyl complex isotopologue (9). While neutron diffraction and 1H NMR spectroscopy give >90% deuterium occupancy at the H3exo and H4exo positions, MRR analysis shows significant loss of isotopic purity, again due to the thermal
decomplexation process used in MRR analysis. Studies regarding the efficient liberation of the cyclohexene organic using oxidants and subsequent analysis by MRR spectroscopy are forthcoming. Table SJ1 provides a composite of the findings for all three analytical methods (HNMR, neutron diffraction, and MRR). All MRR percentages below represent lower limits (owing to the scrambling process that accompanies thermal decomplexation (200 °C) of the cyclohexene.

**Table SJ1.** Deuterium occupancy and percentage composition of various isotopomers and isotopologues.

| Desired Complex | Deuterium Occupancy (NMR) | Percentage of Desired Isotopologue (HRMS) | Percentage of Desired Isotopologue (MRR) (relative to other stereoisotopomers) |
|-----------------|---------------------------|------------------------------------------|--------------------------------------------------------------------------------|
| ![Desired Complex](image) | ![Deuterium Occupancy (NMR)](image) 95% | ![Percentage of Desired Isotopologue (HRMS)](image) 99% >95% | ![Percentage of Desired Stereoisotopomer (MRR)](image) >95% |
| ![Desired Complex](image) | ![Deuterium Occupancy (NMR)](image) 95% 92% | ![Percentage of Desired Isotopologue (HRMS)](image) NA >60% | ![Percentage of Desired Stereoisotopomer (MRR)](image) >66% |
| ![Desired Complex](image) | ![Deuterium Occupancy (NMR)](image) 95% | ![Percentage of Desired Isotopologue (HRMS)](image) NA >82% | ![Percentage of Desired Stereoisotopomer (MRR)](image) >76% |
| ![Desired Complex](image) | ![Deuterium Occupancy (NMR)](image) 95% | ![Percentage of Desired Isotopologue (HRMS)](image) 96% >78% | ![Percentage of Desired Stereoisotopomer (MRR)](image) 100% |
| ![Desired Complex](image) | ![Deuterium Occupancy (NMR)](image) 72% 28% | ![Percentage of Desired Isotopologue (HRMS)](image) 76% >57% | ![Percentage of Desired Stereoisotopomer (MRR)](image) 100% |

Notes:
1. * Difficulty in achieving > 90% deuteration of 4. In this case, estimates of the entire isotopologue distribution are presented instead of occupancy.
2. Samples for HRMS were prepared analogously to those of other methods but these values were prepared from different samples of the same isotopomers.
3. NMR and MRR experiments (and when possible, neutron diffraction) were performed on the same metal-cyclohexene isotopomer samples.
4. " >" Designation implies that the observed free cyclohexene isotopomer by MRR analysis should be regarded as a lower limit of the isotopomer when bound to the metal. For example, in the case of 45, NMR and Neutron Diffraction both give estimates of deuterium occupancy> 90% at the indicated positions. The analysis by MRR, due to the conditions under which the cyclohexene was decomplexed, shows significant scrambling and loss of isotopic purity. Thus the observed species by MRR is a lower limit of the cyclohexene isotopomer observed on the metal BEFORE the scrambling observed in the MRR analysis.
K. Determination of KIE for protonation of 4.

Solutions of HOTf/MeOD were prepared after drying glass pipette and three 4-dram vials in a 150 °C oven overnight. This glassware was then brought into an inert atmosphere (N₂(g)) glovebox. Each of these vials was rinsed with ~ ½ mL of MeOD, dried with a stream of N₂(g) and then 3%, 5% and 10% (mole percent) solutions of HOTf in MeOD were prepared by mass. The goal was to generate known quantities of proto-impurities at various known concentrations to gauge the KIE associated with deuteration after observing difficulty in fully deuterating either 4 or 5 with an acidic deuterium source. Protonation experiments were conducted at -30 °C on 4, the same temperature that protonation was performed at in the synthesis of these complexes. The results were then incorporated into the following equation and solved for the KIE value:

Equation SK1

\[
\text{Theoretical Proton Suppression} \times \text{KIE} = \frac{\text{Theoretical Proton Impurity}}{\text{Observed Proton Suppression}} = \frac{\text{Observed Proton Impurity}}{\text{KIE}}
\]

This equation seeks to determine the KIE by extrapolating the k_H/k_D ratio as a result of observed products distributions in the resulting ¹H NMR. Further discussion on the determination of KIE values can be found in reference 5.

| Theoretical ¹H Impurity | Observed ¹H Impurity | KIE Determination |
|-------------------------|----------------------|------------------|
| 3%                      | 49%                  | 31               |
| 5%                      | 57%                  | 40               |
| 10%                     | 82%                  | 41               |

These results give an average KIE ~ 37.

Analogous experiments with treating 1 with varying amounts of H⁺ impurity in MeOD led to the expected suppression of the proto-signal (i.e., there was not a significant kinetic isotope effect).

Experiment A: 3% Proton Impurity

To a 4-dram vial that had been rinsed with MeOD-d₄ (~ ½ mL) and subsequently dried with N₂(g) was added HOTf (0.131 g, 0.873 mmol) along with MeOD-d₄ (0.997 g, 27.6 mmol) to generate a solution with an estimated 3.1% proton impurity given the ratios of HOTf and MeOD-d₄ in solution. At ambient temperatures the rate of protonation of methanol by triflic acid is estimated as being diffusion controlled. Next complex 4 (0.101 g, 0.173 mmol) was added to MeCN-d₃ (1/2 mL) and cooled to -30 °C. Separately the 3.1 % proto-impurity solution of HOTf/MeOD-d₄ was also cooled to -30 °C. This acidic solution was then added in excess (1/2 mL) to the chilled solution of 4 in MeCN-d₃. Upon addition the reaction mixture turns to a homogeneous yellow color, and this solution was then added to 15 mL of ether and allowed to cool at -30 °C. Over a period of 1 h a yellow crystalline material develops on the side of the vial. The organic layer was decanted, the resulting solid dried with N₂(g) stream and analyzed via ¹H NMR in MeCN-d₃ to give the observed 49% proton impurity.

Once isolated, the product, 26, displays no isotopic scrambling is observed when the complex is re-dissolved in MeCN-d₃ over a week.

Experiment B: 5% Proton Integration

To a 4-dram vial that had been rinsed with MeOD-d₄ (~ ½ mL) and subsequently dried with N₂(g) was added HOTf (0.224 g, 1.49 mmol) along with MeOD-d₄ (1.03 g, 28.6 mmol) to generate a solution with an estimated 5.0% proton
impurity given the ratios of HOTf and MeOD- in solution. At ambient temperatures the rate of protonation of methanol by triflic acid is estimated as being diffusion controlled. Next complex 4 (0.100 g, 0.172 mmol) was added to MeCN-d3 (1/2 mL) and cooled to -30 °C. Separately the 5.0 % proto-impurity solution of HOTf/MeOD- was also cooled to -30 °C. This acidic solution was then added in excess (1/2 mL) to the chilled solution of 4 in MeCN-d3. Upon addition the reaction mixture turns to a homogeneous yellow color, and this solution was then added to 15 mL of ether and allowed to cool at -30 °C. Over a period of 1 h a yellow crystalline material develops on the side of the vial. The organic layer was decanted, the resulting solid dried with N2(g) stream and analyzed via 1H NMR in MeCN-d3 to give the observed 57% proton impurity at the site of protonation/deuteration.

**Experiment C: 10% Proton Integration**

To a 4-dram vial that had been rinsed with MeOD-d4 (~ ½ mL) and subsequently dried with N2(g) was added HOTf (0.465 g, 3.10 mmol) along with MeOD-d4 (0.998 g, 27.7 mmol) to generate a solution with an estimated 10.1% proton impurity given the ratios of HOTf and MeOD in solution. At ambient temperatures the rate of protonation of methanol by triflic acid is estimated as being diffusion controlled. Next complex 4 (0.100 g, 0.172 mmol) was added to MeCN-d3 (1/2 mL) and cooled to -30 °C. Separately the 10.1 % proto-impurity solution of HOTf/MeOD-d3 was also cooled to -30 °C. This acidic solution was then added in excess (1/2 mL) to the chilled solution of 4 in MeCN-d3. Upon addition the reaction mixture turns to a homogeneous yellow color, and this solution was then added to 15 mL of ether and allowed to cool at -30 °C. Over a period of 1 h a yellow crystalline material develops on the side of the vial. The organic layer was decanted, the resulting solid dried with N2(g) stream and analyzed via 1H NMR in MeCN-d3 to give the observed 82% proton impurity protonation/deuteration.

**Experiment D: Nominal 1% Impurity**

When approximately a 1% H+ solution is prepared DPhAT-d2 (0.147 g, 0.456 mmol) with 99% MeOD (2.30 g, 69.6 mmol) in excess is allowed to react with complex 12 (0.221 g, 0.378 mmol) followed by a deuteride source, NaBD4 (0.075 g, 1.81 mmol), at reduced temperatures (-40 C), complex 16 is generated. The site of initial protonation, now the H5-endo resonance, shows ~ 95% proton suppression, implying a mild KIE for the initial protonation. Full determination is obfuscated by overlapping signals.

However, at the H6-exo position, the proton resonance is expected to be suppressed from the second deuteration with an acidic deuterium source, a 28% proton signal remains.

Solving Equation SK1, using 1% for the expected proton resonance and 28% for the observed impurity, yields an approximated KIE of ~38.5, similar to the averaged KIE from previous experiments. A separate sample of 16 prepared by an analogous route and subjected to HRMS shows ~ 24%, % proton impurity, consistent with what is observed by NMR (and indicating difficulty in attaining > 90% levels of deuteration at the H6-exo site) (Figure SK1).
Figure SK1. HNMR spectrum of compound 16 showing incomplete deuterium incorporation at H6exo.

Integration of the proton resonance at 3.55 (the H6exo resonance) was used to determine the KIE of the 1% proton solution (99% D). This is the expected site of deuteration arising from the treatment of the diene complex 4 with DPhAT-d2/MeOD.

The proton resonances at 1.60 (H4endo) and 1.55 (H5exo) are shifted upfield due to secondary isotopic shifts. Residual protons signals from (H4exo) and (H5endo) resonances that would arise from incomplete deuteration at those sites are estimated to be < 10%.

I. Summary of MRR spectroscopic analysis for samples 9-dn as derived 42, 45, 14, 50 and 16

Introduction
Molecular rotational resonance spectroscopy is used to identify and quantitate the relative abundance of the deuterated isomers of cyclohexene. The exceptionally high spectral resolution of spectrometers for rotational spectroscopy make it possible to analyze complex sample mixtures without the need for chemical separation. The spectrum is measured for a gas phase sample produced by pulsed-jet expansion of a dilute mixture of the analyte in an inert gas (neon is used in these measurements). As a result, there are no matrix effects on the transition frequencies and once the signature of a deuterated isotopomer is known, it can be identified to extremely high confidence in other samples by transition frequency. All isotopomers are detected against zero-background and the measurement dynamic range exceeds 100:1 for the samples in this study.

Measurement Principles
The deuterium isomer composition of cyclohexene is analyzed using molecular rotational resonance (MRR) spectroscopy after cyclohexene is removed from the metal by thermal decomposition. The MRR spectrum signature is a sensitive function of the mass distribution relative to the center-of-mass. The spectrum depends on the principal moments-of-inertia, which are inversely proportional to the rotational constants of the rigid-rotor Hamiltonian operator for rotational kinetic energy, and the dipole moment vector in the principal axis system. In the spectrum, the geometry (from which the principal moments-of-inertia can be calculated) determines the quantized energies and the dipole moment determines the transition intensities for allowed rotational transitions. A specific isotopomer of cyclohexene is identified by the comparison between measured rotational constants obtained from a fit using the experimental MRR transition frequencies and the rotational constants calculated from a theoretical structure. Under the Born-Oppenheimer approximation, all isotopomers have the same equilibrium geometry. The rotational kinetic energies depend on a molecular structure that includes zero-point vibrational energy effects, however, the
differences between the equilibrium and zero-point geometries is small. In practice, quantum chemistry is used to provide the initial geometry from the equilibrium structure and this geometry is slightly modified to match the experimental constants. The refined geometry has good accuracy for predicting the rotational constants of the different isotopologues and isotopomers. Transition intensities are needed to convert measured signal strengths into relative populations of the isomers. The dipole moment is calculated from quantum chemistry and is assumed to be the same for all isotopologues. Deuterium substitution does change the bond dipole of the substituted C-H bond, but these changes has been shown to be small and these effects are neglected in the present analysis.\textsuperscript{13}

Rotational Spectroscopy of Deuterated Isomers of Cyclohexene

Cyclohexene has 10 hydrogens and, therefore, there are 1024 different ways to distribute deuterium using a fixed geometry as the reference as seen in Figure SL1. However, not all of these isomers give unique rotational spectra due to the C\textsubscript{2} symmetry axis. Of the 1024 possible isomers, 992 of the geometries are pairs or rotationally equivalent geometries producing only 496 isomers with distinguishable rotational spectra. Using the atom labeling in Figure SL1, the geometries that are equivalent under C\textsubscript{2}-rotation are obtained by the following label changes: H1↔H7, H2↔H6, H3↔H8, H4↔H9, and H5↔H10. There are 32 species that yield identical structure for C\textsubscript{2}-rotation. Therefore, there are 528 different deuterium isomers that have distinguishable rotational spectra (see Table S2 in Supporting Information).

![Figure SL1. Geometry and labeling for cyclohexene conformations.](image)

Labeling convention of cyclohexene used in this document is shown at the top left. For rotationally distinct isotopomers, the positions the deuterium atoms are listed using the H-atom positions 1-10. When chemically distinct isotopomers are described, the carbon atom position (1-6) where the deuteration occurs is given. In most cases, each chemically distinct isotopomer occurs in two rotationally distinct forms due to the transient chirality associated with the ring pucker. The structure of (3)-cyclohexene-d\textsubscript{1} is shown at the top right. In this representation, the chirality of the asymmetric carbon is denoted with its Cahn-Ingold-Prelog notation. The chiral element of the ring pucker is denoted by the (+) notation which gives the slope of the C-C bond where the ring pucker transient chirality occurs. Due to its low interconversion barrier, racemization of the ring pucker chirality will occur so that the sample will have equal amounts of the two diastereomers. In most cases, these diastereomers are rotationally distinct. To determine the H-atom labeling for the diastereomer in the reference configuration, the mirror image of the racemized diastereomer is considered (enantiomers have identical rotational spectra). The mirror image structure is rotationally indistinct from the structure.
obtained by C2-rotation. As a result, the (2)-cyclohexene-d1 rotationally distinct isotopomer has a ring pucker diastereomer that is (1)-cyclohexene-d1.

Cyclohexene has a ring pucker geometry that adds an element of transient chirality. After cyclohexene is liberated from the transition metal, rapid equilibration between the ring pucker isomers occurs. As a result, for a specific deuterium isotopomer produced in the synthesis, there is the possibility that two rotationally distinct isomers will be present in the gas sample when analyzed by MRR spectroscopy. The identity of the second ring-pucker isomer can be determined examining the mirror image of the ring pucker isomer. Figure SL1 shows the ring pucker isomers that occur from the incorporation of deuterium in the carbon-3 position. The ring pucker of (+)-3R-cyclohexene-d1 (2)-d1 or (6)-d1) is (-)-3R-cyclohexene-d1. The enantiomer of this ring pucker is (+)-3S-cyclohexene-d1 ((1)-d1 or (7)-d1). This means that for deuterium incorporation at the 3C position, the two ring pucker isomers that will be observed using MRR are (2)-d1 and (1)-d1. This approach for determining the observed ring puckers also applies to cyclohexene with deuterium incorporated at more than one position. In terms of the reference geometry, the ring-pucker isomerization converts the following H-atom positions: H1→H2, H3→H4, H6→H7, H8→H9, with H5 and H10 unchanged. Finally, most of the possible deuterium isomers of cyclohexene are chiral. However, MRR spectroscopy cannot distinguish enantiomers in a direct measurement. Furthermore, the transition metal complexes used in this study are racemic so no enantiomeric excess is expected.

**Sample Preparation and MRR Spectroscopy Measurements**
The design of the chirped-pulse Fourier transform microwave spectrometer and the experimental principles have been described in detail previously. The technique is briefly summarized here, with emphasis on the sample preparation and MRR measurements unique to the cyclohexene complex that is the subject of this study.

Approximately 30 mg of the cyclohexene transition metal complex per measurement were loaded directly into three stainless steel reservoir nozzles as a solid (~10 mg/reservoir). The samples were stored under inert conditions prior to loading. Loading the sample required exposure to ambient conditions for several minutes before the reservoirs could be reinstalled in the spectrometer and flushed with neon gas. The reservoirs were heated to 60°C, and neon carrier gas was flowed over the reservoirs at 15 psig. Each nozzle was pulsed at 3 Hz and the presence of residual solvents (acetone, water) were monitored by their signatures in the MRR spectrum. The temperature was gradually ramped up to 100°C and pulsing continued until the sample was determined to be sufficiently free of solvent.

To liberate the cyclohexene from the metal complex, the reservoirs were heated to 200°C. The nozzles were not pulsed during this time to allow cyclohexene to accumulate and mix with the Neon carrier gas above the sample, the pressure of which was increased to 45 psig. After 20-30 minutes of heating, the reservoirs were cooled to 140°C, the maximum operating temperature for optimal performance of the pulsed nozzles. Each heating cycle liberated enough cyclohexene gas for ~100 valve pulses. During each injection of gas through the nozzle, the supersonic expansion was excited by a microwave pulse with a 4 µs frequency sweep and 8 free induction decay (FID) emissions were collected and coherently averaged in the time domain. Two different microwave pulses were employed in this study. A 6-18 GHz excitation provided broad spectral coverage to observe six rotational transitions for each cyclohexene isotopologue/isotopomer present in the sample. These six rotational transitions are sufficient to produce an accurate determination of the rotational constants of the isotopomer using nonlinear least squares fitting. The spectra used in the composition analysis were obtained by coadding 200-1000 FID averages in the time domain.

In addition to cyclohexene, other species originating from the metal complex ligands were identified in the MRR spectrum after heating. These thermal decomposition products include trimethyl phosphine and pyrazole (produced through thermal decomposition of theTp-ligand).

The measurement uncertainty for percentage sample composition determination by MRR spectroscopy has been estimated in two ways: 1) Uncertainty in the percentage of 13C-isotopomers in the commercial cyclohexene sample suing the same number of FID averages as a typical analysis in this work (13C is expected at 2% abundance due to the C2-rotation symmetry), and 2) the difference in transition intensity for the ring pucker isomer pairs of the observed, chemically distinct isotopomers (where racemization is expected to produce equal populations of the ring pucker isomers). From these experimental observations, the measurement uncertainty for percentage composition is estimated to be 10% of the reported value.

**The Refined Reference Geometry for Isotopomer Analysis of Cyclohexene**
The rotational constants of the parent species were first reported in 1968, but have been refit here using updated analysis programs. The rotational spectra of the singly-substituted 13C, doubly-substituted 13C, and singly-substituted D isotopomers were assigned in a measurement using a commercial cyclohexene sample. The spectra of each cyclohexene isotopomer were identified with high confidence by comparing the experimentally determined...
rotational constants from this broadband spectrum to those obtained from a quantum chemistry molecular structure (B3LYP D3BJ 6-311++G(d,p) using Gaussian 09). Summaries of the experimental fits for these carbon isotopomers are presented in Table SL1. The fit results for the singly-substituted deuterium isotopologues are listed in Table SL2 (where the rotational constants for all deuterium isotopomers identified in this study are summarized). The assigned transition frequencies for each species are given in Tables SL11-50. A single cyclohexene geometry is used to predict the rotational spectroscopy for all possible deuterium isomers. This geometry is refined from the quantum chemistry equilibrium geometry through a nonlinear least squares fit of the atom coordinates in the principal axis system to the rotational constants for all isotopomers identified in the initial measurement using a commercial sample of cyclohexene. The positions of the nuclei in the principal axis system of the normal species are given in Table SL3 for the reference geometry.
Table SL1. Spectroscopic constants determined for the carbon isotopologues of cyclohexene. Spectral assignments were done by fitting experimental transition to the rigid-rotor Hamiltonian using Pickett’s SPCAT/SPFIT analysis program. All species were observed in natural abundance in a commercial sample.

| Isomer | A (MHz) | B (MHz) | C (MHz) | N² | σ (kHz) |
|--------|---------|---------|---------|----|---------|
| Parent | 4739.1511(26) | 4544.4159(33) | 2562.3985(17) | 22 | 14.6 |
| 13C3-6 | 4738.774(25) | 4555.393(33) | 2534.0678(15) | 11 | 14.7 |
| 13C4-5 | 4679.2185(27) | 4513.7430(39) | 2537.7829(18) | 10 | 15.2 |
| 13C1=2 | 4676.8357(26) | 4518.3805(35) | 2535.9716(16) | 11 | 14.9 |
| 13C3-13C4 | 4675.3239(36) | 4429.882(12) | 2510.3068(22) | 6 | 7.4 |
| 13C4-13C6 | 4676.544(14) | 4427.011(46) | 2509.6874(85) | 6 | 5.8 |
| 13C2-13C3 | 4673.3709(94) | 4434.119(31) | 2508.5169(57) | 6 | 19.1 |
| 13C1-13C3 | 4673.1670(31) | 4432.393(10) | 2507.9307(18) | 6 | 6.3 |
| 13C1-13C2 | 4601.208(32) | 4508.40(12) | 2510.378(24) | 6 | 58.2 |
| 13C3-13C6 | 4738.3999(66) | 4367.752(19) | 2505.6794(39) | 6 | 13.4 |
| 13C4-13C5 | 4606.8606(87) | 4497.374(32) | 2513.9581(54) | 6 | 17.6 |
| 13C1-13C4 | 4637.9591(47) | 4467.863(16) | 2511.2782(29) | 6 | 9.5 |
| 13C2-13C4 | 4600.8(15) | 4503.5(58) | 2511.56(99) | 6 | 85.6 |

²number of experimental transitions in the fit

Table SL2. Spectroscopic constants determined for the deuterium isotopologues of cyclohexene. Spectral assignments were done by fitting experimental transition to the rigid-rotor Hamiltonian using Pickett’s SPCAT/SPFIT analysis program. All species were observed in natural abundance in a commercial sample.

| Isomer | A (MHz) | B (MHz) | C (MHz) | N² | σ (kHz) |
|--------|---------|---------|---------|----|---------|
| d0 | 4739.1511(26) | 4544.4159(33) | 2562.3985(17) | 22 | 15.6 |
| (1)-d1 | 4684.2226(71) | 4358.123(22) | 2517.5716(42) | 6 | 16.0 |
| (2)-d1 | 4728.0271(47) | 4314.894(14) | 2490.7470(28) | 6 | 9.8 |
| (3)-d1 | 4598.9903(53) | 4448.224(19) | 2540.1285(33) | 6 | 13.6 |
| (4)-d1 | 4618.9129(69) | 4402.508(19) | 2482.7260(34) | 9 | 16.5 |
| (5)-d1 | 4628.0530(62) | 4407.556(17) | 2486.8528(31) | 9 | 15.0 |
| (4,9)-d2 | 4421.811(12) | 4375.1906(29) | 2416.4423(19) | 6 | 6.0 |
| (3,8)-d2 | 4456.8531(68) | 4360.890(25) | 2519.1458(43) | 6 | 13.9 |
| (4,8)-d2 | 4480.8460(37) | 4330.5911(38) | 2466.4428(34) | 6 | 6.8 |
| (2,4)-d2 | 4562.8274(31) | 4239.7120(99) | 2419.9967(18) | 6 | 5.7 |
| (1,3)-d2 | 4543.0663(71) | 4269.946(23) | 2496.8638(43) | 6 | 14.5 |
| (2,3)-d2 | 4584.6894(38) | 4233.998(11) | 2469.8934(23) | 6 | 7.9 |
| (1,4)-d2 | 4547.2620(60) | 4258.508(16) | 2445.4059(34) | 8 | 13.9 |
| (1,6)-d2 | 4671.9466(19) | 4143.1205(23) | 2447.6730(10) | 8 | 7.0 |
| (2,9)-d2 | 4581.0458(22) | 4219.0303(92) | 2418.3460(15) | 7 | 7.8 |
| (1,8)-d2 | 4543.0236(66) | 4274.228(21) | 2496.1954(40) | 6 | 13.5 |
| (1,9)-d2 | 4535.3205(19) | 4265.422(20) | 2444.0443(44) | 5 | 8.9 |
| (2,8)-d2 | 4587.8261(63) | 4226.954(19) | 2468.9146(37) | 6 | 12.9 |
| (1,5)-d2 | 4536.705(19) | 4251.294(25) | 2439.7907(5) | 5 | 11.2 |
| (2,5)-d2 | 4549.7472(16) | 4234.144(16) | 2414.7016(16) | 5 | 4.7 |
| (1,10)-d2 | 4519.399(46) | 4270.658(47) | 2441.122(19) | 4 | 19.4 |
| (2,10)-d2 | 4563.4343(31) | 4226.355(31) | 2416.498(13) | 4 | 13.0 |
| (2,3,8)-d3 | 4448.6526(83) | 4148.764(26) | 2449.2613(50) | 6 | 17.0 |
| (1,4,9)-d3 | 4328.3962(65) | 4245.123(27) | 2376.7715(48) | 5 | 11.9 |
| (1,3,8)-d3 | 4405.5468(69) | 4189.116(25) | 2476.7582(48) | 5 | 12.6 |
| (2,4,9)-d3 | 4366.5701(84) | 4202.971(29) | 2352.3619(51) | 6 | 17.0 |
| (2,3,7,8)-d4 | 4396.2294(58) | 3989.815(16) | 2408.5446(34) | 6 | 11.9 |
| (2,4,7,9)-d4 | 4318.2255(35) | 4040.268(11) | 2314.1446(21) | 6 | 7.2 |

²number of experimental transitions in the fit
Table SL3. Refined atomic coordinates (Å) of cyclohexene in the principal axis system. The refinements were done using the experimental constants for the normal species, $^{13}$C, $^{13}$C-$^{13}$C, and D isotopologues observed in natural abundance using a commercial sample of cyclohexene.

|      | a     | b     | c     |
|------|-------|-------|-------|
| C1   | 0.66475 | 1.26747 | 0.08957 |
| C2   | -0.66475 | 1.26747 | -0.08957 |
| C3   | -1.48960 | 0.00604 | -0.17879 |
| C4   | -0.70417 | -1.22101 | 0.30042 |
| C5   | 0.70417  | -1.22101 | -0.30042 |
| C6   | 1.48960  | 0.00604  | 0.17879  |
| H1   | -1.81547 | -0.13878 | -1.21812 |
| H2   | -2.40256 | 0.12761  | 0.41504  |
| H3   | -0.61912 | -1.19277 | 1.39509  |
| H4   | -1.18480 | -2.21303 | 0.18833  |
| H5   | 1.24005  | 2.13513  | 0.05683  |
| H6   | 2.40256  | 0.12761  | -0.41504 |
| H7   | 1.81547  | -0.13878 | 1.21812  |
| H8   | 0.61912  | -1.19277 | -1.39509 |
| H9   | 1.18480  | -2.21303 | -0.18833 |
| H10  | -1.24005 | 2.13513  | 0.05683  |

Example Spectrum Analysis

The spectrum analysis methodology is illustrated using the reaction product from the synthesis targeting trans-4,5-cyclohexene-d2, compound 14 in the paper. For this analysis, the region near the lowest frequency transition ($J_{11/2-000}$ using the usual asymmetric top notation of the rotational kinetic energy levels, $J_{K_aK_c}$) is shown in Figure SL2. This region offers the highest measurement sensitivity. The spectrum is acquired over the 6-18 GHz frequency range but the higher frequency regions are not shown here. Candidate cyclohexene isotopomers in this frequency range are identified by an automated analysis routine. The routine checks each measured transition frequency for a match to the predicted transition frequency of all 528 rotationally distinct isotopomers of cyclohexene calculated using the reference geometry. If an experimental transition frequency is within 500 kHz of a predicted frequency, then the transition frequency for the ring pucker isomer of the candidate match is identified for the list of predicted frequencies. If there is an experimental transition frequency within 500 kHz of the predicted ring pucker transition pair, then these isotopomers are flagged as likely components of the mixture. The presence of a rotationally distinct isotopomer is verified by examining the full measured spectrum region to see that the other rotational transition expected for the isotopomer is present with the correct intensity and that the spectrum can be fit to high accuracy.

For the trans-4,5-cyclohexene-d2 reaction sample, 26 rotationally distinct isotopomers were identified, corresponding to 15 chemically distinct isotopomers. The relative abundance of the rotationally distinct species are determined from the transition intensities using the calculated intensity of the transition in the low frequency region (this calculation includes effects of rotation of the principal axis system upon deuteration). The results for the relative abundance of the rotationally distinct deuterated isomers of cyclohexene in this sample are reported in Table SL6 where the relative abundances of the chemically distinct isotopomers and the isotopologues are also given.

The accuracy of the refined structure makes it straightforward to identify the cyclohexene isotopomer from its spectrum even without the availability of synthesized reference samples. The performance of the reference structure for the rotationally distinct isotopomers observed over all experimental samples is summarized in Table SL4. This table lists the predicted rotational constants for all identified isotopomers. The experimental rotational constants are listed next where the percentage error for each constant is given. As a metric for isotopomer identification, we use the root-mean-squared (RMS) percent error for the three rotational constants of each species. The confidence in the isotopomer identification is assessed by comparing the RMS percent error of the matched geometry to the RMS percent errors of the two next closest geometry matches (the last column of the Table SL4). In all cases, the error for the matched geometry is at least a factor of 10 smaller than the next best geometry match.
Results
A summary of all deuterium isotopomers of cyclohexene identified in the samples for this study is given in Table SL4. The table gives the rotational constants for each isotopomer predicted from the reference geometry and the experimentally determined rotational constants. The assigned transitions for each deuterium isotopomer are given in Tables SL24-50. The percent error for each rotational constant determination is also listed in Table SL4. An assessment of the confidence of each isotopomer identification by MRR spectroscopy is provided by giving the rms error for the three rotational constants for each isotopomer and the rms error to the next closest set of rotational constants from all 528 rotationally distinct deuterated isomers. In all cases, there is a significant increase in the rms error for the next closest possible isotopomer.

The relative abundance of all known isotopomers in each synthetic sample is summarized in Tables SL5-10. The abundance analysis first gives the composition for all rotationally distinct isotopomers. The relative abundance for each chemically distinct deuterated isomer is also given. This value is the sum of the two ring-pucker isomers for each isomer where these give rotationally distinguishable structures. Finally, the relative abundance of the isotopologues, cyclohexene isomers with the same total number of deuterium atoms, is also given in Tables SL5-10.

Discussion
1) Isotopic Scrambling by Internal Rotation of Cyclohexene on the Metal
There were some discrepancies in the relative abundance of the isotopomers in the samples determined by NMR and MRR believed to be caused by isotopic scrambling. This scrambling appears to occur early in the sample processing while the cyclohexene is still attached to the metal. The mechanism of this scrambling is believed to be due to a beta hydride elimination which results in shifting of the deuterium to a new carbon, and in some cases the replacement

Figure SL2. MRR spectrum of trans-4,5-d2-cyclohexene. Twenty-six rotationally distinct isotopomers of cyclohexene, corresponding to 15 chemically distinct species, were identified in the sample and are illustrated by the colored traces below. The simulated spectra were generated using Pickett’s SPCAT/SPFIT software.
with a hydrogen.\textsuperscript{21} Evidence of the isotopic scrambling by internal rotation is illustrated in Figure SL3. \textsuperscript{1}H NMR spectra of a 3-cyclohexene-d\textsubscript{1} sample was taken prior to and directly following an MRR measurement (Figure SL3, Panel A). Prior to MRR, the amount of the H\textsubscript{3}-endo proton impurity in the sample was \textasciitilde5\%, while after MRR it was \textasciitilde30\%. The MRR spectrum of the same sample is shown in Figure SL3, Panel B and the relative amount of 3-cyclohexene-d\textsubscript{1} in this sample was 76\% (10\% d0 impurity, Table SL5). These spectra were acquired using a sample that was bound to a different metal complex than reported on in this study; it did not have the methyl on the nitrosyl group. This metal complex variant is known to be more reactive with oxygen and also binds to the cyclohexene more tightly.

In order to minimize the extent of scrambling, the metal complex that is reported in the body of this paper was used, which is known to be less reactive than the other complex. Figure SL3, Panel C shows the spectrum of a 3-d\textsubscript{1}-cyclohexene sample using the methylated complex where the relative amount of 3-d\textsubscript{1} was determined to be \textasciitilde90\% (Table SL6). In this sample, the relative impurity of cyclohexene d0 was \textasciitilde5\%, while the other 5\% of the sample was made up of the 1-d\textsubscript{1} and 4-d\textsubscript{1} isotopomers. Migration of the metal complex on the ring explains the presence of these isotopomers. The observed scrambling does not change the identity of the most abundant species. The MRR spectrum can therefore be used to confirm the assignment of the dominant isotopomer in a sample, though the values determined by MRR represent a lower limit for the purity of a sample.

\textbf{Figure SL3.} Isotopic scrambling of cyclohexene on the metal complex. Panel A shows \textsuperscript{1}H NMR spectra of a 3-cyclohexene-d\textsubscript{1} sample taken before and after MRR. The amount of H\textsubscript{3}exo proton impurity before and after MRR was \textasciitilde5\% and \textasciitilde30\% respectively. A spectrum of fully protonated cyclohexene is shown for reference. The MRR spectrum of the sample used for the NMR study is shown in Panel B. Analysis of this spectrum by MRR gave a relative amount of the desired product was 76\% 3-d\textsubscript{1}. Panel C shows the MRR spectrum of a different 3-cyclohexene-d\textsubscript{1} sample that was made using a different metal complex. The relative composition of the desired product in this sample was 90\% 3-d\textsubscript{1}.

\textit{Stereoselectivity in the Synthesis}
In this work, MRR spectroscopy is used to analyze isoptalogues and isotopomer purity of the synthetic targets. The analysis is performed on the cyclohexene that is thermally dissociated from the metal by heating. As described above, there is evidence for internal rotation of the cyclohexene on the metal prior to thermal dissociation to produce isotopomer impurities estimated at the 5-10% level. As a result, the stereoisomer purities are lower limits to the values produced directly in the synthesis of the transition metal complex. The main conclusions from MRR analysis are presented below.

**Isotopologue Purity of 3-d1-cyclohexene**

The isotopomer analysis of 3-d1-cyclohexene is presented in Table SL6 for the preferred methylated nitroso complex. The isotopologue purity is 95%. No overdeuteration of the cyclohexene is detected placing d1-isotopomer impurities below 1%. NMR analysis of the cyclohexene transition metal complex prior to sample preparation for MRR spectroscopy indicated that the target cyclohexene isotopomer is synthesized is very high purity, possibly higher than 99%. The MRR measurement detects the other two monodeuterated d1-isotopomers at about 2% each. In addition, MRR measures about 5% of the d0-parent cyclohexene. These results are consistent with isomerization by internal rotation of cyclohexene on the metal prior to dissociation possibly through the agnostic metal complex geometry. This mechanism can also result in reduction of total deuterium content if the sample is in a proton rich environment (possibly from the residual solvents in the samples). In general, MRR analysis indicates lower total deuterium content of the cyclohexene than indicated in the NMR measurements of the synthesized metal complex.

**Cis - Trans Selectivity in d2-isotopomers**

Two d2-isotomers of cyclohexene were analyzed by MRR spectroscopy. The synthesis targets the preparation of trans-4,5-cyclohexene-d2 (Table SL7) and cis-3,4-cyclohexene-d2 (Table SL8). In both cases, the target compound is the dominant isotopomer. Also, in both cases evidence for internal rotation of the cyclohexene on the ring is evident through the detection of other d-2 isotopologues that would be produced through this mechanism. Reduction in total deuterium content relative to expectations from NMR spectroscopy is also indicated by the high relative abundance of the d1-isotopologue. It is noted that the relative abundance of the d1-isotopologue is much higher in cis-3,4-cyclohexene-d2 (30%) than trans-4,5-cyclohexene-d2 (10%). The cis-3,4-cyclohexene-d2 sample provided for MRR analysis had much higher amounts of initial solvent impurities than the other samples analyzed in this project. As a result, it required longer times at solvent removal step where the sample is heated using a temperature ramp from 60°C to 100°C. The prolonged solvent removal step might be expected to increase the isotope scrambling through the agnostic complex intermediate.

The main result that MRR provides for these samples is the stereoselectivity of cis vs. trans isotopomers. For the cyclohexene that is detected with the target deuterium substitution patterns, the stereoselectivity for trans-4,5-cyclohexene-d2 relative to cis-4,5-cyclohexene-d2 is 22:1 and the selectivity for the target cis-3,4-cyclohexene-d2 relative to trans-3,4-cyclohexene-d2 is 39:1. For trans-4,5-cyclohexene-d2, MRR detects about 8% overdeuteration through the presence of two d3-isotopomers. This result is consistent with NMR analysis of the transition metal complex prior to MRR sample preparation. No overdeuteration is detected in the synthesis of cis-3,4-cyclohexene-d2.

**Selectivity in cis,trans-3,4,5-d3-cyclohexene Synthesis**

MRR measures about 20% underdeuteration of this compound entirely from d2-isotopologue impurities as shown in Table 9. Underdeuteration relative to expectations from NMR is a common feature of this analysis and, as mentioned before, could be causes by the proposed mechanism for internal rotation of the cyclohexene on the metal prior to thermal decomposition. No overdeuteration is observed.

In this case, only a single isotopomer, the target cis,trans-3,4,5-d3-cyclohexene, is observed and makes up about 80% of the sample composition. The measurement sensitivity was lower for this compound compared to the d1- and d2-isotopologues. We estimate that all other isotopomer impurities are below 2% giving a stereoselectivity of the synthesis of 40:1 or higher.
Selectivity in the cis,trans,trans-3,4,5,6-d4-cyclohexene Synthesis
MRR analysis of this sample gives a high level of underdeuteration with about 40% of total d3-isotopologue. This high abundance of d3-isotopologues was also inferred from the NMR analysis. The origin of this isotopomer impurity through slow reaction at the exo-H6 position is described in the main paper. For d-4 isotopologues, only a single isotopomer is detected – the target cis,trans,trans-3,4,5,6-d4-cyclohexene. This species makes up 55% of the sample composition. No other d4-isotopomers are detected in a spectrum where the detection limit is 1%. The stereoselectivity in this synthesis is 55:1 or higher.

Summary
MRR provides a simple method to quantitatively analyze the isotopomer content of cyclohexene. The measurement is performed by transferring the reaction product to the MRR spectrometer and then removing the cyclohexene ligand with heat. This sample preparation process is found to cause about 10% scrambling of the isotopomers possibly through internal rotation on the metal complex via an agnostic geometry. As a result, MRR composition analysis provides a lower limit to the isotopomer purity of the prepared transition metal complex. MRR analysis shows that overdeuteration of the samples is low – only being detected in one sample at less than 10% composition. MRR also demonstrates that the synthesis has high stereoselectivity. Undesired cis/trans isomers were typically a factor of 40 or more lower in abundance than the described isomer.
Table SL4. Comparison between calculated and experimental rotational constants of deuterium isotopologues of cyclohexene. The theoretical rotational constants are scaled using the refined structure determined from the isotopologues observed in natural abundance. Experimental fits were done using Pickett’s SPCAT/SPFIT analysis program.

|              | Theoretical Rotational Constants | Experimental Rotational Constants | RMS error (%) | RMS closest (%) |
|--------------|----------------------------------|-----------------------------------|---------------|-----------------|
|              | A (MHz)  | B (MHz)  | C (MHz)  | A (MHz)  | B (MHz)  | C (MHz)  |               |                |
| (1)-d1       | 4684.219 | 4358.111 | 2517.572 | 4684.2226 (0.00008%) | 4358.123 (0.0003%) | 2517.5716 (-0.000016%) | 0.0004 | 0.9989, 1.1854 |
| (2)-d1       | 4728.048 | 4314.878 | 2490.756 | 4728.0271 (-0.0004%) | 4314.894 (0.0004%) | 2490.7470 (-0.0004%) | 0.0004 | 1.0037, 1.7424 |
| (3)-d1       | 4598.989 | 4448.217 | 2540.135 | 4598.9903 (0.00003%) | 4448.224 (0.00016%) | 2540.1285 (-0.0003%) | 0.0005 | 1.3708, 1.4541 |
| (4)-d1       | 4618.901 | 4402.491 | 2482.75  | 4618.9129 (0.0003%) | 4402.508 (0.0004%) | 2482.7260 (-0.0010%) | 0.0011  | 0.163, 1.2893  |
| (5)-d1       | 4628.066 | 4407.568 | 2486.842 | 4628.0530 (-0.0003%) | 4407.556 (-0.0003%) | 2486.8528 (0.0004%) | 0.0004  | 0.1626, 1.1914 |
| (4,9)-d2     | 4421.288 | 4375.256 | 2416.333 | 4421.811 (0.012%)  | 4375.1906 (-0.0015%) | 2416.4423 (0.005%)  | 0.0076  | 0.3695, 0.485  |
| (3,8)-d2     | 4456.721 | 4360.738 | 2519.087 | 4456.8531 (0.003%)  | 4360.890 (0.003%)  | 2519.1458 (0.002%)  | 0.003   | 1.312, 1.4409  |
| (4,8)-d2     | 4480.6184 | 4330.3479 | 2466.3685 | 4480.8460 (0.005%)  | 4330.5911 (0.006%)  | 2466.4428 (0.003%)  | 0.0047  | 0.2001, 0.9340  |
| (2,4)-d2     | 4562.684 | 4239.535 | 2419.902 | 4562.8274 (0.003%)  | 4239.7120 (0.004%)  | 2419.9967 (0.004%)  | 0.004   | 0.1973, 0.2273  |
| (1,3)-d2     | 4542.793 | 4269.867 | 2496.803 | 4543.0663 (0.006%)  | 4269.946 (0.0019%)  | 2496.8638 (0.002%)  | 0.0043  | 0.0562, 0.7313  |
| (2,3)-d2     | 4584.407 | 4233.947 | 2469.753 | 4584.6894 (0.006%)  | 4233.998 (0.0012%)  | 2469.8934 (0.006%)  | 0.0047  | 0.1083, 0.8206  |
| (1,4)-d2     | 4546.732 | 4258.462 | 2445.308 | 4547.2620 (0.012%)  | 4258.508 (0.0011%)  | 2445.4059 (0.004%)  | 0.0095  | 0.1763, 0.2178  |
| (1,6)-d2     | 4671.5817 | 4143.0032 | 2447.6479 | 4671.9466 (0.008%)  | 4143.1205 (0.003%)  | 2447.6730 (0.0010%) | 0.0048  | 0.1188, 0.9342  |
| (2,9)-d2     | 4581.0412 | 4218.6573 | 2418.2439 | 4581.0458 (0.00010%) | 4219.0130 (0.008%) | 2418.3460 (0.004%) | 0.0054  | 0.2548, 0.0042  |
| (1,8)-d2     | 4542.8417 | 4273.9475 | 2496.0786 | 4543.0236 (0.004%) | 4274.228 (0.007%) | 2496.1954 (0.005%) | 0.0052  | 0.0606, 0.7041  |
| (1,9)-d2     | 4535.321 | 4265.041 | 2443.964 | 4535.320 (-0.00002%) | 4265.422 (0.009%) | 2444.0443 (0.003%) | 0.0055  | 0.1757, 0.2145  |
| (2,8)-d2     | 4587.667 | 4226.731 | 2468.865 | 4587.8261 (0.003%) | 4226.954 (0.005%) | 2468.9146 (0.002%) | 0.0038  | 0.1066, 0.8276  |
| (1,5)-d2     | 4536.012 | 4251.504 | 2439.721 | 4536.705 (0.015%) | 4251.294 (-0.005%) | 2439.7907 (0.003%) | 0.0094  | 0.2069, 0.2119 |
| (2,5)-d2     | 4549.062 | 4234.304 | 2414.656 | 4549.7472 (0.015%) | 4234.144(-0.004%) | 2414.7016 (0.0019%) | 0.0090  | 0.2005, 0.2187 |
|        |      |      |      |      |      |      |
|--------|------|------|------|------|------|------|
| (1,10)-d2 | 4519.2719 | 4270.5929 | 2441.0246 | 4519.399 (0.003%) | 4270.658 (-0.0015%) | 2441.122 (0.004%) | 0.003 | 0.2273, 0.3364 |
| (2,10)-d2 | 4563.1005 | 4226.7668 | 2416.2462 | 4563.434 (0.007%) | 4226.355 (-0.010%) | 2416.498 (0.010%) | 0.0093 | 0.1978, 0.2163 |
| (2,3,8)-d3 | 4448.28 | 4148.446 | 2449.104 | 4448.655 (0.008%) | 4148.763 (0.008%) | 2449.763 (0.03%) | 0.0162 | 0.5691, 0.6681 |
| (1,4,9)-d3 | 4328.111 | 4244.478 | 2376.592 | 4328.3962 (0.007%) | 4245.123 (0.015%) | 2376.7715 (0.008%) | 0.0108 | 0.3581, 0.3627 |
| (2,4,9)-d3 | 4405.188 | 4188.755 | 2476.620 | 4405.5468 (0.008%) | 4189.116 (0.009%) | 2476.7582 (0.006%) | 0.0076 | 0.7374, 0.8750 |
| (1,3,8)-d3 | 4366.493 | 4202.289 | 2352.164 | 4366.570 (0.0018%) | 4202.971 (0.016%) | 2352.3619 (0.008%) | 0.0106 | 0.3785, 0.3787 |
| (2,3,7,8)-d4 | 4395.524 | 3989.456 | 2408.355 | 4396.2300 (0.016%) | 3989.815 (0.009%) | 2408.5446 (0.008%) | 0.0116 | 0.1099, 0.8497 |
| (2,4,7,9)-d4 | 4317.699 | 4039.583 | 2313.929 | 4318.2255 (0.012%) | 4040.268 (0.017%) | 2314.1446 (0.009%) | 0.0135 | 0.1087, 0.2349 |
Table SL5. Composition of 3-d1-cyclohexene sample determined by MRR (Figure L2B). Sample was on metal that did not have a methyl group on the nitrosyl group.

| Rotational Isomer | Percent | Chemically Distinct | Percent | Isotopologue | Percent |
|-------------------|---------|---------------------|---------|---------------|---------|
| Parent            | 9.4     | d0                  | 9.4     | d0            | 9.4     |
| (1)-d1            | 39.6    | 3-d1                | 75.9    | d1            | 90.6    |
| (2)-d1            | 36.3    |                     |         |               |         |
| (3)-d1            | 3.8     | 4-d1                | 7.8     |               |         |
| (4)-d1            | 4.0     | 1-d1                | 6.8     |               |         |
| (5)-d1            | 6.8     |                     |         |               |         |

Table SL6. Composition of 3-d1-cyclohexene sample determined by MRR. (Figure L2C)

| Rotational Isomer | Percent | Chemically Distinct | Percent | Isotopologue | Percent |
|-------------------|---------|---------------------|---------|---------------|---------|
| Parent            | 5.4     | d0                  | 5.4     | d0            | 5.4     |
| (1)-d1            | 47.0    | 3-d1                | 90.3    | d1            | 94.6    |
| (2)-d1            | 43.3    |                     |         |               |         |
| (3)-d1            | 1.3     | 4-d1                | 3.2     |               |         |
| (4)-d1            | 1.9     |                     |         |               |         |
| (5)-d1            | 1.1     | 1-d1                | 1.1     |               |         |

Table SL7. Composition of trans-4,5-d2-cyclohexene determined by MRR.

| Rotational Isomer | Percent | Chemically Distinct | Percent | Isotopologue | Percent |
|-------------------|---------|---------------------|---------|---------------|---------|
| Parent            | 3.9     | d0                  | 3.9     | d0            | 3.9     |
| (1)-d1            | 1.5     | 3-d1                | 2.7     | d1            | 10.0    |
| (2)-d1            | 1.2     |                     |         |               |         |
| (3)-d1            | 3.0     | 4-d1                | 6.1     |               |         |
| (4)-d1            | 3.1     |                     |         |               |         |
| (5)-d1            | 1.3     | 1-d1                | 1.3     |               |         |
| (4,9)-d2          | 27.8    | trans-4,5-d2        | 52.6    | d2            | 78.3    |
| (3,8)-d2          | 24.8    |                     |         |               |         |
| (4,8)-d2          | 2.4     | cis-4,5-d2          | 2.4     |               |         |
| (2,4)-d2          | 3.6     | trans-3,4-d2        | 7.0     |               |         |
| (1,3)-d2          | 3.4     |                     |         |               |         |
| (2,3)-d2          | 1.0     | cis-3,4-d2          | 2.2     |               |         |
| (1,4)-d2          | 1.2     |                     |         |               |         |
| (1,6)-d2          | 0.8     | cis-3,6-d2          | 0.8     |               |         |
| (2,9)-d2          | 1.2     | cis-3,5-d2          | 2.6     |               |         |
| (1,8)-d2          | 1.4     |                     |         |               |         |
| (1,9)-d2          | 1.8     | trans-3,5-d2        | 3.8     |               |         |
| (2,8)-d2          | 2.0     |                     |         |               |         |
| (1,5)-d2          | 2.1     | 1,3-d2              | 3.8     |               |         |
| (2,5)-d2          | 1.7     |                     |         |               |         |
| (1,10)-d2         | 1.3     | 2,3-d2              | 3.0     |               |         |
| (2,10)-d2         | 1.7     |                     |         |               |         |
| (2,3,8)-d3        | 1.2     | cis,trans-3,4,5-d3  | 2.3     |               |         |
| (1,4,9)-d3        | 1.1     |                     |         |               |         |
| (1,3,8)-d3        | 1.8     | trans,trans-3,4,5-d3| 5.6     |               |         |
| (2,4,9)-d3        | 3.8     |                     |         |               |         |
### Table SI.8. Composition of \textit{cis}-3,4-d\textsubscript{2}-cyclohexene determined by MRR.

| Rotational Isomer | Percent | Chemically Distinct | Percent | Isotopologue | Percent |
|-------------------|---------|---------------------|---------|--------------|---------|
| Parent            | 9.4     | d0                  | 9.4     | d0           | 9.4     |
| (1)-d\textsubscript{1} | 8.4     | 3-d\textsubscript{1} | 18.1    | d\textsubscript{1} | 30.1    |
| (2)-d\textsubscript{1} | 9.7     | 4-d\textsubscript{1} | 9.8     | d\textsubscript{1} | 60.6    |
| (3)-d\textsubscript{1} | 5.1     | 1-d\textsubscript{1} | 2.2     | d\textsubscript{1} | 60.6    |
| (4)-d\textsubscript{1} | 2.2     | 1,3-d\textsubscript{2} | 4.7     | d\textsubscript{1} | 60.6    |

### Table SI.9. Composition of \textit{cis,trans}-3,4,5-d\textsubscript{3}-cyclohexene determined by MRR.

| Rotational Isomer | Percent | Chemically Distinct | Percent | Isotopologue | Percent |
|-------------------|---------|---------------------|---------|--------------|---------|
| (4,9)-d\textsubscript{2} | 6.1     | \textit{trans}-4,5-d\textsubscript{2} | 10.1    | d\textsubscript{2} | 21.9    |
| (3,8)-d\textsubscript{2} | 4.0     | \textit{trans}-3,4-d\textsubscript{2} | 4.3     | d\textsubscript{2} | 21.9    |
| (2,4)-d\textsubscript{2} | 2.2     | \textit{trans}-3,4-d\textsubscript{2} | 4.3     | d\textsubscript{2} | 21.9    |
| (1,3)-d\textsubscript{2} | 2.1     | \textit{cis}-3,4-d\textsubscript{2} | 4.4     | d\textsubscript{2} | 21.9    |
| (2,3)-d\textsubscript{2} | 1.8     | \textit{cis}-3,4-d\textsubscript{2} | 4.4     | d\textsubscript{2} | 21.9    |
| (1,4)-d\textsubscript{2} | 1.3     | 2,3-d\textsubscript{2} | 3.1     | d\textsubscript{2} | 21.9    |
| (2,10)-d\textsubscript{2} | 1.8     | 2,3-d\textsubscript{2} | 3.1     | d\textsubscript{2} | 21.9    |
| (2,3,8)-d\textsubscript{3} | 46.1    | \textit{cis,trans}-3,4,5-d\textsubscript{3} | 78.1    | d\textsubscript{3} | 78.1    |
| (1,4,9)-d\textsubscript{3} | 32.0    | \textit{cis,trans}-3,4,5-d\textsubscript{3} | 78.1    | d\textsubscript{3} | 78.1    |
Table SI.10. Composition of *cis,trans,trans*-3,4,5,6-d4-cyclohexene determined by MRR.

| Rotational Isomer | Percent | Chemically Distinct | Percent | Isotopologue | Percent |
|-------------------|---------|---------------------|---------|--------------|---------|
| (4,9)-d2          | 1.2     | *trans*-4,5-d2      | 1.2     | d2           | 3.4     |
| (3,8)-d2          | 0.0     | *cis*-3,4-d2        | 2.2     | d2           |         |
| (2,3)-d2          | 1.1     | *cis*-3,4-d2        |         | d2           | 3.4     |
| (1,4)-d2          | 1.1     | *cis*-3,4-d2        |         | d2           | 3.4     |
| (2,3,8)-d3        | 21.2    | *cis,trans*-3,4,5-d3| 37.7    | d3           | 41.0    |
| (1,4,9)-d3        | 16.5    | *trans,trans*-3,4,5-d3| 3.3     | d3           | 41.0    |
| (1,3,8)-d3        | 2.1     | *trans,trans*-3,4,5-d3| 3.3     | d3           | 41.0    |
| (2,4,9)-d3        | 1.2     | *cis,trans,trans*-3,4,5-d3| 55.5    | d4           | 55.5    |
| (2,3,7,8)-d4      | 35.6    | *cis,trans,trans*-3,4,5,6-d4| 55.5    | d4           | 55.5    |
| (2,4,7,9)-d4      | 19.9    | *cis,trans,trans*-3,4,5,6-d4| 55.5    | d4           | 55.5    |
Table SL11. Measured rotational transitions ($\nu_{\text{obs}}$, MHz) of the parent and residuals ($\nu_{\text{obs}}$-$\nu_{\text{calc}}$, MHz).

| J$'$ | $K_a$' | $K_b$' | ← | J$''$ | $K_a$'' | $K_b$'' | $\nu_{\text{obs}}$, MHz | $\nu_{\text{obs}}$-$\nu_{\text{calc}}$, MHz |
|------|--------|--------|----|------|--------|--------|----------------|----------------|
| 2    | 2      | 1      | ← | 2    | 1      | 2      | 6530.228       | -0.006         |
| 3    | 3      | 1      | ← | 3    | 2      | 2      | 6830.559       | -0.0002        |
| 4    | 4      | 1      | ← | 4    | 3      | 2      | 7234.95        | 0.0049         |
| 1    | 1      | 1      | ← | 0    | 0      | 0      | 7301.565       | 0.015          |
| 5    | 5      | 1      | ← | 5    | 4      | 2      | 7745.158       | 0.003          |
| 4    | 2      | 2      | ← | 4    | 1      | 3      | 10244.94       | -0.0075        |
| 3    | 1      | 2      | ← | 3    | 0      | 3      | 10337.86       | -0.0039        |
| 4    | 2      | 2      | ← | 3    | 1      | 3      | 10405.1        | -0.0097        |
| 4    | 3      | 2      | ← | 4    | 2      | 3      | 10441.27       | -0.0198        |
| 5    | 4      | 2      | ← | 5    | 3      | 3      | 10512.48       | -0.0305        |
| 2    | 0      | 2      | ← | 1    | 1      | 1      | 12217.98       | 0.0131         |
| 2    | 1      | 2      | ← | 1    | 0      | 1      | 12426.38       | 0.0174         |
| 6    | 3      | 3      | ← | 6    | 2      | 4      | 14459.67       | 0.014          |
| 5    | 2      | 3      | ← | 5    | 1      | 4      | 14505.09       | -0.009         |
| 5    | 3      | 3      | ← | 5    | 2      | 4      | 14521.58       | -0.0042        |
| 2    | 2      | 1      | ← | 1    | 1      | 0      | 16779.85       | 0.0114         |
| 3    | 0      | 3      | ← | 2    | 1      | 2      | 17444.95       | -0.0129        |
| 3    | 1      | 3      | ← | 2    | 0      | 2      | 17459.21       | -0.0201        |
| 6    | 4      | 3      | ← | 6    | 3      | 4      | 14508.23       | -0.0111        |
| 4    | 1      | 3      | ← | 4    | 0      | 4      | 14528.16       | 0.0249         |
| 4    | 2      | 3      | ← | 4    | 1      | 4      | 14532.33       | 0.0248         |
| 5    | 3      | 2      | ← | 5    | 2      | 3      | 10073.87       | 0.0052         |

Table SL12. Measured rotational transitions ($\nu_{\text{obs}}$, MHz) of the $^{13}$C1=2 isotopologue and residuals ($\nu_{\text{obs}}$-$\nu_{\text{calc}}$, MHz).

| J$'$ | $K_a$' | $K_b$' | ← | J$''$ | $K_a$'' | $K_b$'' | $\nu_{\text{obs}}$, MHz | $\nu_{\text{obs}}$-$\nu_{\text{calc}}$, MHz |
|------|--------|--------|----|------|--------|--------|----------------|----------------|
| 3    | 2      | 2      | ← | 3    | 1      | 3      | 10313.64       | -0.0223        |
| 3    | 0      | 3      | ← | 2    | 1      | 2      | 17271.62       | -0.0191        |
| 2    | 1      | 2      | ← | 1    | 0      | 1      | 12284.78       | 0.0186         |
| 3    | 1      | 3      | ← | 2    | 0      | 2      | 17281.08       | -0.017         |
| 1    | 1      | 1      | ← | 0    | 0      | 0      | 7212.823       | 0.015          |
| 2    | 0      | 2      | ← | 1    | 1      | 1      | 12117.2        | 0.0148         |
| 4    | 1      | 3      | ← | 4    | 0      | 4      | 14413.26       | 0.0132         |
| 2    | 2      | 1      | ← | 1    | 1      | 0      | 16566.48       | 0.0132         |
| 3    | 3      | 1      | ← | 3    | 2      | 2      | 6665.764       | -0.0016        |
| 3    | 2      | 2      | ← | 3    | 1      | 3      | 10313.64       | -0.0223        |

Table SL13. Measured rotational transitions ($\nu_{\text{obs}}$, MHz) of the $^{13}$C3=6 isotopologue and residuals ($\nu_{\text{obs}}$-$\nu_{\text{calc}}$, MHz).

| J$'$ | $K_a$' | $K_b$' | ← | J$''$ | $K_a$'' | $K_b$'' | $\nu_{\text{obs}}$, MHz | $\nu_{\text{obs}}$-$\nu_{\text{calc}}$, MHz |
|------|--------|--------|----|------|--------|--------|----------------|----------------|
| 1    | 1      | 1      | ← | 0    | 0      | 0      | 7272.856       | 0.0141         |
| 2    | 0      | 2      | ← | 1    | 1      | 1      | 12028.53       | 0.0127         |
| 2    | 1      | 2      | ← | 1    | 0      | 1      | 12341.01       | 0.0199         |
| 2    | 2      | 1      | ← | 1    | 1      | 0      | 16750.39       | 0.0135         |
| 3    | 0      | 3      | ← | 2    | 1      | 2      | 17248.24       | -0.0165        |
| 3    | 1      | 3      | ← | 2    | 0      | 2      | 17279.21       | -0.019         |
| 3    | 1      | 2      | ← | 3    | 0      | 3      | 10190.72       | -0.0109        |
| 4    | 1      | 3      | ← | 4    | 0      | 4      | 14380.37       | 0.0176         |
| 3    | 2      | 2      | ← | 3    | 1      | 3      | 10332.33       | -0.0175        |
| 2    | 2      | 1      | ← | 2    | 1      | 2      | 6614.089       | -0.0039        |
| 3    | 3      | 1      | ← | 3    | 2      | 2      | 7056.459       | -0.0071        |
Table SL.14. Measured rotational transitions ($\nu_{obs}$, MHz) of the $^{13}$C4=5 isotopologue and residuals ($\nu_{obs}$-$\nu_{calc}$, MHz).

| $J'$ | $K_a'$ | $K_b'$ | $\rightarrow$ J'' | $K_a''$ | $K_b''$ | $\nu_{obs}$ / MHz | $\nu_{obs}$-$\nu_{calc}$ / MHz |
|------|--------|--------|-------------------|--------|--------|-----------------|-----------------------------|
| 1    | 1      | 1      | 0 0 0 0           | 2      | 2      | 7217.016        | 0.0136                      |
| 3    | 3      | 1      | 2 2 2 2           | 1      | 2      | 6678.509        | -0.0045                     |
| 2    | 1      | 2      | 1 2 1 2           | 3      | 0      | 6424.276        | -0.0076                     |
| 3    | 1      | 2      | 3 0 3 3           | 1      | 3      | 10250.25        | -0.0067                     |
| 3    | 2      | 2      | 3 1 3 3           | 1      | 0      | 10299.44        | -0.0259                     |
| 2    | 1      | 2      | 1 0 1 0           | 3      | 2      | 12292.6         | 0.0181                      |
| 4    | 1      | 3      | 4 0 4 4           | 2      | 1      | 14390.98        | 0.0232                      |
| 2    | 2      | 1      | 1 1 1 0           | 3      | 0      | 16755.44        | 0.0094                      |
| 3    | 1      | 3      | 2 0 2 2           | 0      | 1      | 17289.34        | -0.019                      |
| 3    | 0      | 3      | 2 1 2 2           | 1      | 2      | 17279.01        | -0.0038                     |

Table SL.15. Measured rotational transitions ($\nu_{obs}$, MHz) of the $^{13}$C1-$^{13}$C2 isotopologue and residuals ($\nu_{obs}$-$\nu_{calc}$, MHz).

| $J'$ | $K_a'$ | $K_b'$ | $\rightarrow$ J'' | $K_a''$ | $K_b''$ | $\nu_{obs}$ / MHz | $\nu_{obs}$-$\nu_{calc}$ / MHz |
|------|--------|--------|-------------------|--------|--------|-----------------|-----------------------------|
| 1    | 1      | 1      | 0 0 0 0           | 2      | 2      | 7111.4627       | -0.1313                     |
| 2    | 0      | 2      | 1 1 1 1           | 2      | 1      | 12036.3678      | -0.0175                     |
| 2    | 1      | 2      | 1 0 1 1           | 1      | 0      | 12132.3530      | -0.0298                     |
| 2    | 2      | 1      | 1 1 1 0           | 3      | 2      | 16314.0378      | 0.0443                      |
| 3    | 0      | 3      | 2 1 2 2           | 0      | 1      | 17104.7015      | -0.0416                     |
| 3    | 1      | 3      | 2 0 2 2           | 1      | 2      | 17108.0584      | 0.0874                      |

Table SL.16. Measured rotational transitions ($\nu_{obs}$, MHz) of the $^{13}$C1-$^{13}$C3 isotopologue and residuals ($\nu_{obs}$-$\nu_{calc}$, MHz).

| $J'$ | $K_a'$ | $K_b'$ | $\rightarrow$ J'' | $K_a''$ | $K_b''$ | $\nu_{obs}$ / MHz | $\nu_{obs}$-$\nu_{calc}$ / MHz |
|------|--------|--------|-------------------|--------|--------|-----------------|-----------------------------|
| 1    | 1      | 1      | 0 0 0 0           | 2      | 2      | 7181.1065       | 0.0087                      |
| 2    | 0      | 2      | 1 1 1 1           | 2      | 1      | 11934.9819      | 0.0039                      |
| 2    | 1      | 2      | 1 0 1 1           | 1      | 0      | 12196.9647      | 0.0056                      |
| 2    | 2      | 1      | 1 1 1 0           | 3      | 2      | 16527.4280      | -0.0038                     |
| 3    | 0      | 3      | 2 1 2 2           | 0      | 1      | 17078.5335      | -0.0094                     |
| 3    | 1      | 3      | 2 0 2 2           | 1      | 2      | 17100.9264      | 0.0027                      |

Table SL.17. Measured rotational transitions ($\nu_{obs}$, MHz) of the $^{13}$C2-$^{13}$C3 isotopologue and residuals ($\nu_{obs}$-$\nu_{calc}$, MHz).

| $J'$ | $K_a'$ | $K_b'$ | $\rightarrow$ J'' | $K_a''$ | $K_b''$ | $\nu_{obs}$ / MHz | $\nu_{obs}$-$\nu_{calc}$ / MHz |
|------|--------|--------|-------------------|--------|--------|-----------------|-----------------------------|
| 1    | 1      | 1      | 0 0 0 0           | 2      | 2      | 7181.9110       | 0.0150                      |
| 2    | 0      | 2      | 1 1 1 1           | 2      | 1      | 11938.7447      | 0.0136                      |
| 2    | 1      | 2      | 1 0 1 1           | 1      | 0      | 12198.939       | 0.0343                      |
| 2    | 2      | 1      | 1 1 1 0           | 3      | 2      | 16528.6427      | -0.0112                     |
| 3    | 0      | 3      | 2 1 2 2           | 0      | 1      | 17082.6048      | -0.0184                     |
| 3    | 1      | 3      | 2 0 2 2           | 1      | 2      | 17104.7015      | -0.0110                     |

Table SL.18. Measured rotational transitions ($\nu_{obs}$, MHz) of the $^{13}$C4-$^{13}$C6 isotopologue and residuals ($\nu_{obs}$-$\nu_{calc}$, MHz).

| $J'$ | $K_a'$ | $K_b'$ | $\rightarrow$ J'' | $K_a''$ | $K_b''$ | $\nu_{obs}$ / MHz | $\nu_{obs}$-$\nu_{calc}$ / MHz |
|------|--------|--------|-------------------|--------|--------|-----------------|-----------------------------|
| 1    | 1      | 1      | 0 0 0 0           | 2      | 2      | 7186.2421       | 0.0099                      |
| 2    | 0      | 2      | 1 1 1 1           | 2      | 1      | 11933.2710      | 0.0029                      |
| 2    | 1      | 2      | 1 0 1 1           | 1      | 0      | 1205.6139       | 0.0069                      |
| 2    | 2      | 1      | 1 1 1 0           | 3      | 2      | 16539.3174      | -0.0042                     |
### Table SL19. Measured rotational transitions ($\nu_{\text{obs}}, \text{MHz}$) of the $^{13}\text{C}_3^{13}\text{C}_4$ isotopologue and residuals ($\nu_{\text{obs}}-\nu_{\text{calc}}, \text{MHz}$).

| $J'$ | $K_a'$ | $K_b'$ | $\rightarrow$ | $J''$ | $K_a''$ | $K_b''$ | $\nu_{\text{obs}} \text{ / MHz}$ | $\nu_{\text{obs}}-\nu_{\text{calc}} \text{ / MHz}$ |
|------|--------|--------|---------------|------|--------|--------|-----------------|-----------------|
| 1    | 1      | 1      | $\rightarrow$ | 0    | 0      | 0      | 7185.6385       | 0.0078          |
| 2    | 0      | 2      | $\rightarrow$ | 1    | 1      | 1      | 11936.7447      | 0.0053          |
| 2    | 1      | 2      | $\rightarrow$ | 1    | 0      | 1      | 12206.2557      | 0.0115          |
| 2    | 2      | 1      | $\rightarrow$ | 1    | 1      | 0      | 16536.2737      | 0.0046          |
| 3    | 0      | 3      | $\rightarrow$ | 2    | 1      | 2      | 17089.6622      | 0.0088          |
| 3    | 1      | 3      | $\rightarrow$ | 2    | 0      | 2      | 17112.9780      | 0.0018          |

### Table SL20. Measured rotational transitions ($\nu_{\text{obs}}, \text{MHz}$) of the $^{13}\text{C}_2^{13}\text{C}_4$ isotopologue and residuals ($\nu_{\text{obs}}-\nu_{\text{calc}}, \text{MHz}$).

| $J'$ | $K_a'$ | $K_b'$ | $\rightarrow$ | $J''$ | $K_a''$ | $K_b''$ | $\nu_{\text{obs}} \text{ / MHz}$ | $\nu_{\text{obs}}-\nu_{\text{calc}} \text{ / MHz}$ |
|------|--------|--------|---------------|------|--------|--------|-----------------|-----------------|
| 1    | 1      | 1      | $\rightarrow$ | 0    | 0      | 0      | 7112.3747       | 0.0242          |
| 2    | 0      | 2      | $\rightarrow$ | 1    | 1      | 1      | 12034.8535      | 0.1829          |
| 2    | 1      | 2      | $\rightarrow$ | 1    | 0      | 1      | 12135.4391      | 0.0816          |
| 2    | 2      | 1      | $\rightarrow$ | 1    | 1      | 0      | 16314.0378      | 0.0371          |
| 3    | 0      | 3      | $\rightarrow$ | 2    | 1      | 2      | 17107.7335      | 0.0082          |
| 3    | 1      | 3      | $\rightarrow$ | 2    | 0      | 2      | 17111.2749      | 0.0276          |

### Table SL21. Measured rotational transitions ($\nu_{\text{obs}}, \text{MHz}$) of the $^{13}\text{C}_1^{13}\text{C}_4$ isotopologue and residuals ($\nu_{\text{obs}}-\nu_{\text{calc}}, \text{MHz}$).

| $J'$ | $K_a'$ | $K_b'$ | $\rightarrow$ | $J''$ | $K_a''$ | $K_b''$ | $\nu_{\text{obs}} \text{ / MHz}$ | $\nu_{\text{obs}}-\nu_{\text{calc}} \text{ / MHz}$ |
|------|--------|--------|---------------|------|--------|--------|-----------------|-----------------|
| 1    | 1      | 1      | $\rightarrow$ | 0    | 0      | 0      | 7149.2501       | 0.0128          |
| 2    | 0      | 2      | $\rightarrow$ | 1    | 1      | 1      | 11991.0813      | -0.0012         |
| 2    | 1      | 2      | $\rightarrow$ | 1    | 0      | 1      | 12171.7931      | -0.0004         |
| 2    | 2      | 1      | $\rightarrow$ | 1    | 1      | 0      | 16425.1520      | -0.0034         |
| 3    | 0      | 3      | $\rightarrow$ | 2    | 1      | 2      | 17102.4608      | 0.0131          |
| 3    | 1      | 3      | $\rightarrow$ | 2    | 0      | 2      | 17113.4635      | 0.0039          |
Table SL.22. Measured rotational transitions ($v_{\text{obs}}$, MHz) of the $^{13}$C4-13C5 isotopologue and residuals ($v_{\text{obs}}$-$v_{\text{calc}}$, MHz).

| $J'$ | $K_a'$ | $K_b'$ | ← | $J''$ | $K_a''$ | $K_b''$ | $v_{\text{obs}}$ / MHz | $v_{\text{obs}}$-$v_{\text{calc}}$ / MHz |
|------|-------|-------|---|-------|-------|-------|-----------------|-----------------|
| 1    | 1     | 1     | ← | 0     | 0     | 0     | 7120.8353       | 0.0165          |
| 2    | 0     | 2     | ← | 1     | 1     | 1     | 12034.8531      | 0.0128          |
| 2    | 1     | 2     | ← | 1     | 0     | 1     | 12148.7618      | 0.0268          |
| 2    | 2     | 1     | ← | 1     | 1     | 0     | 16334.5295      | -0.0103         |
| 3    | 0     | 3     | ← | 2     | 1     | 2     | 17119.0710      | -0.0241         |
| 3    | 1     | 3     | ← | 2     | 0     | 2     | 17123.6139      | -0.0009         |

Table SL.23. Measured rotational transitions ($v_{\text{obs}}$, MHz) of the $^{13}$C2-13C5 isotopologue and residuals ($v_{\text{obs}}$-$v_{\text{calc}}$, MHz).

| $J'$ | $K_a'$ | $K_b'$ | ← | $J''$ | $K_a''$ | $K_b''$ | $v_{\text{obs}}$ / MHz | $v_{\text{obs}}$-$v_{\text{calc}}$ / MHz |
|------|-------|-------|---|-------|-------|-------|-----------------|-----------------|
| 1    | 1     | 1     | ← | 0     | 0     | 0     | 7244.0910       | 0.0117          |
| 2    | 0     | 2     | ← | 1     | 1     | 1     | 11834.7816      | 0.0101          |
| 2    | 1     | 2     | ← | 1     | 0     | 1     | 12255.4600      | 0.0218          |
| 2    | 2     | 1     | ← | 1     | 1     | 0     | 16720.8712      | -0.0079         |
| 3    | 0     | 3     | ← | 2     | 1     | 2     | 17047.7867      | -0.0171         |
| 3    | 1     | 3     | ← | 2     | 0     | 2     | 17102.0857      | -0.0028         |

Table SL.24. Measured rotational transitions ($v_{\text{obs}}$, MHz) of the (1)-d1 isotopologue and residuals ($v_{\text{obs}}$-$v_{\text{calc}}$, MHz).

| $J'$ | $K_a'$ | $K_b'$ | ← | $J''$ | $K_a''$ | $K_b''$ | $v_{\text{obs}}$ / MHz | $v_{\text{obs}}$-$v_{\text{calc}}$ / MHz |
|------|-------|-------|---|-------|-------|-------|-----------------|-----------------|
| 1    | 1     | 1     | ← | 0     | 0     | 0     | 7201.807        | 0.0128          |
| 2    | 0     | 2     | ← | 1     | 1     | 1     | 11871.22        | -0.0053         |
| 2    | 1     | 2     | ← | 1     | 0     | 1     | 12236.94        | 0.0018          |
| 2    | 2     | 1     | ← | 1     | 1     | 0     | 16570.24        | -0.0033         |
| 3    | 0     | 3     | ← | 2     | 1     | 2     | 17082.6         | 0.0232          |
| 3    | 1     | 3     | ← | 2     | 0     | 2     | 17125.2         | -0.0229         |

Table SL.25. Measured rotational transitions ($v_{\text{obs}}$, MHz) of the (2)-d1 isotopologue and residuals ($v_{\text{obs}}$-$v_{\text{calc}}$, MHz).

| $J'$ | $K_a'$ | $K_b'$ | ← | $J''$ | $K_a''$ | $K_b''$ | $v_{\text{obs}}$ / MHz | $v_{\text{obs}}$-$v_{\text{calc}}$ / MHz |
|------|-------|-------|---|-------|-------|-------|-----------------|-----------------|
| 1    | 1     | 1     | ← | 0     | 0     | 0     | 7218.795        | 0.0207          |
| 2    | 0     | 2     | ← | 1     | 1     | 1     | 11724.58        | 0.0038          |
| 2    | 1     | 2     | ← | 1     | 0     | 1     | 12200.27        | 0.0000          |
| 2    | 2     | 1     | ← | 1     | 1     | 0     | 16674.82        | -0.0064         |
| 3    | 0     | 3     | ← | 2     | 1     | 2     | 16932.66        | -0.0086         |
| 3    | 1     | 3     | ← | 2     | 0     | 2     | 17001.23        | 0.0035          |
Table SL.26. Measured rotational transitions ($\nu_{\text{obs}}, \text{MHz}$) of the (3)-d1 isotopologue and residuals ($\nu_{\text{obs}}-\nu_{\text{calc}}, \text{MHz}$).

| $J'$ | $K_a'$ | $K_b'$ | ← | $J''$ | $K_a''$ | $K_b''$ | $\nu_{\text{obs}} / \text{MHz}$ | $\nu_{\text{obs}}-\nu_{\text{calc}} / \text{MHz}$ |
|------|--------|--------|---|-------|--------|--------|-----------------|-----------------|
| 1    | 1      | 1      | ← | 0     | 0      | 0      | 7139.141        | 0.0219          |
| 2    | 0      | 2      | ← | 1     | 1      | 1      | 12060.02        | -0.0011         |
| 2    | 1      | 2      | ← | 1     | 0      | 1      | 12219.36        | -0.0113         |
| 2    | 2      | 1      | ← | 1     | 1      | 0      | 16337.1         | -0.0044         |
| 3    | 0      | 3      | ← | 2     | 1      | 2      | 17218.72        | -0.0039         |
| 3    | 1      | 3      | ← | 2     | 0      | 2      | 17227.62        | 0.008           |

Table SL.27. Measured rotational transitions ($\nu_{\text{obs}}, \text{MHz}$) of the (4)-d1 isotopologue and residuals ($\nu_{\text{obs}}-\nu_{\text{calc}}, \text{MHz}$).

| $J'$ | $K_a'$ | $K_b'$ | ← | $J''$ | $K_a''$ | $K_b''$ | $\nu_{\text{obs}} / \text{MHz}$ | $\nu_{\text{obs}}-\nu_{\text{calc}} / \text{MHz}$ |
|------|--------|--------|---|-------|--------|--------|-----------------|-----------------|
| 1    | 1      | 1      | ← | 0     | 0      | 0      | 7114.911        | 0.0053          |
| 2    | 0      | 2      | ← | 1     | 1      | 1      | 11850.18        | -0.0243         |
| 2    | 1      | 2      | ← | 1     | 1      | 1      | 11868.15        | 0.0321          |
| 2    | 1      | 2      | ← | 1     | 0      | 1      | 12088.62        | 0.0056          |
| 2    | 2      | 1      | ← | 1     | 1      | 0      | 16371.01        | -0.0033         |
| 3    | 0      | 3      | ← | 2     | 1      | 2      | 16940.39        | 0.0116          |
| 3    | 1      | 3      | ← | 2     | 1      | 2      | 16941.28        | -0.0122         |
| 3    | 0      | 3      | ← | 2     | 0      | 2      | 16958.29        | -0.0032         |
| 3    | 1      | 3      | ← | 2     | 0      | 2      | 16959.2         | -0.0046         |

Table SL.28. Measured rotational transitions ($\nu_{\text{obs}}, \text{MHz}$) of the (5)-d1 isotopologue and residuals ($\nu_{\text{obs}}-\nu_{\text{calc}}, \text{MHz}$).

| $J'$ | $K_a'$ | $K_b'$ | ← | $J''$ | $K_a''$ | $K_b''$ | $\nu_{\text{obs}} / \text{MHz}$ | $\nu_{\text{obs}}-\nu_{\text{calc}} / \text{MHz}$ |
|------|--------|--------|---|-------|--------|--------|-----------------|-----------------|
| 1    | 1      | 1      | ← | 0     | 0      | 0      | 7101.647        | 0.0083          |
| 2    | 0      | 2      | ← | 1     | 1      | 1      | 11833.4         | -0.0049         |
| 2    | 1      | 2      | ← | 1     | 1      | 1      | 11850.68        | -0.0059         |
| 2    | 1      | 2      | ← | 1     | 0      | 1      | 12067.08        | -0.0082         |
| 2    | 2      | 1      | ← | 1     | 1      | 0      | 16339.47        | 0.0002          |
| 3    | 0      | 3      | ← | 2     | 1      | 2      | 16913.08        | 0.0085          |
| 3    | 1      | 3      | ← | 2     | 1      | 2      | 16913.98        | 0.0382          |
| 3    | 0      | 3      | ← | 2     | 0      | 2      | 16930.33        | -0.0221         |
| 3    | 1      | 3      | ← | 2     | 0      | 2      | 16931.21        | -0.0147         |

Table SL.29. Measured rotational transitions ($\nu_{\text{obs}}, \text{MHz}$) of the (4,9)-d2 isotopomer and residuals ($\nu_{\text{obs}}-\nu_{\text{calc}}, \text{MHz}$).

| $J'$ | $K_a'$ | $K_b'$ | ← | $J''$ | $K_a''$ | $K_b''$ | $\nu_{\text{obs}} / \text{MHz}$ | $\nu_{\text{obs}}-\nu_{\text{calc}} / \text{MHz}$ |
|------|--------|--------|---|-------|--------|--------|-----------------|-----------------|
| 1    | 0      | 1      | ← | 0     | 0      | 0      | 6791.637        | 0.0044          |
| 2    | 1      | 2      | ← | 1     | 1      | 1      | 11624.51        | -0.0116         |
| 2    | 0      | 2      | ← | 1     | 0      | 1      | 11670.31        | -0.0042         |
| 2    | 1      | 1      | ← | 1     | 1      | 0      | 15542.02        | 0.001           |
| 3    | 1      | 3      | ← | 2     | 1      | 2      | 16480.21        | 0.0063          |
| 3    | 0      | 3      | ← | 2     | 0      | 2      | 16481.02        | 0.0021          |
Table SL30. Measured rotational transitions ($v_{obs}$, MHz) of the (3,8)-d2 isotopomer and residuals ($v_{obs}$-$v_{calc}$, MHz).

| $J'$ | $K_{a}'$ | $K_{b}'$ | $J''$ | $K_{a}''$ | $K_{b}''$ | $v_{obs}$ / MHz | $v_{obs}$-$v_{calc}$ / MHz |
|-----|----------|----------|------|----------|----------|-----------------|---------------------------|
| 1   | 1        | 1        | 0    | 0        | 0        | 6975.987       | -0.0123                   |
| 2   | 0        | 2        | 1    | 1        | 1        | 11914.68       | 0.009                     |
| 2   | 1        | 2        | 1    | 0        | 1        | 12014.32       | 0.0271                    |
| 2   | 2        | 1        | 1    | 1        | 0        | 15889.70       | -0.0015                   |
| 3   | 0        | 3        | 2    | 1        | 2        | 17002.26       | -0.0095                   |
| 3   | 1        | 3        | 2    | 0        | 2        | 17006.00       | -0.0094                   |

Table SL31. Measured rotational transitions ($v_{obs}$, MHz) of the (4,8)-d2 isotopomer and residuals ($v_{obs}$-$v_{calc}$, MHz).

| $J'$ | $K_{a}'$ | $K_{b}'$ | $J''$ | $K_{a}''$ | $K_{b}''$ | $v_{obs}$ / MHz | $v_{obs}$-$v_{calc}$ / MHz |
|-----|----------|----------|------|----------|----------|-----------------|---------------------------|
| 1   | 1        | 1        | 0    | 0        | 0        | 6947.28         | -0.0088                   |
| 1   | 0        | 1        | 0    | 0        | 0        | 6797.043        | 0.0088                    |
| 2   | 2        | 1        | 2    | 2        | 2        | 6051.937        | 0.0054                    |
| 2   | 2        | 1        | 2    | 1        | 2        | 6043.207        | -0.0028                   |
| 2   | 1        | 1        | 2    | 0        | 2        | 5601.171        | 0.0048                    |
| 2   | 1        | 1        | 2    | 1        | 2        | 5592.438        | -0.0074                   |

Table SL32. Measured rotational transitions ($v_{obs}$, MHz) of the (2,4)-d2 isotopomer and residuals ($v_{obs}$-$v_{calc}$, MHz).

| $J'$ | $K_{a}'$ | $K_{b}'$ | $J''$ | $K_{a}''$ | $K_{b}''$ | $v_{obs}$ / MHz | $v_{obs}$-$v_{calc}$ / MHz |
|-----|----------|----------|------|----------|----------|-----------------|---------------------------|
| 1   | 1        | 1        | 0    | 0        | 0        | 6982.827        | 0.0027                    |
| 2   | 0        | 2        | 1    | 1        | 1        | 11460.38        | 0.0025                    |
| 2   | 1        | 2        | 1    | 0        | 1        | 11822.83        | 0.011                     |
| 2   | 2        | 1        | 1    | 1        | 0        | 16108.48        | -0.0028                   |
| 3   | 0        | 3        | 2    | 1        | 2        | 16474.99        | -0.0007                   |
| 3   | 1        | 3        | 2    | 0        | 2        | 16517.33        | -0.0073                   |

Table SL33. Measured rotational transitions ($v_{obs}$, MHz) of the (1,3)-d2 isotopomer and residuals ($v_{obs}$-$v_{calc}$, MHz).

| $J'$ | $K_{a}'$ | $K_{b}'$ | $J''$ | $K_{a}''$ | $K_{b}''$ | $v_{obs}$ / MHz | $v_{obs}$-$v_{calc}$ / MHz |
|-----|----------|----------|------|----------|----------|-----------------|---------------------------|
| 1   | 1        | 1        | 0    | 0        | 0        | 7039.932        | 0.002                     |
| 2   | 0        | 2        | 1    | 1        | 1        | 11731.36        | 0.0108                    |
| 2   | 1        | 2        | 1    | 0        | 1        | 12033.69        | 0.0279                    |
| 2   | 2        | 1        | 1    | 1        | 0        | 16126.06        | -0.0061                   |
| 3   | 0        | 3        | 2    | 1        | 2        | 16871.49        | -0.0168                   |
| 3   | 1        | 3        | 2    | 0        | 2        | 16902.65        | -0.0056                   |

Table SL34. Measured rotational transitions ($v_{obs}$, MHz) of the (2,3)-d2 isotopomer and residuals ($v_{obs}$-$v_{calc}$, MHz).

| $J'$ | $K_{a}'$ | $K_{b}'$ | $J''$ | $K_{a}''$ | $K_{b}''$ | $v_{obs}$ / MHz | $v_{obs}$-$v_{calc}$ / MHz |
|-----|----------|----------|------|----------|----------|-----------------|---------------------------|
| 1   | 1        | 1        | 0    | 0        | 0        | 7054.597        | 0.0142                    |
| 2   | 0        | 2        | 1    | 1        | 1        | 11596.4        | -0.003                    |
| 2   | 1        | 2        | 1    | 0        | 1        | 11994.36       | -0.0115                   |
| 2   | 2        | 1        | 1    | 1        | 0        | 16223.96       | -0.002                    |
| 3   | 0        | 3        | 2    | 1        | 2        | 16727          | 0.0046                    |
| 3   | 1        | 3        | 2    | 0        | 2        | 16782.98       | 0.0016                    |

Table SL35. Measured rotational transitions ($v_{obs}$, MHz) of the (1,4)-d2 isotopomer and residuals ($v_{obs}$-$v_{calc}$, MHz).
| $J'$ | $K_a'$ | $K_b'$ | $\leftarrow$ | $J''$ | $K_a''$ | $K_b''$ | $\nu_{\text{obs}} / \text{MHz}$ | $\nu_{\text{obs}} - \nu_{\text{calc}} / \text{MHz}$ |
|-----|--------|--------|--------------|-----|--------|--------|----------------|----------------|
| 1   | 1      | 1      | $\leftarrow$ | 0   | 0      | 0      | 6992.662       | -0.006         |
| 2   | 0      | 2      | $\leftarrow$ | 1   | 1      | 1      | 11562.9        | -0.0113        |
| 2   | 1      | 2      | $\leftarrow$ | 1   | 1      | 1      | 11594.75       | 0.0245         |
| 2   | 0      | 2      | $\leftarrow$ | 1   | 0      | 1      | 11851.67       | 0.0043         |
| 2   | 1      | 2      | $\leftarrow$ | 1   | 0      | 1      | 11883.5        | 0.0222         |
| 2   | 2      | 1      | $\leftarrow$ | 1   | 1      | 0      | 16087.19       | -0.0039        |
| 3   | 0      | 3      | $\leftarrow$ | 2   | 1      | 2      | 16608.8        | -0.011         |
| 3   | 1      | 3      | $\leftarrow$ | 2   | 0      | 2      | 16642.82       | -0.0109        |

**Table SL.36.** Measured rotational transitions ($\nu_{\text{obs}}$, MHz) of the (1,6)-d2 isotopomer and residuals ($\nu_{\text{obs}} - \nu_{\text{calc}}$, MHz).

| $J'$ | $K_a'$ | $K_b'$ | $\leftarrow$ | $J''$ | $K_a''$ | $K_b''$ | $\nu_{\text{obs}} / \text{MHz}$ | $\nu_{\text{obs}} - \nu_{\text{calc}} / \text{MHz}$ |
|-----|--------|--------|--------------|-----|--------|--------|----------------|----------------|
| 1   | 1      | 1      | $\leftarrow$ | 0   | 0      | 0      | 7119.61        | -0.0076        |
| 2   | 2      | 1      | $\leftarrow$ | 2   | 1      | 2      | 6672.827       | 0.0052         |
| 4   | 4      | 0      | $\leftarrow$ | 4   | 3      | 1      | 5649.124       | 0.01           |
| 2   | 0      | 2      | $\leftarrow$ | 1   | 1      | 1      | 11380.55       | 0.0115         |
| 2   | 1      | 2      | $\leftarrow$ | 1   | 0      | 1      | 12014.98       | 0.0131         |
| 2   | 2      | 1      | $\leftarrow$ | 1   | 1      | 0      | 16463.5        | -0.006         |
| 3   | 0      | 3      | $\leftarrow$ | 2   | 1      | 2      | 16571.87       | 0.0012         |
| 3   | 1      | 3      | $\leftarrow$ | 2   | 0      | 2      | 16690.97       | 0.0052         |
| 1   | 1      | 1      | $\leftarrow$ | 0   | 0      | 0      | 7119.61        | -0.0076        |
| 2   | 2      | 1      | $\leftarrow$ | 2   | 1      | 2      | 6672.827       | 0.0052         |

**Table SL.37.** Measured rotational transitions ($\nu_{\text{obs}}$, MHz) of the (2,9)-d2 isotopomer and residuals ($\nu_{\text{obs}} - \nu_{\text{calc}}$, MHz).

| $J'$ | $K_a'$ | $K_b'$ | $\leftarrow$ | $J''$ | $K_a''$ | $K_b''$ | $\nu_{\text{obs}} / \text{MHz}$ | $\nu_{\text{obs}} - \nu_{\text{calc}} / \text{MHz}$ |
|-----|--------|--------|--------------|-----|--------|--------|----------------|----------------|
| 1   | 1      | 1      | $\leftarrow$ | 0   | 0      | 0      | 6999.398       | 0.0056         |
| 2   | 0      | 2      | $\leftarrow$ | 1   | 1      | 1      | 11424.75       | 0.0002         |
| 2   | 1      | 2      | $\leftarrow$ | 1   | 0      | 1      | 11836.09       | 0.0088         |
| 2   | 2      | 1      | $\leftarrow$ | 1   | 1      | 0      | 16161.48       | -0.0004        |
| 3   | 0      | 3      | $\leftarrow$ | 2   | 1      | 2      | 16458.56       | 0.0079         |
| 3   | 1      | 3      | $\leftarrow$ | 2   | 0      | 2      | 16512.08       | -0.0156        |
| 2   | 2      | 1      | $\leftarrow$ | 2   | 1      | 2      | 6488.097       | -0.002         |

**Table SL.38.** Measured rotational transitions ($\nu_{\text{obs}}$, MHz) of the (1,8)-d2 isotopomer and residuals ($\nu_{\text{obs}} - \nu_{\text{calc}}$, MHz).

| $J'$ | $K_a'$ | $K_b'$ | $\leftarrow$ | $J''$ | $K_a''$ | $K_b''$ | $\nu_{\text{obs}} / \text{MHz}$ | $\nu_{\text{obs}} - \nu_{\text{calc}} / \text{MHz}$ |
|-----|--------|--------|--------------|-----|--------|--------|----------------|----------------|
| 1   | 1      | 1      | $\leftarrow$ | 0   | 0      | 0      | 7039.215       | -0.0039        |
| 2   | 0      | 2      | $\leftarrow$ | 1   | 1      | 1      | 11734.59       | 0.0079         |
| 2   | 1      | 2      | $\leftarrow$ | 1   | 0      | 1      | 12031.64       | 0.0279         |
| 2   | 2      | 1      | $\leftarrow$ | 1   | 1      | 0      | 16125.26       | -0.004         |
| 3   | 0      | 3      | $\leftarrow$ | 2   | 1      | 2      | 16870.93       | -0.0063        |
| 3   | 1      | 3      | $\leftarrow$ | 2   | 0      | 2      | 16901.01       | -0.0135        |

**Table SL.39.** Measured rotational transitions ($\nu_{\text{obs}}$, MHz) of the (1,9)-d2 isotopomer and residuals ($\nu_{\text{obs}} - \nu_{\text{calc}}$, MHz).

| $J'$ | $K_a'$ | $K_b'$ | $\leftarrow$ | $J''$ | $K_a''$ | $K_b''$ | $\nu_{\text{obs}} / \text{MHz}$ | $\nu_{\text{obs}} - \nu_{\text{calc}} / \text{MHz}$ |
|-----|--------|--------|--------------|-----|--------|--------|----------------|----------------|
| 1   | 1      | 1      | $\leftarrow$ | 0   | 0      | 0      | 6979.3558      | -0.0080        |
| 2   | 0      | 2      | $\leftarrow$ | 1   | 1      | 1      | 11569.7327     | 0.0052         |
| 2   | 1      | 2      | $\leftarrow$ | 1   | 0      | 1      | 11867.4637     | 0.0111         |
| 3   | 0      | 3      | $\leftarrow$ | 2   | 1      | 2      | 16602.1963     | -0.0125        |
### Table SL.40. Measured rotational transitions (ν<sub>obs</sub>, MHz) of the (2,8)-d<sub>2</sub> isotopomer and residuals (ν<sub>obs</sub>−ν<sub>calc</sub>, MHz).

| J' | K<sub>a</sub>' | K<sub>b</sub>' | ← | J'' | K<sub>a</sub>'' | K<sub>b</sub>'' | ν<sub>obs</sub> / MHz | ν<sub>obs</sub>−ν<sub>calc</sub> / MHz |
|----|-------------|-------------|---|----|-------------|-------------|----------------|------------------|
| 1  | 1           | 1           | ← | 0  | 0           | 0           | 7056.7581     | 0.0173           |
| 2  | 0           | 2           | ← | 1  | 1           | 1           | 11583.6441    | 0.0093           |
| 2  | 1           | 2           | ← | 1  | 0           | 1           | 11994.5828    | 0.0127           |
| 2  | 2           | 1           | ← | 1  | 1           | 0           | 16232.2730    | -0.0080          |
| 3  | 0           | 3           | ← | 2  | 1           | 2           | 16718.1684    | -0.0190          |
| 3  | 1           | 3           | ← | 2  | 0           | 2           | 16772.6454    | -0.0039          |

### Table SL.41. Measured rotational transitions (ν<sub>obs</sub>, MHz) of the (1,5)-d<sub>2</sub> isotopomer and residuals (ν<sub>obs</sub>−ν<sub>calc</sub>, MHz).

| J' | K<sub>a</sub>' | K<sub>b</sub>' | ← | J'' | K<sub>a</sub>'' | K<sub>b</sub>'' | ν<sub>obs</sub> / MHz | ν<sub>obs</sub>−ν<sub>calc</sub> / MHz |
|----|-------------|-------------|---|----|-------------|-------------|----------------|------------------|
| 1  | 1           | 1           | ← | 0  | 0           | 0           | 6976.4853     | -0.0099          |
| 2  | 0           | 2           | ← | 1  | 1           | 1           | 11539.5296    | 0.0022           |
| 2  | 1           | 2           | ← | 1  | 0           | 1           | 11856.0937    | 0.0171           |
| 3  | 0           | 3           | ← | 2  | 1           | 2           | 16572.3148    | 0.0047           |
| 3  | 1           | 3           | ← | 2  | 0           | 2           | 16605.7533    | -0.0143          |

### Table SL.42. Measured rotational transitions (ν<sub>obs</sub>, MHz) of the (2,5)-d<sub>2</sub> isotopomer and residuals (ν<sub>obs</sub>−ν<sub>calc</sub>, MHz).

| J' | K<sub>a</sub>' | K<sub>b</sub>' | ← | J'' | K<sub>a</sub>'' | K<sub>b</sub>'' | ν<sub>obs</sub> / MHz | ν<sub>obs</sub>−ν<sub>calc</sub> / MHz |
|----|-------------|-------------|---|----|-------------|-------------|----------------|------------------|
| 1  | 1           | 1           | ← | 0  | 0           | 0           | 6964.4579     | 0.0091           |
| 2  | 1           | 2           | ← | 1  | 0           | 1           | 11793.8472    | -0.0048          |
| 2  | 2           | 1           | ← | 1  | 1           | 0           | 16063.9435    | 0.0002           |
| 3  | 0           | 3           | ← | 2  | 1           | 2           | 16440.3788    | 0.0000           |
| 3  | 2           | 1           | ← | 2  | 1           | 2           | 6405.1353     | -0.0016          |

### Table SL.43. Measured rotational transitions (ν<sub>obs</sub>, MHz) of the (1,10)-d<sub>2</sub> isotopomer and residuals (ν<sub>obs</sub>−ν<sub>calc</sub>, MHz).

| J' | K<sub>a</sub>' | K<sub>b</sub>' | ← | J'' | K<sub>a</sub>'' | K<sub>b</sub>'' | ν<sub>obs</sub> / MHz | ν<sub>obs</sub>−ν<sub>calc</sub> / MHz |
|----|-------------|-------------|---|----|-------------|-------------|----------------|------------------|
| 1  | 1           | 1           | ← | 0  | 0           | 0           | 6960.5413     | 0.0208           |
| 2  | 0           | 2           | ← | 1  | 1           | 1           | 11570.3628    | 0.0177           |
| 2  | 1           | 2           | ← | 1  | 1           | 1           | 11842.7463    | -0.0175          |
| 1  | 0           | 1           | ← | 0  | 0           | 0           | 6711.7580     | -0.0212          |

### Table SL.44. Measured rotational transitions (ν<sub>obs</sub>, MHz) of the (2,10)-d<sub>2</sub> isotopomer and residuals (ν<sub>obs</sub>−ν<sub>calc</sub>, MHz).

| J' | K<sub>a</sub>' | K<sub>b</sub>' | ← | J'' | K<sub>a</sub>'' | K<sub>b</sub>'' | ν<sub>obs</sub> / MHz | ν<sub>obs</sub>−ν<sub>calc</sub> / MHz |
|----|-------------|-------------|---|----|-------------|-------------|----------------|------------------|
| 1  | 1           | 1           | ← | 0  | 0           | 0           | 6979.9469     | 0.0141           |
| 2  | 0           | 2           | ← | 1  | 1           | 1           | 11433.0191    | 0.0115           |
| 2  | 1           | 2           | ← | 1  | 1           | 1           | 11812.9179    | -0.0113          |
| 1  | 0           | 1           | ← | 0  | 0           | 0           | 6642.8384     | -0.0145          |

### Table SL.45. Measured rotational transitions (ν<sub>obs</sub>, MHz) of the (2,3,8)-d<sub>3</sub> isotopomer and residuals (ν<sub>obs</sub>−ν<sub>calc</sub>, MHz).

| J' | K<sub>a</sub>' | K<sub>b</sub>' | ← | J'' | K<sub>a</sub>'' | K<sub>b</sub>'' | ν<sub>obs</sub> / MHz | ν<sub>obs</sub>−ν<sub>calc</sub> / MHz |
|----|-------------|-------------|---|----|-------------|-------------|----------------|------------------|
| 1  | 1           | 1           | ← | 0  | 0           | 0           | 6897.8888     | -0.0258          |
| 2  | 0           | 2           | ← | 1  | 1           | 1           | 11460.26      | 0.0081           |
Table SL.46. Measured rotational transitions (ν_{obs}, MHz) of the (1,4,9)-d3 isotopomer and residuals (ν_{obs}-ν_{calc}, MHz).

| J' | K_a' | K_b' | ← | J'' | K_a'' | K_b'' | ν_{obs} / MHz | ν_{obs}-ν_{calc} / MHz |
|----|------|------|← |      |       |       |              |                        |
| 1  | 1    | 1    | ← | 0    | 0     | 0     | 6705.143     | -0.0246                |
| 2  | 0    | 2    | ← | 1    | 1     | 1     | 11372.71     | -0.002                 |
| 2  | 1    | 1    | ← | 1    | 1     | 0     | 15361.97     | 0.0073                 |
| 3  | 0    | 3    | ← | 2    | 1     | 2     | 16168.89     | -0.0015                |
| 3  | 1    | 3    | ← | 2    | 0     | 2     | 16171.67     | 0.0062                 |

Table SL.47. Measured rotational transitions (ν_{obs}, MHz) of the (1,3,8)-d3 isotopomer and residuals (ν_{obs}-ν_{calc}, MHz).

| J' | K_a' | K_b' | ← | J'' | K_a'' | K_b'' | ν_{obs} / MHz | ν_{obs}-ν_{calc} / MHz |
|----|------|------|← |      |       |       |              |                        |
| 1  | 1    | 1    | ← | 0    | 0     | 0     | 6882.2833    | -0.0216                |
| 2  | 0    | 2    | ← | 1    | 1     | 1     | 11600.1449   | 0.0009                 |
| 2  | 1    | 0    | ← | 1    | 1     | 0     | 15693.4047   | 0.0061                 |
| 3  | 0    | 3    | ← | 2    | 1     | 2     | 16668.4997   | -0.0106                |
| 3  | 1    | 3    | ← | 2    | 0     | 2     | 16688.8445   | 0.0131                 |

Table SL.48. Measured rotational transitions (ν_{obs}, MHz) of the (2,4,9)-d3 isotopomer and residuals (ν_{obs}-ν_{calc}, MHz).

| J' | K_a' | K_b' | ← | J'' | K_a'' | K_b'' | ν_{obs} / MHz | ν_{obs}-ν_{calc} / MHz |
|----|------|------|← |      |       |       |              |                        |
| 1  | 1    | 1    | ← | 0    | 0     | 0     | 6718.8997    | -0.0323                |
| 2  | 0    | 2    | ← | 1    | 1     | 1     | 11249.6884   | 0.0057                 |
| 2  | 1    | 2    | ← | 1    | 0     | 1     | 11423.6757   | 0.0198                 |
| 2  | 2    | 1    | ← | 1    | 1     | 0     | 15452.0779   | 0.0055                 |
| 3  | 0    | 3    | ← | 2    | 1     | 2     | 16039.8632   | -0.0145                |
| 3  | 1    | 3    | ← | 2    | 0     | 2     | 16050.6683   | 0.0045                 |
Table SL49. Measured rotational transitions ($\nu_{\text{obs}}, \text{MHz}$) of the (2,3,7,8)-d$_4$ isotopomer and residuals ($\nu_{\text{obs}}-\nu_{\text{calc}}, \text{MHz}$).

| J' | K$_a'$ | K$_b'$ | ← | J'' | K$_a''$ | K$_b''$ | $\nu_{\text{obs}}/ \text{MHz}$ | $\nu_{\text{obs}}-\nu_{\text{calc}}/ \text{MHz}$ |
|----|-------|-------|---|------|-------|-------|----------------|----------------|
| 1  | 1     | 1     | ← | 0    | 0     | 0     | 6804.767       | -0.0069        |
| 2  | 0     | 2     | ← | 1    | 1     | 1     | 11146.7        | 0.008          |
| 2  | 1     | 2     | ← | 1    | 0     | 1     | 11621.89       | 0.0236         |
| 2  | 2     | 1     | ← | 1    | 1     | 0     | 15597.23       | -0.0025        |
| 3  | 0     | 3     | ← | 2    | 1     | 2     | 16188.47       | -0.012         |
| 3  | 1     | 3     | ← | 2    | 0     | 2     | 16264.63       | -0.005         |

Table SL50. Measured rotational transitions ($\nu_{\text{obs}}, \text{MHz}$) of the (2,4,7,9)-d$_4$ isotopomer and residuals ($\nu_{\text{obs}}-\nu_{\text{calc}}, \text{MHz}$).

| J' | K$_a'$ | K$_b'$ | ← | J'' | K$_a''$ | K$_b''$ | $\nu_{\text{obs}}/ \text{MHz}$ | $\nu_{\text{obs}}-\nu_{\text{calc}}/ \text{MHz}$ |
|----|-------|-------|---|------|-------|-------|----------------|----------------|
| 1  | 1     | 1     | ← | 0    | 0     | 0     | 6632.364       | -0.0064        |
| 2  | 0     | 2     | ← | 1    | 1     | 1     | 10951.76       | -0.0037        |
| 2  | 1     | 2     | ← | 1    | 0     | 1     | 11260.65       | -0.0127        |
| 2  | 2     | 1     | ← | 1    | 1     | 0     | 15268.83       | 0.0042         |
| 3  | 0     | 3     | ← | 2    | 1     | 2     | 15729.43       | 0.0019         |
| 3  | 1     | 3     | ← | 2    | 0     | 2     | 15762.55       | 0.0084         |
M. Mechanistic Considerations.

In principle, protonation of the \( \eta^2 \)-benzene ligand of 1 could occur at any one of the six carbons. Several mechanisms that would give rise to 2 are shown in supplementary materials (Fig. S8), which include direct protonation of the benzene endo or exo to the metal, as well as indirect protonation via a metal hydride. The reaction of 1 with \( \text{D}^+ \) to form 11 (e.g. 2-d1) results in deuterium incorporation exclusively endo to the metal, but this does not definitively show which carbon is initially protonated. Given that the endo proton of the benzene ligand in 1 completely preempts protonation from an exogenous acid (exo), we propose that the protonation must be concerted— that C-H bond formation is intramolecular and simultaneous with electronic changes at the metal, which could lower the activation barrier for this process (relative to protonation by an external acid). Such a mechanism could occur via a hydride intermediate, but this seems sterically untenable. Rather, we propose a mechanism (Fig. S14) in which the nitrosyl ligand first is protonated to form a hydroxylimido ligand analogous to that reported by Legzdins et al.\(^{22}\) This would be followed by a concerted proton transfer in which a gamma carbon of the benzene is protonated simultaneously with release of electron density back into the tungsten through the NO group. Such action would stabilize the emerging benzenium ligand (Fig. S14; 2*). An analogous protonation at the other gamma carbon would lead to the minor isomer 3, via 3*. DFT calculations indicate that the \( \eta^1 \)-benzenium complex 2 is only 2.4 kcal/mol lower in energy than the protonated nitrosyl (1H\(^{+} \)), and the activation barrier for this process (transition state shown in Fig. S14) is only \( \sim 12 \) kcal/mol. The role of nitrosyl ligands in intramolecular proton transfer has been previously documented.\(^ {23}\)

NOESY data for a sample of 1 in acidic solution (S9) include chemical exchange correlations (Fig. S9; circled correlations) that indicate the interconversion of 2 and 3 (Fig. S14). The chemical exchange between seven pairs of protons from the two isomers (each pair indicated by a different color) reveal that an intermolecular spin transfer occurs between 2 to 3 with a concomitant 60° ccw rotation of the benzene ring (looking from benzene to tungsten). Further, an intramolecular spin transfer is indicated for 2 that involves a 120° cw rotation (Fig S9; boxed correlations). We propose that these exchanges occur via the intermediate species 1H\(^{+} \) (Figure S14), where a reversible nitrosyl proton transfer can involve either gamma carbon. Note that isomerization of 2/3 occurs at a rate similar to, but not significantly slower than the purported benzene ring-walk, because the latter isomerization does not completely scramble the benzene proton spin density. The chemical exchange data rules out the direct isomerization of 2 and 3, as well as \( \alpha \) or \( \beta \) protonation as the dominant isomerization mechanism, since these pathways would result in different exchange patterns (Fig. S14).

Regarding the stereochemistry and kinetics of \( \eta^2 \)-diene protonation, the reaction of complexes 4 and 5 with a deuterated acid indicates that at -30 °C, the hydrogen is delivered exogenously, exo to the tungsten (Fig 1). The allyl complex 26 was prepared from the 1,3-cyclohexadiene species 4, while treatment of the stereoisomer 5 reacts to form the isotopomer 24. In contrast to the \( \eta^2 \)-benzene complex 1, a metal- or nitrosyl-assisted mechanism does not appear to be involved at this temperature. We speculate that while endo protonation may still be accessible for these 1,3-cyclohexadiene complexes, the less-delocalized diene ligand is more basic than its \( \eta^1 \)-benzene predecessor, and its direct exo protonation apparently preempts the endo mechanism at -30 °C.

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