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Supporting Information

Thermal Decomposition Modes for Four Coordinate Ruthenium Phosphonium Alkylidene Olefin Metathesis Catalysts.

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Supporting Information

1. General Information.

1.A. Reagents and General Procedures. Most operations involving ruthenium complexes were performed under a purified argon atmosphere using glove box or vacuum line techniques. Preparations of organic compounds were done in air. Ether, pentane, hexanes, dichloromethane, and toluene were all pre-dried in CaH_2 or sodium/benzophenone or sodium/potassium alloy. Borane dimethylsulfide adduct (1 M in CH_2Cl_2), chloral acetyl chloride, chloral hydrate, 1,1-dichloroethene, 4-dimethylaminopyridine, 2,4-dimethyl aniline, dioxane, hexamethyldisiloxane, hydroxylamine hydrochloride, iodomethane, iodomethane-d_3, 98%-D $LiAlD_4$, 98%-D mesitylene-d_{12}, oxalyl chloride, potassium hexamethyldisilazane, sodium borohydride, tricyclohexylphosphine, triethyl orthoformate, triisopropylphosphine, and zinc powder were purchased from Aldrich. Hydrogen peroxide (30 wt%) and sodium iodide were purchased from EM Science. Pyridine was purchased from EMD Chemicals Inc. A gas cylinder of hydrochloric acid was purchased from Matheson Gas Products Canada. $B(C_6F_5)_3$ (97%, Strem) was purified to >99 % purity by sublimation in vacuo at 70°C. Generation 1 and 2 Grubbs catalysts were provided by Materia, and Feist's ester[1] and Jutzi's acid[2] were prepared by published procedures. NMR spectra for the ruthenium complexes were recorded in dry (over CaH_2), oxygen free CD_2Cl_2 or $C_2D_2Cl_4$. NMR spectra for organic compounds were run in $CDCl_3$, CD_2Cl_2 or acetone-d_6, which were used as received. All NMR solvents are from Cambridge Isotope Laboratories Inc. purchased from ACP Chemicals.

1.B. Instrumentation. Nuclear magnetic resonance spectroscopy (^1H, ^2H, $^{13}C\{^1H\}$, $^{31}P\{^1H\}$, DEPT-135, HMQC and COSY) was performed on Bruker AMX-300, DMX-300, UGI-400, DRY-400 or DRX-400. All ^1H and ^{13}C spectra were referenced to Me_4Si at 0 ppm through the residual ^1H signal(s) of the deuterated solvents used. ^2H NMR spectra were referenced by locking and measuring a ^1H NMR spectrum with an equivalent amount of solvent. ^{31}P NMR spectra were referenced to an aqueous external standard of H_3PO_4 in D_2O at δ 0.0 ppm. Elemental analyses, High-Resolution Mass Spectrometry (HRMS), and Electrospray Ionization Mass Spectrometry (ESI MS) were performed at the University of Calgary.

2. Quantitative ESI MS.

2.A. Synthesis of CD_3PCy_3I/CH_3PCy_3I.[3]

In a glove box, PCy_3 (100 mg; 0.36 mmol) was weighed into a 2-necked 50 mL round bottom flask equipped with stir bar. 10 mL of hexanes was added and then on the vacuum line 10 mL of diethyl ether was vacuum transferred to the flask (at -78°C). In a separate 2-necked round bottom flask methyl iodide (or d_3-methyl iodide) was weighed (507 mg/522 mg; 3.60 mmol), degassed, and added via syringe to the phosphine (at 25°C) to produce a white precipitate within seconds. After stirring at room temperature overnight, the precipitate was filtered, washed with pentane (3 X 20 mL), and dried further on the vacuum line. Yield = 141 mg (92%; 0.33 mmol). **CH_3PCy_3I:** ^{1}H NMR (399.6 MHz, CD_2Cl_2, 298 K): δ 2.50 (ps q, 3H, Cy C*H*), 1.96-1.80 (m, 18H, overlapping C*H*$_3$ and Cy C*H*$_2$), 1.54-1.36 (m, 15H, Cy C*H*$_2$). ^{31}P{^{1}H} NMR (161.8 MHz, CD_2Cl_2, 298 K) δ 34.61(s). ^{13}C{^{1}H} NMR (100.5 MHz, CD_2Cl_2, 298 K): δ 30.14 (d, $^1J_{CP}$ = 42 Hz, Cy *C*H), 26.69 (d, $^2J_{CP}$ = 4 Hz, Cy *C*H$_2$), 26.20 (d, $^3J_{CP}$ = 12 Hz, Cy *C*H$_2$), 25.24 (d, $^4J_{CP}$ = 2 Hz, Cy *C*H$_2$), 0.48 (d, $^1J_{CP}$ = 49 Hz, *C*H$_3$). ESI MS: $C_{19}H_{36}P^+$ [M – I$^-$]: 295 m/z. HRMS: Calcd for $C_{19}H_{36}P^+$ 295.2555, Observed 295.2553. **CD_3PCy_3I:** ^{1}H NMR (399.6 MHz, CD_2Cl_2, 298 K): δ 2.50 (ps q, 3H, Cy C*H*), 1.96-1.80 (m, 15H, Cy C*H*$_2$), 1.54-1.31 (m, 15H, Cy C*H*$_2$). ^{31}P{^{1}H} NMR (161.8 MHz, CD_2Cl_2, 298 K) δ 34.28 (s). ^{13}C{^{1}H} NMR (100.5 MHz, CD_2Cl_2, 298 K): δ 30.08 (d, $^1J_{CP}$ = 42 Hz, Cy *C*H), 26.69 (d, $^2J_{CP}$ = 4 Hz, Cy *C*H$_2$), 26.20 (d, $^3J_{CP}$ = 12 Hz, Cy *C*H$_2$), 25.22 (d, $^4J_{CP}$ = 2 Hz, Cy *C*H$_2$), *C*D$_3$ resonance not resolved. ESI MS: $C_{19}H_{33}D_3P^+$ [M – I$^-$]: 298 m/z. HRMS: Calcd for $C_{19}H_{33}D_3P^+$ 298.2743, Observed 298.2738.

Similarly, P^{i}Pr$_3$ derivatives can be prepared:

CH_3 P^{i}Pr$_3$I: ^{1}H NMR (399.6 MHz, CD_2Cl_2, 298 K): δ 2.86 (ps s, 3H, ^{i}Pr C*H*), 1.92 (d, 3H, C*H*$_3$), 1.45 (dd, $^1J_{CH}$ = 20 Hz, 18H, ^{i}Pr C*H*$_3$). ^{31}P{^{1}H} NMR (161.8 MHz, CD_2Cl_2, 298 K) δ 45.59(s). ^{13}C{^{1}H} NMR (100.5 MHz, CD_2Cl_2, 298 K): δ 21.01 (d, $^1J_{CP}$ = 43 Hz, ^{i}Pr *C*H), 16.82 (d, $^2J_{CP}$ = 3 Hz, ^{i}Pr *C*H$_3$), 0.50 (d, $^1J_{CP}$ = 49 Hz, *C*H$_3$). ESI MS: $C_{10}H_{24}P^+$ [M – I$^-$]: 175 m/z. HRMS: Calcd for $C_{10}H_{24}P^+$ 175.1616, Observed 175.1614. **CD_3 P^{i}Pr$_3$I:** ^{1}H NMR (399.6 MHz, CD_2Cl_2, 298 K): δ 2.59 (ps s, 3H, ^{i}Pr C*H*), 1.43 (dd, $^1J_{CH}$ = 20 Hz, 18H, ^{i}Pr C*H*$_3$). ^{31}P{^{1}H} NMR (161.8 MHz, CD_2Cl_2, 298 K) δ 45.28 (s). ^{13}C{^{1}H} NMR (100.5 MHz, CD_2Cl_2, 298 K): δ 20.95 (d, $^1J_{CP}$ = 43 Hz, ^{i}Pr *C*H), 16.81 (d, $^2J_{CP}$ = 3 Hz, ^{i}Pr *C*H$_3$), *C*D$_3$ resonance not resolved. ESI MS: $C_{10}H_{21}D_3P^+$ [M – I$^-$]: 178 m/z. HRMS: Calcd for $C_{10}H_{21}D_3P^+$ 178.1804, Observed 178.1808.

2.B. Correlation Curve by ESI MS.

Samples of varying ratios of CH_3PCy_3I to CD_3PCy_3I (0, 1, 2, 3, 4, 5) were prepared from stock solutions (0.00205 mg/mL $CD_3PCy_3^+$, 0.00208 mg/mL $CH_3PCy_3^+$) in water, which were measured using automatic volumetric pipettes to form solutions with a total analyte concentration of 0.00164 mg/mL in 80% water/20% acetonitrile (eg. 1/1: 1600 μL $CH_3PCy_3^+$ stock solution, 1600 μL $CD_3PCy_3^+$ stock solution, and 800 μL acetonitrile). Each of these solutions was run on the ESI MS instrument three times with an acquisition time of 30 minutes per trial. The absolute intensities obtained were corrected for the

natural isotopic abundance (based on a sample containing only CH_3PCy_3I), and a correlation curve was produced (Figure 1).

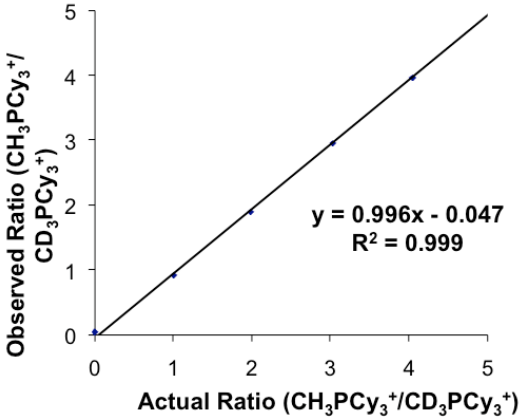


Figure 1- Comparison of Ratio In (by Known Concentrations) to Ratio Out (by ESI-MS Relative Integrations)

2.C. ESI MS Verification Against NMR Spectroscopy.

Several labeled samples (298 K/343 K decomposition of d_{11}-**1-^{i}Pr/Cy**, 343 K decomposition of d_6-**1-^{i}Pr/Cy**) were completely decomposed (monitored by ^{31}P NMR for disappearance of starting material) and then the resulting mixture was measured using ESI MS (see Experimental) and then also measured by relating the peak integrations ($CH_3PR_3^+$ vs. $CHD_2PR_3^+$; R = ^{i}Pr, Cy) using a Bruker BioSpin Canada Avance III 600 MHz NMR to give a quantitative $^{31}P\{^1H\}$ NMR (242.9 MHz, CD_2Cl_2, 298 K, 90 degree pulse, d_1 = 100 s, ns = 512) for comparison (Table 1).

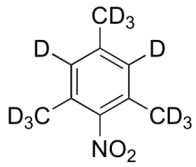
	KIE by ESI MS /±0.4	**KIE by NMR Spectroscopy /±0.4**
d_{11}-1-^{i}Pr, 343 K	6.2	5.8
d_6-1-^{i}Pr, 343 K	5.9	7.2
d_{11}-1-^{i}Pr, 298 K	9.4	8.9
d_{11}-1-Cy, 343 K	6.9	6.6
d_6-1-Cy, 343 K	6.8	7.1
d_{11}-1-Cy, 298 K	9.8	9.6

Table 1- ESI MS and NMR Spectroscopy Comparison of KIEs

3. Labeled Ligand Synthesis.

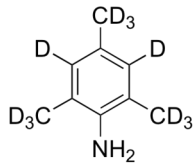
3.A. Synthesis of d_{11}-Mesityl Aniline.

Synthesis of d_{11}-Nitromesityl[4]



In a 100 mL round bottom flask, equipped with stir bar, d_{12}-mesitylene (5.157 g, 39.0 mmol) was charged along with 10 mL of acetic anhydride. The flask was placed in an ice bath (0°C). In a separate flask (125 mL), acetic anhydride (20 mL) and nitric acid (2.60 mL, 40.9 mmol) were combined and cooled (0°C). The nitric acid mixture was added to the mesitylene mixture drop wise via syringe, causing the solution to become orange upon addition, disappearing after a few minutes. The reaction stirred for 1 hour at room temperature, and the reaction progress was monitored by TLC (1:8 ethyl acetate/hexanes). The reaction mixture was then poured into 250 mL of ice water to precipitate, was filtered, and washed with water yielding light-yellow crystalline solids. Yield = 6.565 g (96%, 37.2 mmol). ^{2}H NMR (46.1 MHz, $CHCl_3$, 298 K): δ 6.20 (br s, 2H, Mes C*D*), 1.52, 1.49 (overlapping br s, 9H, Mes CD_3). HRMS: Calcd for $C_9D_{11}O_2N$ 176.14890, Observed 176.14802.

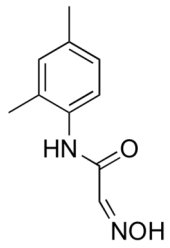
Synthesis of d_{11}-Mesityl Aniline[5]



In a 250 mL round bottom flask equipped with stir bar, d_{11}-nitromesityl (6.565 g, 37.2 mmol) was added along with 125 mL of ethanol. Zinc powder (12.097 g, 185 mmol) was then added and the mixture was cooled to 0°C (ice/water bath). 15 mL of concentrated acetic acid was added drop wise (very slowly!) and the solution left to slowly warm to room temperature over 5 hours. Reaction completion was tested by TLC (1:4 ethyl acetate/hexanes) against starting material and completed reaction was worked up by extracting with 1 M $NaOH_{(aq)}$ and petroleum ether (3 X 50 mL). Petroleum ether extracts were combined, dried ($MgSO_4$), filtered, and concentrated to a clear orange oil. Yield = 4.472 g (82%, 30.6 mmol). ^{1}H NMR (300.1 MHz, $CDCl_3$, 298 K): δ 3.46 (br s, 2H, NH_2). ^{2}H NMR (46.1 MHz, $CHCl_3$, 298 K): δ 6.16 (br s, 2H, Mes C*D*), 1.41, 1.36 (overlapping s, 9H total, o/p-Mes CD_3). HRMS: Calcd for $C_9D_{11}H_2N$ 146.17398, Observed 146.17384.

3.B. Synthesis of *ortho-d_3*-Mesityl Aniline.[6]

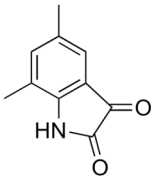
Synthesis of 2,4-Dimethylisonitrosoacetanilide[3a]



Chloral hydrate (27.316 g, 165 mmol) was charged into a 2-necked, 2 L round bottom flask equipped with stir bar and 800 mL of distilled water was added. In a 250 mL flask hydroxylamine hydrochloride (34.973 g, 495 mmol) was dissolved in 200 mL of distilled water and then added to the 2 L flask. In another 250 mL flask 2,4-dimethyl aniline (20.5 mL, 165 mmol) was dissolved in 1.2 M HCl (16 mL $HCl_{(conc.)}$ in 160 mL of H_2O) and then added to the 2 L flask. Finally, anhydrous sodium sulfate (238.442 g, 1650 mmol) was added and solution was slowly heated to 80°C over 3 hours. Reaction solution became brown over the 3 hours. Reaction was

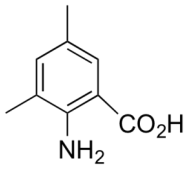
cooled to room temperature and then was filtered, washed with H_2O, benzene, and hexanes respectively. Resulting wet brown solids were further dried in vacuo and then recrystallized from ethyl acetate and hexanes. Yield = 20.386 g (64%, 106 mmol). ^{1}H NMR (399.6 MHz, acetone-d_6, 298 K): δ 11.35 (s, 1H, N*H*), 8.62 (br s, 1H, C*H*NOH), 7.66 (d, J = 8 Hz, 1H, ortho-C*H*), 7.55 (s, 1H, meta-C*H*), 7.00 (d, J = 8 Hz, 1H, meta-C*H*), 3.05 (br s, 1H, NO*H*), 2.27, 2.25 (overlapping s, 6H total, CH_3). ^{13}C{^{1}H} NMR (100.5 MHz, acetone-d_6, 298 K): δ 160.08 (s, N*C*O), 144.06 (s, *C*HNOH), 134.89, 133.16, 129.73 (s, tertiary *C*), 130.86, 126.70, 123.22 (s, aromatic *C*H), 16.79, 16.77 (s, *C*H_3). Anal. Calcd. for $C_{10}H_{12}O_2N_2$: C, 62.49; H, 6.29; N, 14.57. Found: C, 62.08; H, 6.17; N, 14.24.

Synthesis of 5,7-Dimethyl-2,3-indoledione[3b]



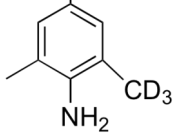
Made as per literature procedure with 88% H_2SO_4. Crude Yield = 90%. Used crude solids to make 2-amino-3,5-dimethylbenzoic acid. Crude ^{13}C{^{1}H} NMR (100.5 MHz, acetone-d_6, 298 K): δ 184.31 (s, N*C*O), 159.52 (s, *C*O), 147.04, 121.40, 117.96, 107.73 (s, tertiary *C*), 140.06, 132.41, 122.01 (s, aromatic *C*H), 19.49, 14.66 (s, *C*H_3).

Synthesis of 2-Amino-3,5-dimethylbenzoic Acid[3a]



In a 500 mL round bottom flask equipped with stir bar, 2-amino-3,5-dimethylbenzoic acid (16.423 g, 93.7 mmol), sodium hydroxide (4.151 g, 103 mmol), potassium chloride (17.516 g, 235 mmol) and 200 mL of distilled water were added. Contents of the flask were cooled to 0°C (ice/water bath) and in a separate flask (also cooled to 0°C) 200 mL of distilled water, sodium hydroxide (15.034 g, 376 mmol), and 30% wt/wt hydrogen peroxide (20 g) were combined. The peroxide solution was added to the round bottom flask through a dropping funnel over 1 hour. Flask was then left to stir for 30 minutes without replenishing ice bath followed by drop wise addition of glacial acetic acid (44 mL). A brown precipitate formed which was filtered and washed with water and pentane, and then were further dried in vacuo. Crude solids purified by sublimation at 140°C. Yield = 10.192 g (66%, 61.7 mmol). ^{1}H NMR (399.6 MHz, acetone-d_6, 298 K): δ 7.57, 7.05 (s, 2H, aromatic C*H*), 7.66 (br s, NH_2), 2.18, 2.15 (overlapping s, 6H total, CH_3). ^{13}C{^{1}H} NMR (100.5 MHz, acetone-d_6, 298 K): δ 169.62 (s, CO_2H), 147.90, 123.32, 123.14, 111.42 (s, tertiary *C*), 135.91, 128.89 (s, aromatic *C*H), 19.34, 16.63 (s, *C*H_3). Anal. Calcd. for $C_9H_{11}O_2N$: C, 65.44; H, 6.71; N, 8.48. Found: C, 65.36; H, 6.89; N, 8.46. No resolution of carboxylic acid proton suggests that this compound likely exists in the zwitterionic form.

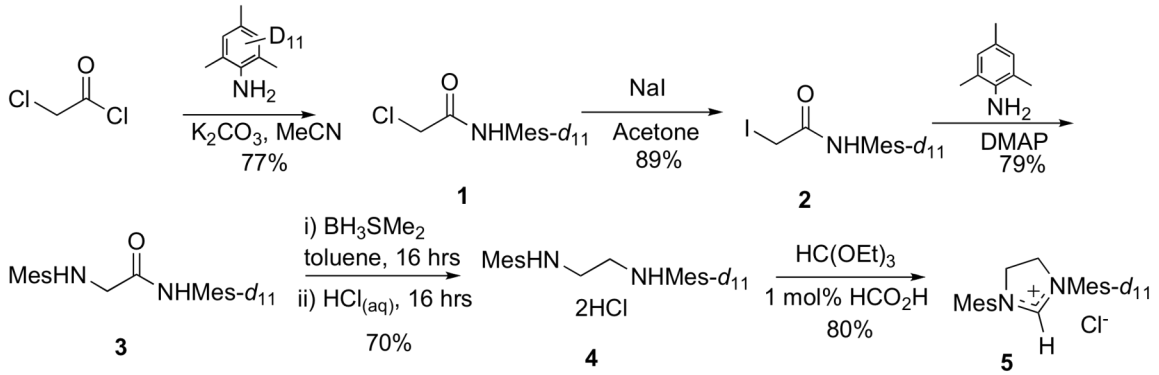
Synthesis of *ortho*-d_3-Mesityl Aniline[3c]



In a 1 L 3-necked round bottom flask equipped with stir bar and a condenser under argon, $LiAlD_4$ (2.850 g, 67.8 mmol) was added along with 1 L of dioxane and finally 2-amino-3,5-dimethyl benzoic acid (1.402g, 8.5 mmol) was added slowly. Aluminum trichloride (2.274 g, 17.0 mmol) was carefully added (some gas evolution) and reaction was stirred at room temperature for 20 minutes before heating to reflux overnight. Cooled

reaction mixture was quenched with sequentially with ethyl acetate, ethanol and 1 M $NaOH_{(aq)}$ until pH > 12. Mixture was extracted with ether (3 X 500 mL) and ether extracts were combined, dried ($MgSO_4$), filtered and concentrated to dryness yielding a clear orange oil. Crude oil was purified by short path distillation (85°C under dynamic vacuum). Yield = 0.817 g (71%, 6.0 mmol). ^{1}H NMR (300.1 MHz, $CDCl_3$, 298 K): δ 6.79 (s, 2H, Mes C*H*), 3.46 (br s, NH_2), 2.23, 2.18 (s, 3H each, Mes CH_3). ^{2}H NMR ($CHCl_3$, 46.1 MHz, 298 K) δ 1.88 (s, 3H, Mes CD_3). ^{13}C{^{1}H} NMR (100.5 MHz, $CDCl_3$, 298 K): δ 140.34, 127.33, 122.03, 131.94 (s, tertiary *C*), 129.02 (s, Mes *C*H), 20.53, 17.74 (s, Mes *C*H_3), 17.02 (septet, Mes *C*D_3). HRMS: Calcd for $C_9H_{10}D_3N$ 138.1236, Observed 138.1238.

3.C. Synthesis of asymmetric d_{11}-NHC.



Synthesis of the labeled (d_{11}) version of N-chloroacetylmesitylamine (**1**)[7], N,N'-(dimesityl) ethane 1,2-diamine dichloride salt (**4**)[8] and 1,3-dimesityl-4,5-dihydroimidazolinium (**5**)[9] were prepared by modifying published procedures with deuterium-containing starting materials.

(**1**): Spectral data are consistent with literature.[7] ^{2}H NMR (46.1 MHz, $CHCl_3$, 298 K): δ 6.19 (br s, 2H, Mes C*D*), 1.48, 1.40 (overlapping s, 9H total, o/p-Mes CD_3).

(**4**): Spectral data are consistent with literature.[8b] ^{2}H NMR (46.1 MHz, $CHCl_3$, 298 K): δ 6.85 (br s, 2H, Mes C*D*), 1.88, 1.63 (overlapping s, 9H total, o/p-Mes CD_3).

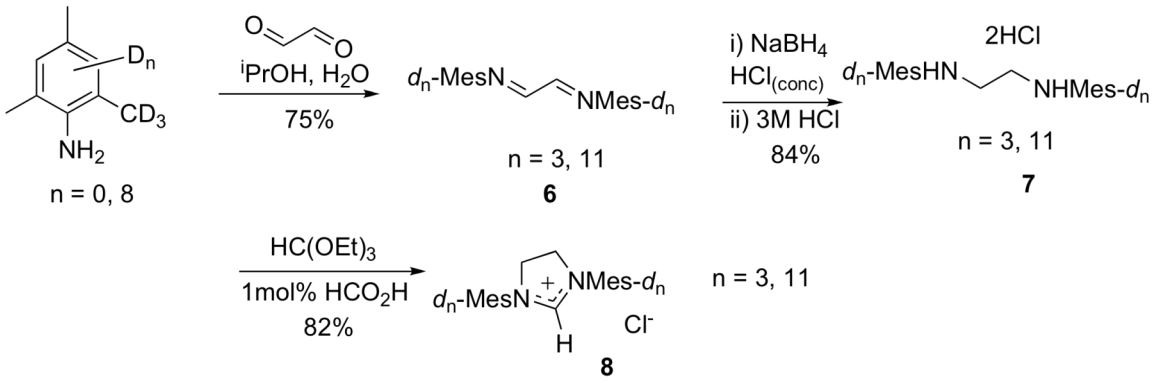
(**5**): Spectral data are consistent with literature.[8b] ^{2}H NMR (46.1 MHz, $CHCl_3$, 298 K): δ 6.76 (br s, 2H, Mes C*D*), 1.78, 1.67 (overlapping s, 9H total, o/p-Mes CD_3).

Synthesis of N-iodoacetyl(d_{11}-mesityl)amine (2) In a 250 mL round bottom flask, equipped with stir bar, N-chloroacetyl(d_{11}-mesityl)amine (1.333 g, 5.98 mmol) was dissolved in 50 mL of acetone. In a separate flask sodium iodide (1.311 g, 8.75 mmol) was dissolved in 50 mL of acetone and then was added to the round bottom flask. Reaction was stirred at room temperature overnight. A fine white precipitate (NaCl) was observed after the reaction time, which was filtered and washed with acetone (3 X 10 mL). The filtrate was concentrated to dryness and then washed with water. Solids remaining were recrystallized from ethyl acetate. Yield = 1.673 g (89%, 5.32 mmol). ^{1}H NMR (300.1 MHz, $CDCl_3$, 298 K): δ 7.30 (br s, 2H, N*H*), 3.88 (s, 2H, CH_2). ^{2}H NMR (46.1 MHz, $CHCl_3$, 298 K): δ 6.15 (br s, 2H, Mes C*D*), 1.46, 1.39 (overlapping s, 9H

total, o/p-Mes CD_3). $^{13}C\{^1H\}$ NMR (100.5 MHz, $CDCl_3$, 298 K): δ 165.33 (s, *C*O), -1.08 (s, *C*H_2I). No d_{11}-Mes ^{13}C NMR signals were resolved. HRMS: Calcd for $C_{11}H_3D_{11}NOI$ 314.0811, Observed 314.0818.

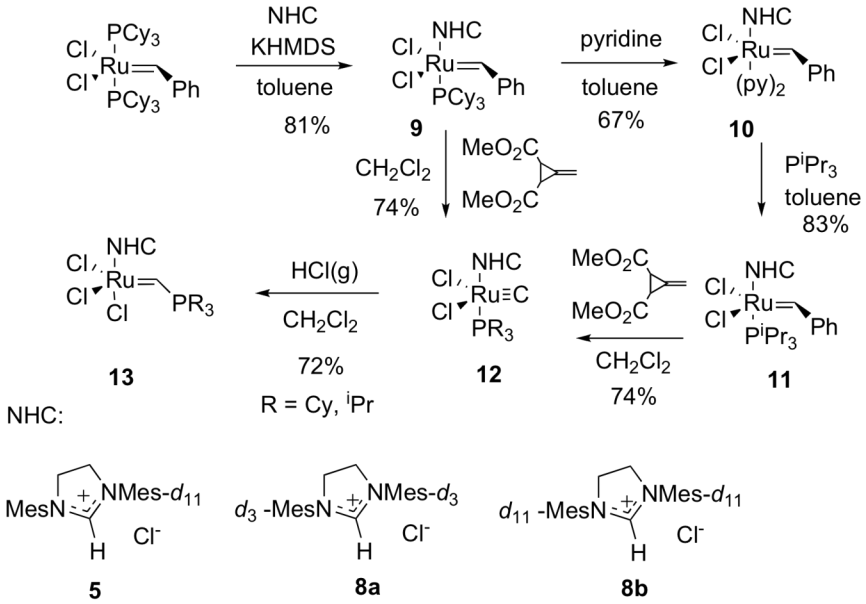
Synthesis of N-(d_{11}-mesityl)-N'-(mesityl) ethane 2-amine amide (3) In a 100 mL round bottom flask equipped with stir bar, N-iodoacetyl(d_{11}-mesityl)amine (5.100 g, 16.2 mmol) was added along with mesityl aniline (35 mL, 249 mmol) and a small chunk of 4-dimethylaminopyridine (DMAP) and mixture was stirred at room temperature for three days. Reaction progress was monitored by TLC (1:4 ethyl acetate/hexanes) and once complete (no more N-iodoacetyl (d_{11}-mesityl)amine), the solution was distilled to recover excess mesityl aniline. Remaining residue was extracted with 1 M $NaOH_{(aq)}$ (100 mL) and dichloromethane (3 X 50 mL) and the organic extracts were combined, dried ($MgSO_4$), filtered and concentrated to give brown solids. Solids were recrystallized from ethyl acetate. Yield = 4.123 g (79%, 12.8 mmol). ^1H NMR (300.1 MHz, $CDCl_3$, 298 K): δ 8.52 (br s, 1H, N*H*CO), 6.88 (s, 2H, Mes C*H*), 3.80 (s, 2H, CH_2), 3.55 (br s, 1H, N*H*CH_2), 2.35, 2.26 (overlapping s, 9H total). ^2H NMR (46.1 MHz, $CHCl_3$, 298 K): δ 6.45 (br s, 2H, Mes C*D*), 1.65, 1.61 (overlapping s, 9H total, o/p-Mes CD_3). ^{13}C NMR (100.5 MHz, $CDCl_3$, 298 K): δ 169.55 (s, *C*O), 142.23, 136.77, 134.69, 132.82, 130.91 (s, tertiary *C*), 129.94, 129.81 (s, Mes *C*H), 129.58, 129.31, 129.05, 128.85, 128.73, 128.53 (overlapping *C*D and tertiary *C* on d_{11}-Mes), 52.45 (s, *C*H_2), 20.57, 18.30 (s, Mes *C*H_3), 17.87, 17.48 (overlapping septets for o/p Mes *C*D_3). HRMS: Calcd for $C_{20}H_{15}D_{11}ON_2$ 321.2736, Observed 321.2743.

3.D. Synthesis of symmetric d_n-NHC (n = 6, 22)



Synthesis of the labeled versions of N,N'-(dimesityl) ethylenediimine (**6**), N,N'-(dimesityl) ethane 1,2-diamine dichloride salt (**7**) and 1,3-dimesityl-4,5-dihydroimidazolinium (**8**) were all prepared by published procedures with deuterium-containing starting materials.[9] Spectral data is consistent with literature (^2H NMR chemical shifts are very similar to the shifts in the asymmetric NHC analogue).[9]

4. Synthesis of labeled ruthenium phosphonium alkylidene catalysts



Synthesis of (9), (10), (11), (12), (13) were all prepared by published procedures with deuterium-containing N-heterocyclic carbene (NHC) ligands.[1,10] Spectral data is consistent with literature (^{2}H NMR chemical shifts do not deviate significantly from those of the respective non-coordinated NHC ligands).[1,10]

5. NMR Spectrum

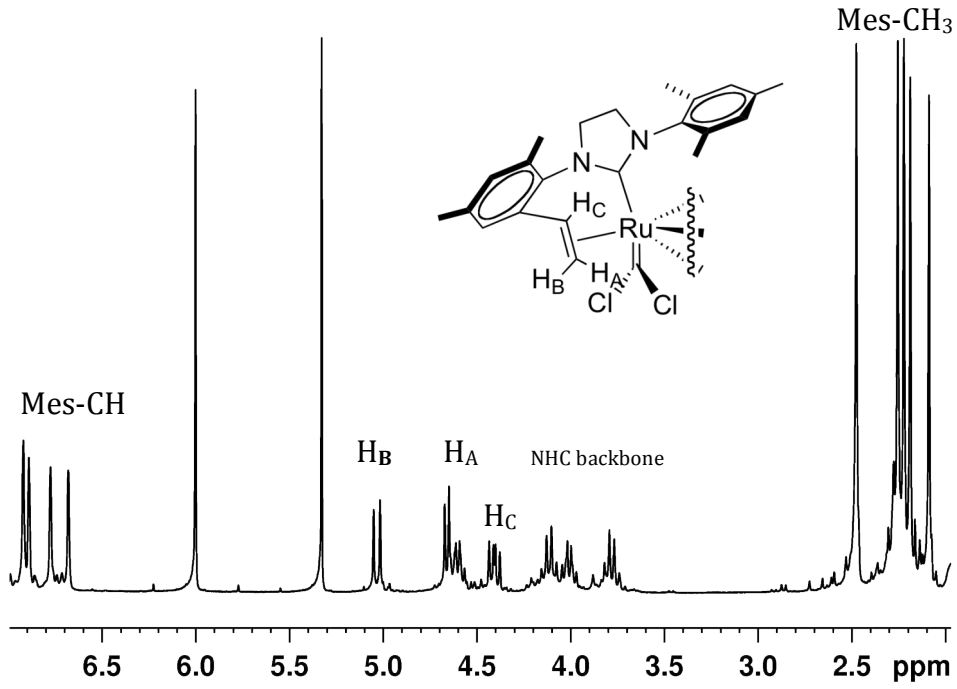


Figure 2- ^{1}H NMR Spectrum of Compound **2** in $(CDCl_2)_2$

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