Supporting information For: Preparation and Reactivity of A Ru(0) Phosphino-Carbene Complex

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1. General remarks.

All manipulations were carried out under an atmosphere of dry, O_2-free N_2 employing a VAC atmospheres glove box and a Schlenk vacuum-line. Solvents were purified with a Grubbs-type column system manufactured by Innovative Technology and dispensed into thick-walled Schlenk glass flasks equipped with Teflon-valve stopcocks (pentanes, hexanes, toluene, tetrahydrofuran, and dichloromethane). Anhydrous benzene was purchased from Sigma-Aldrich and used without further purification. Deuterated solvents were dried over the appropriate agents, vacuum-transferred into storage flasks with Young-type Teflon stopcocks and degassed accordingly (C_6D_6, CD_2Cl_2, THF-d_8, and $CDCl_3$). ^1H and $^{31}P\{^1H\}$ NMR spectra were recorded at 25 °C on a Bruker 400 MHz spectrometer. $^{13}C\{^1H\}$ NMR spectra were recorded at 25 ^oC on a Bruker 500 MHz spectrometer equipped with a cold probe. $^{29}Si\{^1H\}$ NMR data were obtained via ^{29}Si DEPT-135 experiments recorded at 25 ^oC on a Varian 500 MHz spectrometer. Chemical shifts are given relative to $SiMe_4$ and referenced to the residue solvent signal (^1H, ^{13}C, ^{29}Si) or relative to a standard (^{31}P: 85% H_3PO_4). Chemical shifts are reported in ppm and coupling constants as scalar values in Hz. Potassium bis(trimethylsilyl)amide (KHMDS), bis(mercaptoethyl)ether ($(HSC_2H_5)_2O$), $HPhSiCl_2$, triphenylsilane, and diphenylsilane were purchased from Sigma-Aldrich, while $RuHCl(CO)(PPh_3)_3$ was acquired from Strem and used without further purification. Despite long acquisition times on a 500 MHz cryoprobe instrument, some quarternary carbons in the ^{13}C NMR spectra were not observed. Furthermore, for quarternary Si atoms, ^{29}Si DEPT-135 proved unsuccessful in obtaining ^{29}Si NMR spectra, again despite prolonged acquisition times. Such instances are specifically mentioned for each occurence.

2. Synthesis of 1-(di(*tert*-butyl)phosphinoyl)-3-methyl-imidazolium tetrafluoroborate.

1-(di(*tert*-butyl)phosphanyl)-3-methyl imidazolium tetrafluoroborate was prepared according to literature procedures, with some modifications[1,2]. In a 20 mL scintillation vial 1-methylimidazole (1.0914 g, 13.29 mmol) and sodium tetrafluoroborate (1.5953 g, 14.53 mmol) were combined in THF (5 mL) and cooled to -35 ^{o}C. While stirring, a solution of di-*t*-butylchlorophosphine (2.6640 g, 14.75 mmol) in THF (3 mL) was added drop-wise to the cold solution. Mixture immediately became cloudy as a white precipitate formed. The reaction was stirred at -35 ^{o}C for 30 minutes and then allowed to warm to room temperature. Stirring continued at room temperature overnight. Upon completion of reaction the suspension was concentrated to dryness and the resulting white solid washed with dichloromethane (2 x 5 mL) to extract product. Extracts were filtered over a Celite plug and concentrated under vacuum to afford a white solid, which was washed with pentane (3 x 15 mL) and diethyl ether (3 x 15 mL). The resulting residue was dried under vacuum to afford the product as a crystalline white solid (2.8749 g, 69%).

^{1}H NMR (CD_2Cl_2): δ 3.15 (d, $^{3}J_{P\text{-}H}$= 14 Hz, 18 H, C(C*H*$_3$)$_3$), 5.94 (s, 3 H, N-C*H*$_3$), 9.35 (s, 1 H, C*H* on backbone), 9.36 (s, 1 H, C*H* on backbone), 10.68 (s, 1 H, N-C*H*-N). **^{31}P{^{1}H} NMR (CD_2Cl_2):** δ 123.3 (s, *P*(^{t}Bu)$_2$). **^{13}C{^{1}H} NMR (CD_2Cl_2):** δ 28.1 (d, $^{2}J_{C\text{-}P}$= 16 Hz, C(*C*H$_3$)$_3$), 35.0 (d, $^{1}J_{C\text{-}P}$= 30 Hz, *C*(CH$_3$)$_3$), 36.7 (s, N-*C*H$_3$), 124.5 (s, *C*H on backbone), 126.6 (s, *C*H on backbone), 141.8 (s, N-*C*H-N). **^{19}F{^{1}H} NMR (CD_2Cl_2):** δ -149.8 (s, B*F*$_4^-$). **^{11}B{^{1}H} NMR (CD_2Cl_2):** δ -1.0 (*B*F$_4^-$).

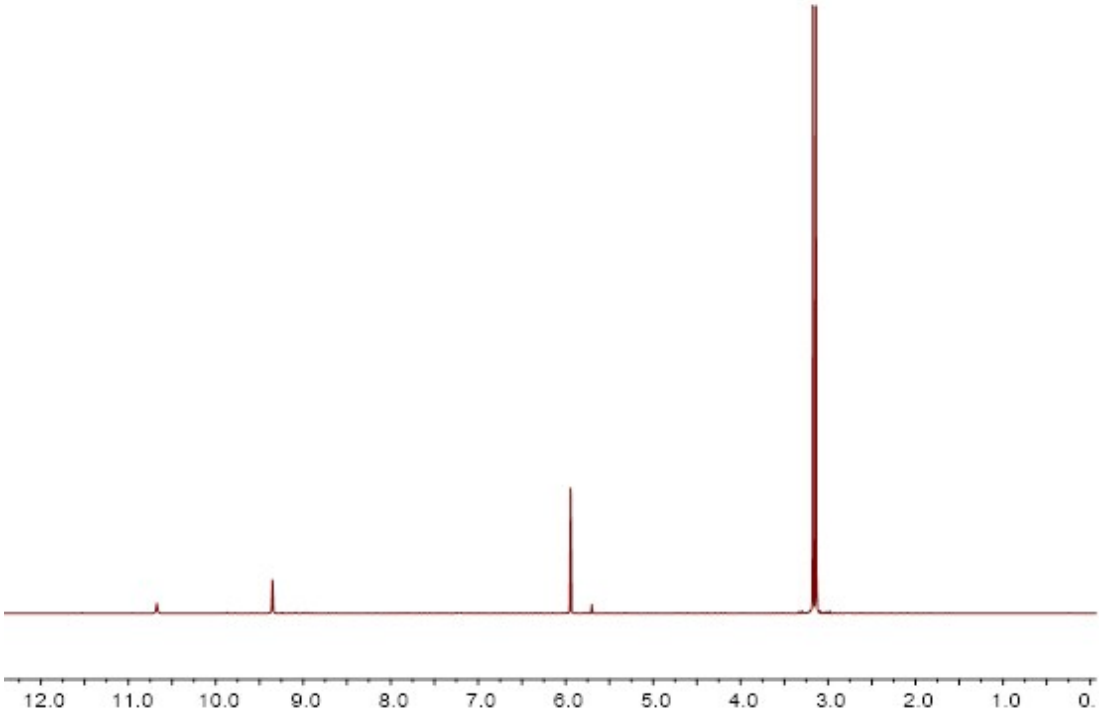


Figure S1: ^{1}H NMR spectrum of imidazolium tetrafluoroborate in CD_2Cl_2.

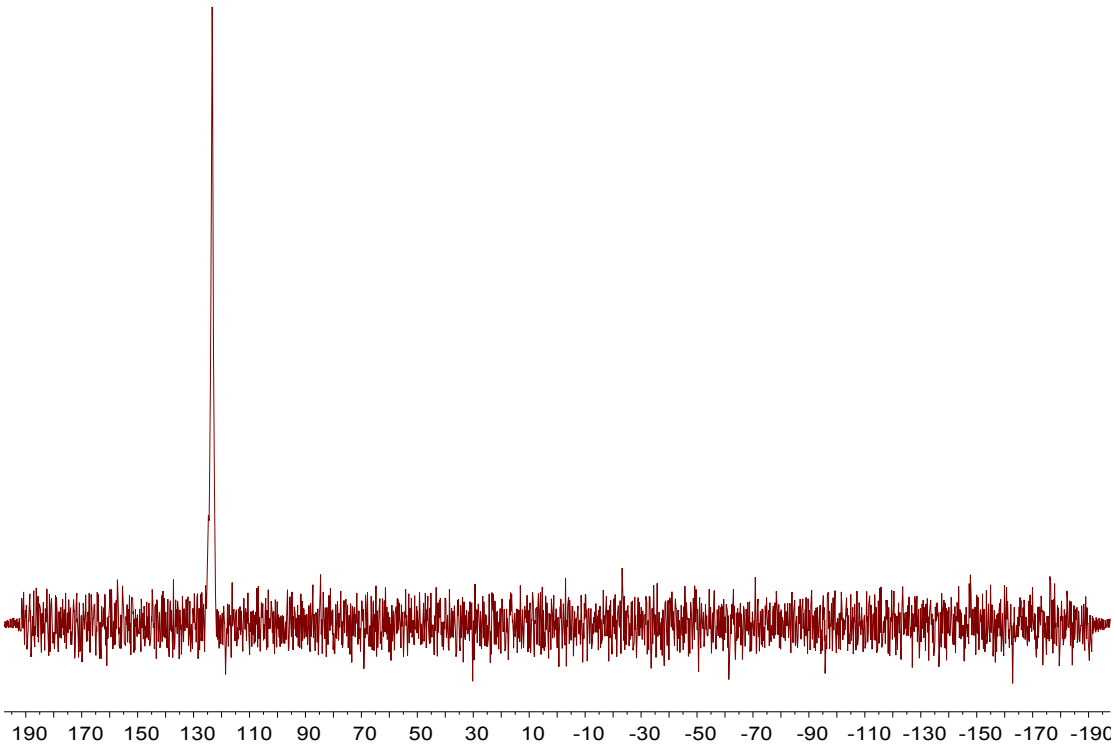


Figure S2: $^{31}P\{^{1}H\}$ NMR spectrum of imidazolium tetrafluoroborate in CD_2Cl_2.

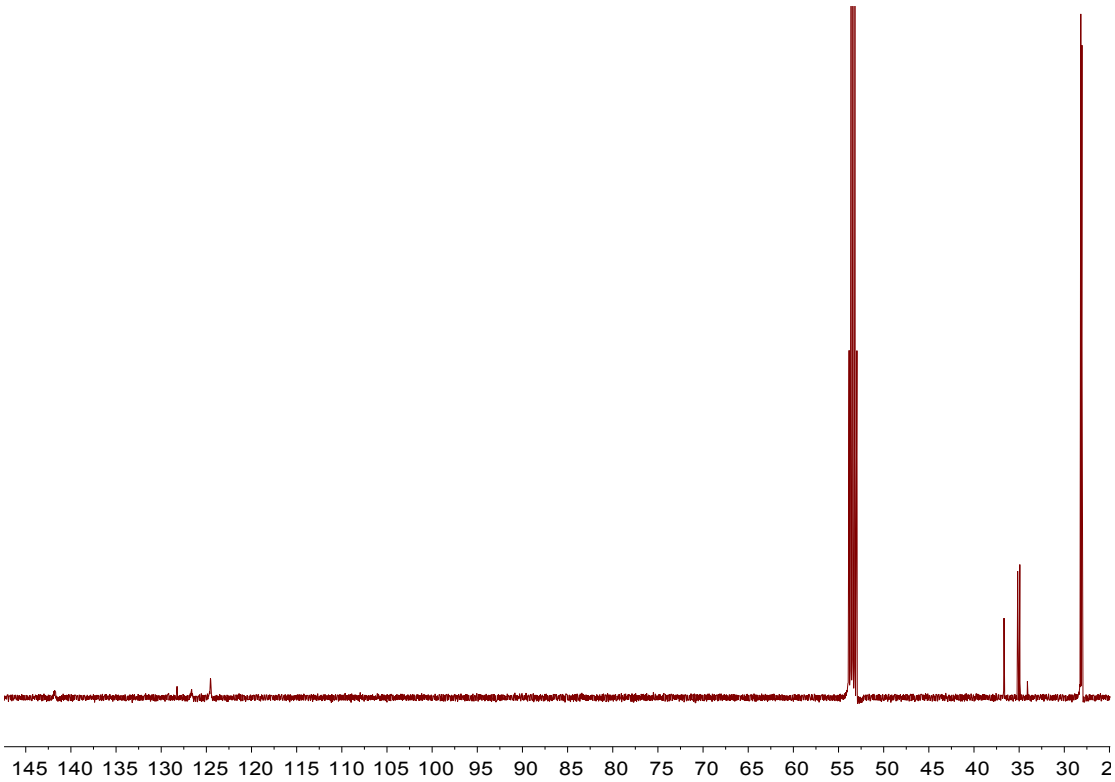


Figure S3: $^{13}C\{^{1}H\}$ NMR spectrum of imidazolium tetrafluoroborate in CD_2Cl_2.

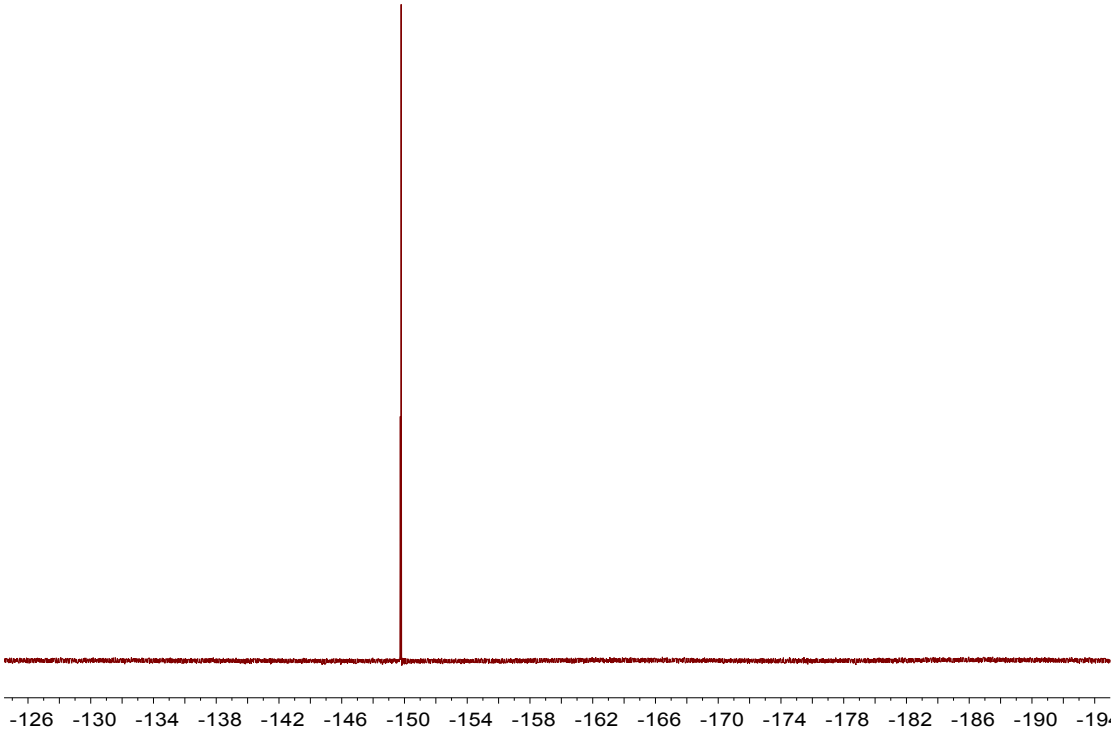


Figure S4: $^{19}F\{^{1}H\}$ NMR spectrum of imidazolium tetrafluoroborate in CD_2Cl_2.

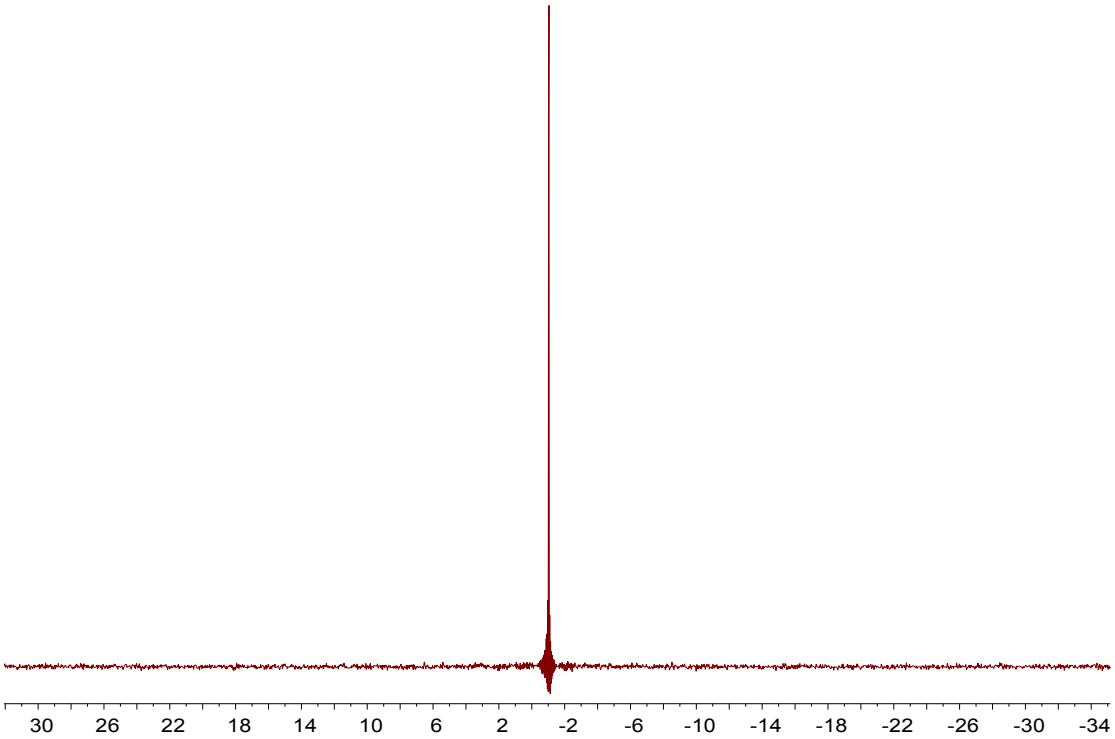
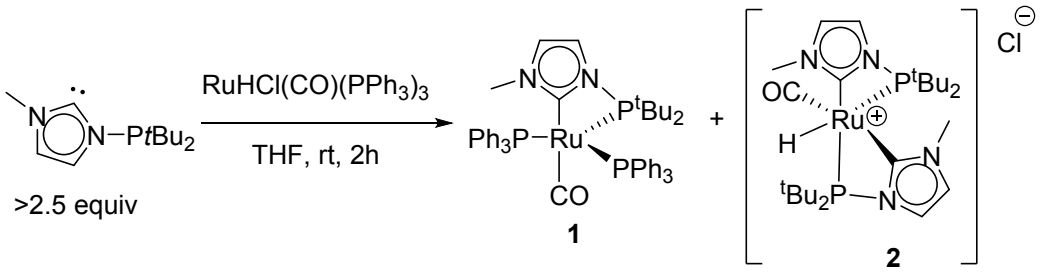


Figure S5: $^{11}B\{^{1}H\}$ NMR spectrum of imidazolium tetrafluoroborate in CD_2Cl_2.

3. Synthesis of 1-(di(*tert*-butyl)phosphanyl)-3-methyl-imidazolylidene.

A 20 mL vial was charged with above imidazolium tetrafluoroborate salt (0.5971 g, 1.909 mmol), suspended in diethyl ether (8 mL), and cooled to -35 ^{o}C. KHMDS (0.4026 g, 2.018 mmol) in diethyl ether (4 mL) was added drop-wise to the stirring suspension to immediately afford a pale yellow solution. Mixture was warmed to room temperature and stirred for a further 30 minutes. Concentration of mixture afforded an off-white residue that was washed with pentane (2 x 4 mL) and filtered through a Celite plug. The yellow filtrate was concentrated to 1 mL and a pale-yellow precipitate was observed. Vial was placed in freezer overnight to complete precipitation of product. The yellow supernatant was then syringed off and discarded. Residue was dried under vacuum to afford pale yellow crystals (0.3030 g, 70%). Characterization of product is consistent with literature values[2].

4. Synthesis of complex 1 and 2.



1-(di(*tert*-butyl)phosphanyl)-3-methyl-imidazolylidene (0.086 g, 0.380 mmol) and $RuHCl(CO)(PPh_3)_3$ (0.1370, 0.1438 mmol) were added to a vial equipped with stir bar and dissolved in THF (5 mL) to afford a beige suspension. After stirring for 15 minutes the mixture became a bright orange suspension. The mixture was stirred at room temperature for 2 hours. The vial was concentrated to dryness and the residue was extracted with hexanes (2 × 5 mL). Complex **1** (0.014 g, 11%) was obtained as orange-red crystals from the concentrated hexane solution overnight. The pale yellow residue was further washed with benzene (4 mL), then dissolved in 8 mL of CH_2Cl_2. Layering of CH_2Cl_2 solution with pentane afforded colorless x-ray quality crystals of complex **2** (0.049 g, 55%).

Characterization of Ru(0) complex 1:

^{1}H NMR (C_6D_6): 1.13 (d, $^3J_{P\text{-}H}$ = 13 Hz, 18 H, $C(CH_3)_3$), 1.57 (s, 3 H, N-CH_3), 5.67 (s, 1 H, C*H* on backbone of carbene), 6.20 (dd, $^3J_{H\text{-}P}$ = 3 Hz, $^3J_{H\text{-}H}$ = 2 Hz, 1 H, C*H* on carbene), 6.96–7.07 (m, 18 H, PPh_3), 7.66–7.70 (m, 12 H, PPh_3). **^{31}P{^{1}H} NMR (C_6D_6):** 48.8 (d, $^2J_{P\text{-}P}$ = 99 Hz), 119.8 (t, $^2J_{P\text{-}P}$ = 99 Hz). **^{13}C{^{1}H} NMR (C_6D_6):** 30.0 (d, $^2J_{C\text{-}P}$ = 10 Hz, $C(CH_3)_3$), 35.1 (s, N-CH_3), 38.30 (d, $^1J_{C\text{-}P}$ = 11 Hz, $C(CH_3)_3$), 122.0 (s, *C*H on carbene), 122.5 (d, $^2J_{C\text{-}P}$ = 7 Hz, *C*H on backbone of carbene), 127.6 (s, *m*-PPh_3), 129.0 (s, *p*-PPh_3), 134.2 (s, *o*- PPh_3). ν_{CO}= 1909 cm^{-1}. **Elemental Analysis:** Calcd C: 66.88, H: 6.07, N: 3.18. Found C: 66.01, H: 5.98, N: 3.79;

* Peaks corresponding to the CO, carbene and *ipso*- carbons were not found despite long acquisition times.

Characterization of Ru(II) complex 2:

^{1}H NMR (CD_2Cl_2): -12.42 (dd, $^{2}J_{P-H}$ = 103 Hz, $^{2}J_{P-H}$ = 17 Hz, 1 H, Ru-*H*), 1.28 (dd, $^{3}J_{P-H}$ = 54 Hz, $^{3}J_{P-H}$ = 14 Hz, 9 H, C(CH_3)$_3$), 1.45 (dd, $^{3}J_{P-H}$= 38 Hz, $^{3}J_{P-H}$ = 15 Hz, 9 H, C(CH_3)$_3$), 3.19 (s, 3 H, N-CH_3), 3.78 (s, 3 H, N-CH_3), 7.07 (dt, $^{3}J_{P-H}$= 21 Hz, $^{3}J_{H-H}$ = 2 Hz, 2 H, C*H* on backbone of carbene), 7.21 (s, 1 H, C*H* on backbone of carbene), 7.36 (s, 1 H, C*H* on backbone of carbene). **^{31}P{^{1}H} NMR (CD_2Cl_2):** 101.1 (d, $^{2}J_{P-P}$ = 187 Hz, *P*(^{t}Bu)$_2$), 129.8 (d, $^{2}J_{P-P}$ = 190 Hz , *P*(^{t}Bu)$_2$). **^{13}C{^{1}H} NMR (CD_2Cl_2):** 28.9 (d, $^{2}J_{C-P}$ = 8 Hz, C(*C*H$_3$)$_3$), 29.6 (d, $^{2}J_{C-P}$ = 5 Hz, C(*C*H$_3$)$_3$), 37.8 (d, $^{1}J_{C-P}$ = 14 Hz, *C*(CH$_3$)$_3$), 38.8 (d, $^{1}J_{C-P}$ = 10 Hz, *C*(CH$_3$)$_3$), 39.0 (d, $^{1}J_{C-P}$ = 7 Hz, *C*(CH$_3$)$_3$), 36.2 (s, N-*C*H$_3$), 36.9 (s, N-*C*H$_3$), 123.2 (d, $^{2}J_{C-P}$ = 7 Hz, *C*H on backbone of carbene), 123.4 (d, $^{2}J_{C-P}$ = 7 Hz, *C*H on backbone of carbene), 125.1 (s, *C*H on backbone of carbene), 125.3 (s, *C*H on backbone of carbene), 182.4 (m, *C*O), 214.0 (m, N-*C*-N). ν_{CO}= 1937 cm^{-1}. **Elemental Analysis:** Calcd C: 48.58, H: 7.66, N: 9.06; Found C: 47.95, H: 6.95, N: 9.25.

* Peaks corresponding to the other carbene carbon was not found despite long acquisition times.

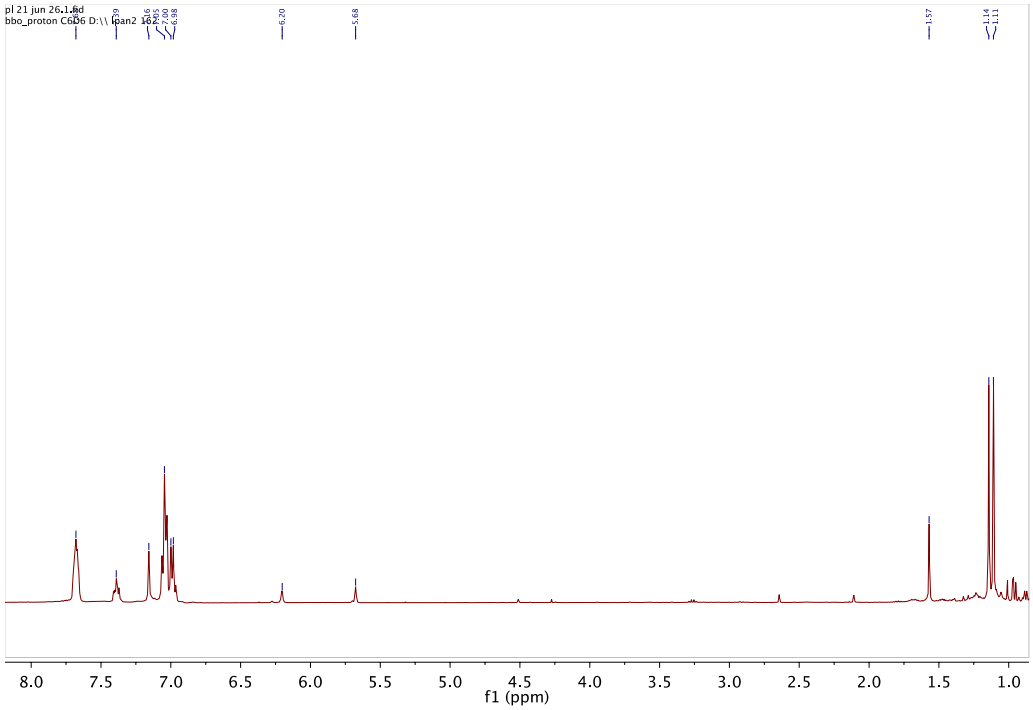


Figure S6: ^{1}H NMR spectrum of complex **1** in C_6D_6.

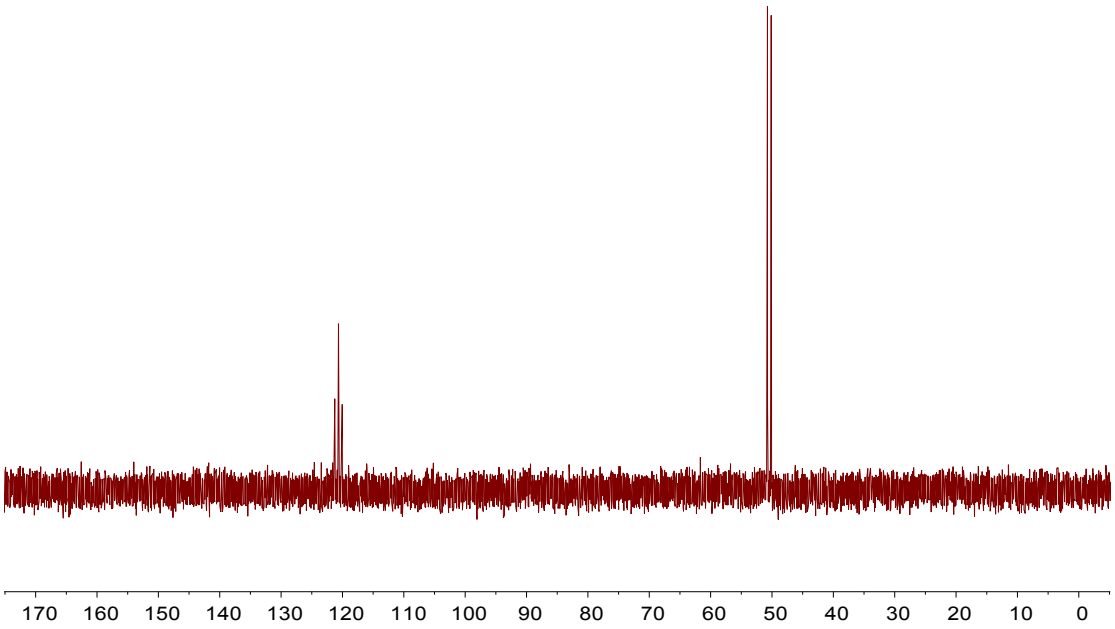


Figure S7: $^{31}P\{^{1}H\}$ NMR spectrum of complex **1** in d_8-THF.

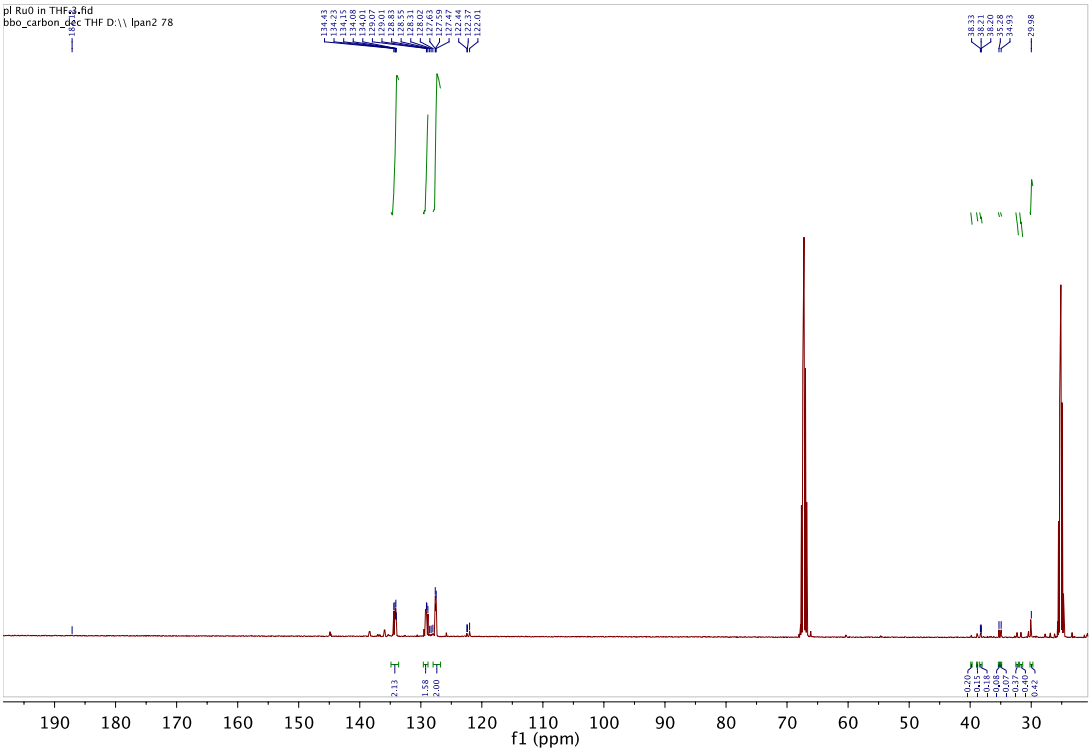


Figure S8: $^{13}C\{^{1}H\}$ NMR spectrum of complex **1** in d_8-THF.

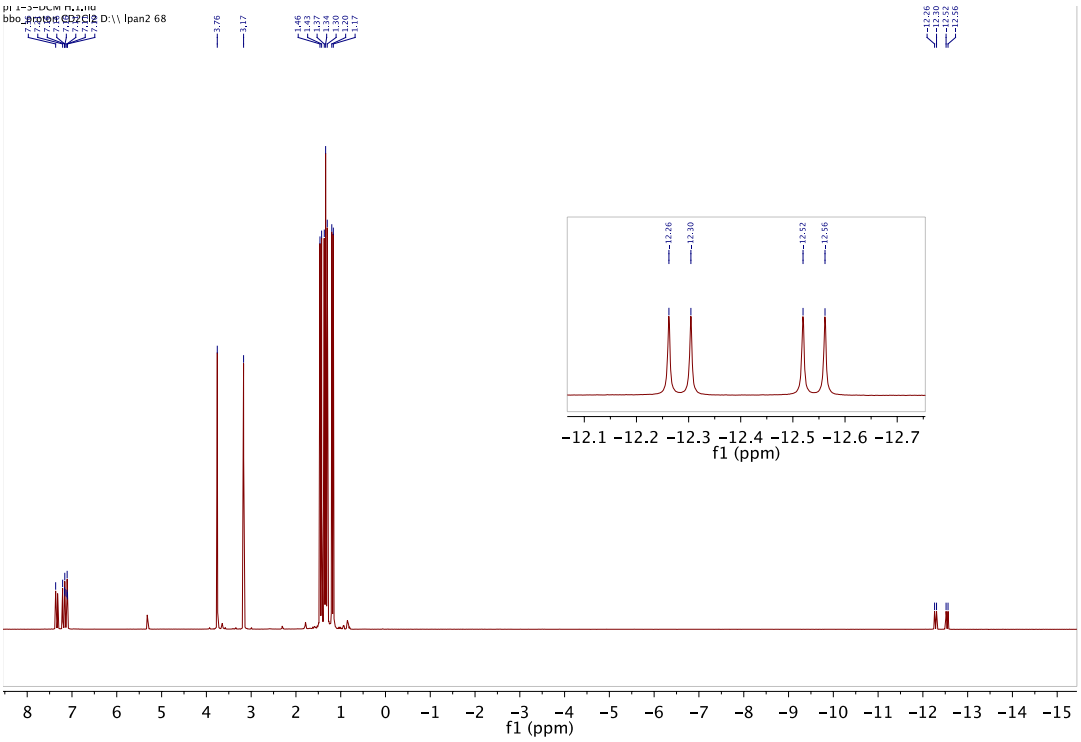


Figure S9: ^{1}H NMR spectrum of complex **2** in CD_2Cl_2.

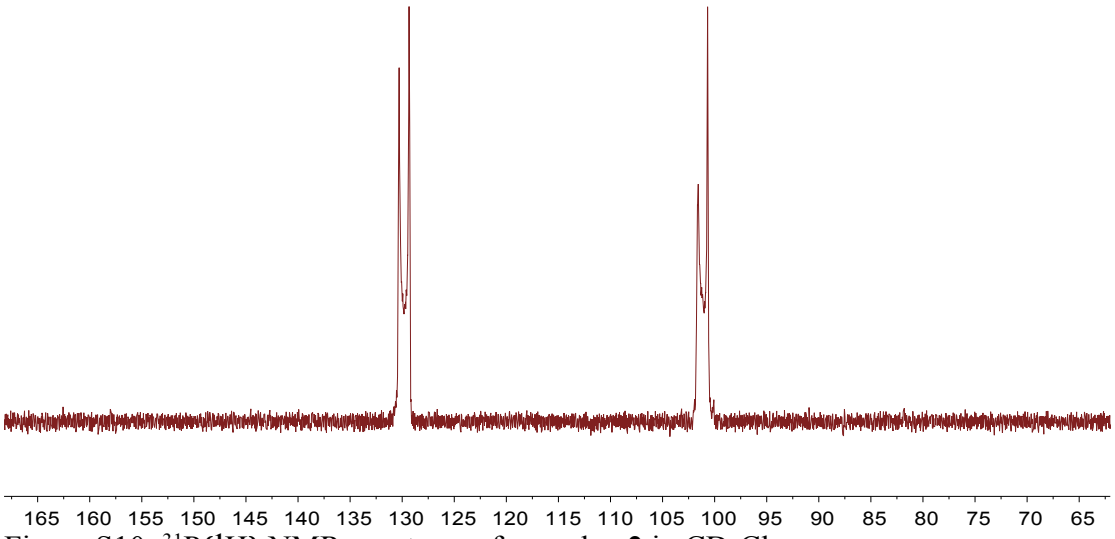


Figure S10: $^{31}P\{^{1}H\}$ NMR spectrum of complex **2** in CD_2Cl_2.

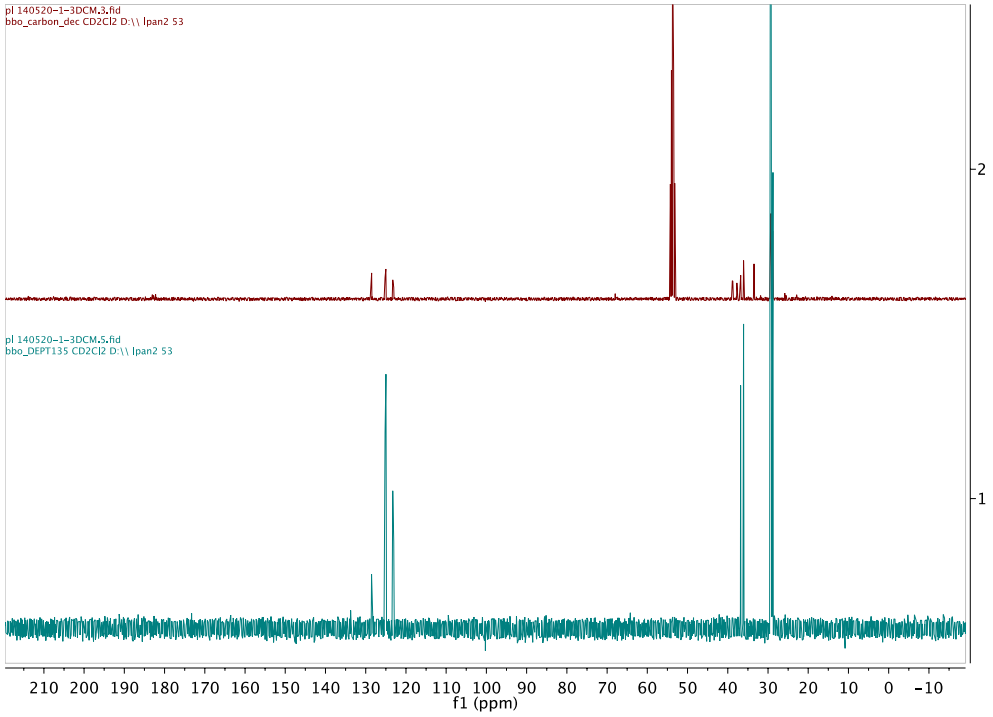
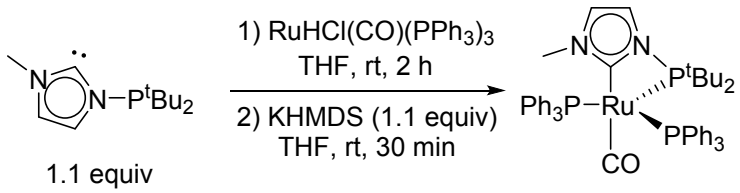


Figure S11: $^{13}C\{^{1}H\}$ NMR spectrum (top) and dept135 NMR spectrum (bottom) of complex **2** in CD_2Cl_2.

5. Selective synthesis of complex 1.

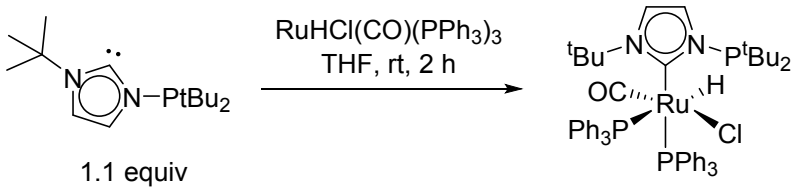


1

A 20 mL scintillation vial was equipped with a stir bar and $RuHCl(CO)(PPh_3)_3$ (0.6732 g, 0.7068 mmol). 1-(di(*tert*-butyl)phosphanyl)-3-methylimidazolylidene (0.1738 g, 0.7680 mmol) in THF (10 mL) was added to the vial to afford a beige suspension. Vial stirred at room temperature for 2 hours. Within 15 minutes a colour change from beige to bright orange/red was observed. Upon completion of reaction the color of the suspension was bright orange. KHMDS (0.2341 g, 1.174 mmol) in THF (2 mL) was added drop-wise to the orange suspension. Mixture immediately became a dark red solution. Reaction was allowed to carry on at room temperature for 1 hour; in the meantime the colour of the mixture became a very dark crimson red. Vial was concentrated to dryness and dark red residue washed with benzene (3 x 4 mL) to extract product. Extracts were filtered through celite and filtrate was

concentrated to 2 mL. Vial left standing overnight to precipitate product. Dark red supernatant syringed off and product dried under vacuum to afford complex **1** as a bright orange solid (0.2023 g, 33%). Characterization of product consistent with data reported above.

6. *In-situ* generation of complex 3



1.1 equiv

3

NMR tube charged with 1-(di(*tert*-butyl)phosphanyl)-3-*tert*-butyl-imidazolylidene (0.0194 g, 0.0724 mmol) and $RuHCl(CO)(PPh_3)_3$ (0.0500 g, 0.0658 mmol) in C_6D_6 (0.5 mL). NMR tube sealed and reaction allowed to proceed for 2 hours. Completion of reaction was confirmed by ^1H and ^{31}P NMR spectroscopy whereby all the starting material had been consumed.

^{1}H NMR (C_6D_6): -7.90 (dd, $^2J_{P-H}$= 102 Hz, $^2J_{P-H}$= 30 Hz, 1 H, Ru-*H*), 0.86 (d, $^3J_{P-H}$= 12 Hz, 9 H, P-C(C*H*$_3$)$_3$), 1.29 (d, $^3J_{P-H}$= 12 Hz, 9 H, P-C(C*H*$_3$)$_3$), 1.33 (s, 9 H, C(C*H*$_3$)$_3$), 6.51 (s, 1 H, C*H* backbone of carbene), 6.90 (s, 1 H, C*H* backbone of carbene), 7.16-7.63 (m, 30H, PPh_3). **^{31}P{^{1}H} NMR (C_6D_6):** -5.4 (s, free PPh_3), 33.6 (d, $^2J_{P-P}$= 14 Hz, PPh_3), 56.9 (d, $^2J_{P-P}$= 15 Hz), 86.4 (s, P^tBu_2).

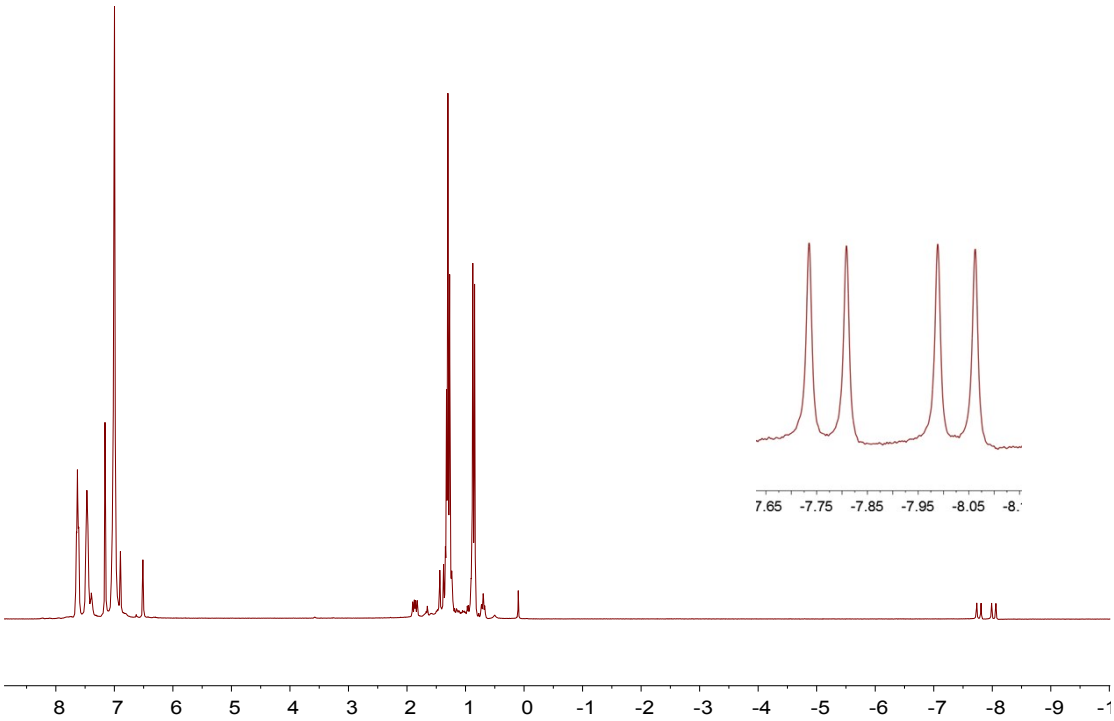


Figure S12: ^{1}H NMR spectrum of complex **3** in C_6D_6.

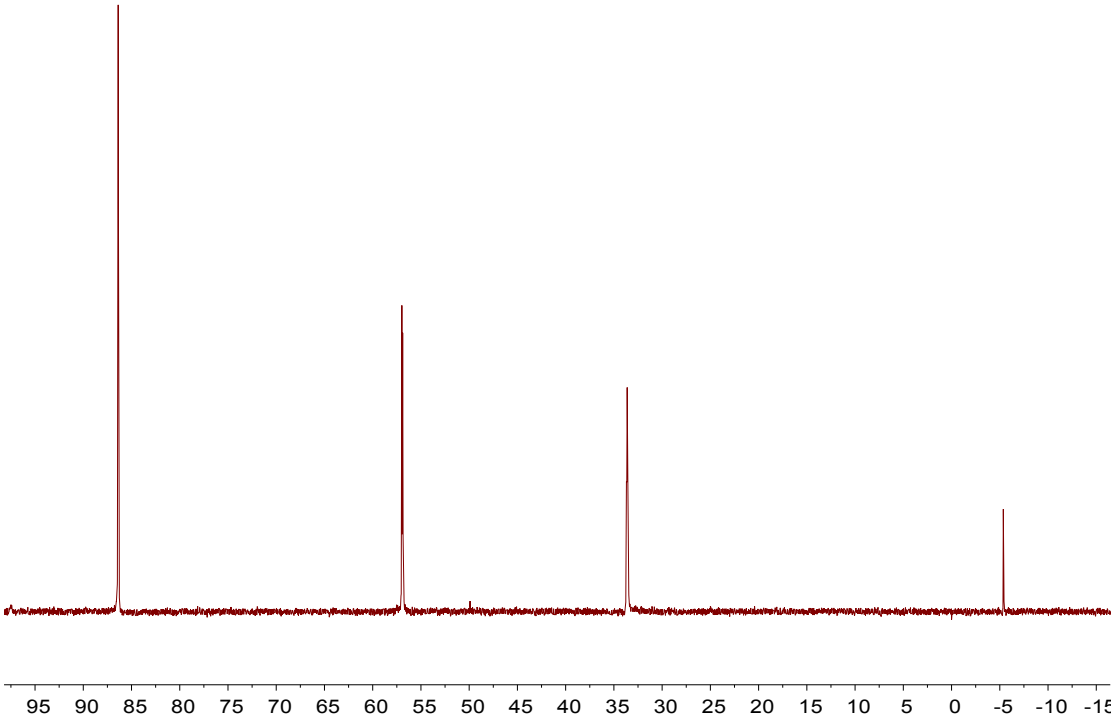
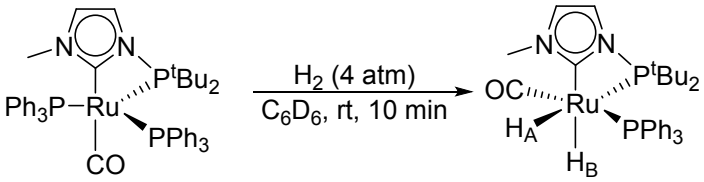


Figure S13: $^{31}P\{^{1}H\}$ NMR spectrum of complex **3** in C_6D_6.

7. Generation of complex 4.



1 **4**

J-Young NMR tube charged with complex **1** (0.0526 g, 0.0598 mmol) in C_6D_6 (1 mL). The bright orange solution was degassed using three consecutive cycles of freeze-pump-thaw and backfilled with H_2 (4 atm). The color of the mixture changed from orange to pale yellow in 10 minutes. ^{31}P NMR data indicates the dissociation of one triphenylphosphine moiety from complex **1**. Isolation of complex **4** for the purposes of IR and crystallographic analyses has proven difficult as the product appears to proceed in the reverse fashion under vacuum.

^{1}H NMR (C_6D_6): -10.38 (ddd, $^2J_{P-H}$ = 103 Hz, $^2J_{P-H}$ = 23 Hz, $^2J_{H-H}$ = 5 Hz, 1 H, Ru-*H*$_A$), -5.12 (ddd, $^2J_{P-H}$ = 24 Hz, $^2J_{P-H}$ = 17 Hz, $^2J_{H-H}$ = 5 Hz, 1 H, Ru-*H*$_B$), 1.01 (d, $^3J_{P-H}$ = 13 Hz, 9 H, C(C*H*$_3$)$_3$), 1.17 (d, $^3J_{P-H}$ = 13 Hz, 9 H, C(C*H*$_3$)$_3$), 3.17 (s, 3 H, N-C*H*$_3$), 5.84 (br s, 1H, C*H* on backbone of carbene), 6.12-6.13 (m, 1 H, C*H* backbone of carbene), 7.00 – 7.14 (m, 18 H, PPh$_3$), 7.37 – 8.17 (m, 12 H, PPh$_3$). **^{31}P{^{1}H} NMR (C_6D_6):** -5.4 (s, free PPh$_3$), 65.4 (d, $^2J_{P-P}$ = 13 Hz, PPh$_3$), 125.2 (d, $^2J_{P-P}$ = 13 Hz, N-P(^{t}Bu$_2$)). **^{13}C{^{1}H} NMR (C_6D_6):** 27.5 (d, $^2J_{C-P}$ = 2 Hz, C(*C*H$_3$)$_3$), 27.6 (d, $^2J_{C-P}$ = 2 Hz, C(*C*H$_3$)$_3$), 34.0 (s, N-*C*H$_3$), 34.1 (d, $^1J_{C-P}$ = 9 Hz *C*(CH$_3$)$_3$), 35.0 (d, $^1J_{C-P}$ = 11 Hz *C*(CH$_3$)$_3$) 118.2 (d, $^2J_{C-P}$ = 4 Hz, *C*H on backbone of carbene), 119.5 (d, $^2J_{C-P}$ = 2 Hz, *C*H on backbone of carbene), 132.1 (s, *p*-PPh$_3$), 132.6 (s, *m*-PPh$_3$), 136.0 (s, *o*-PPh$_3$), 140.8 (dd, $^1J_{C-P}$ = 35 Hz, $^3J_{C-P}$ = 3 Hz, *ipso*-PPh$_3$), 189.8 (dd, $^2J_{C-P}$ = 77 Hz, $^2J_{C-P}$ = 8 Hz, *C*O), 209.6 (dd, $^2J_{C-P}$ = 9 Hz, $^2J_{C-P}$ = 4 Hz, N-*C*-N).

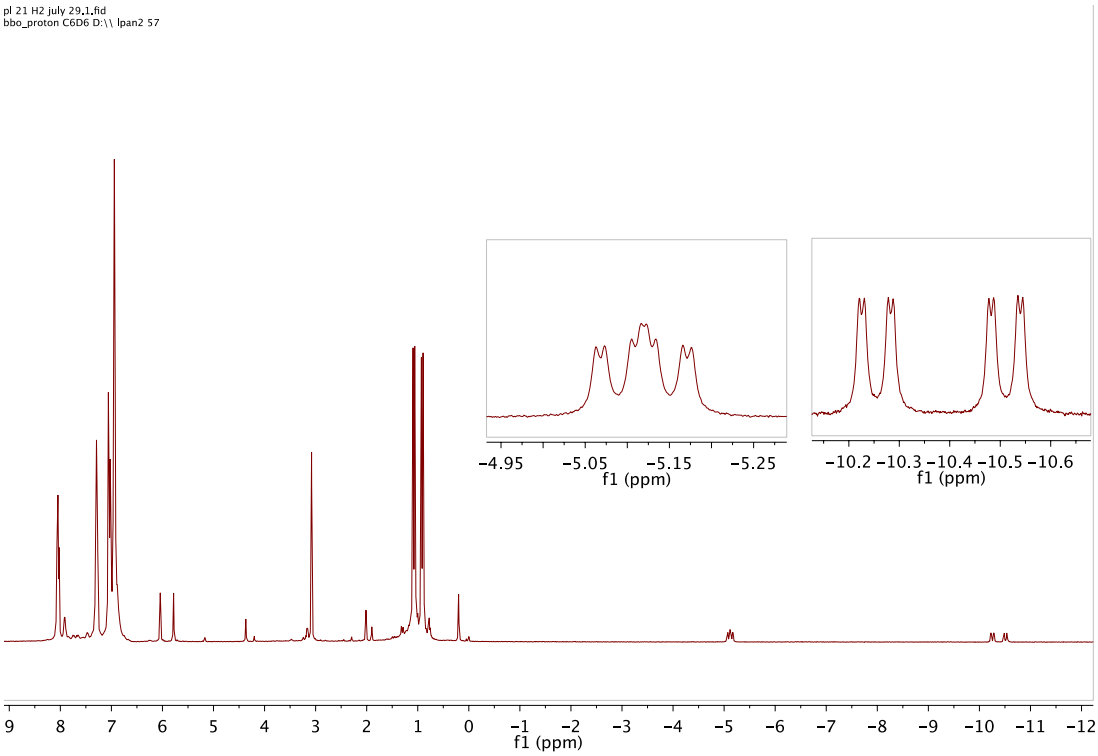


Figure S14: ^{1}H NMR spectrum of complex **4** in C_6D_6.

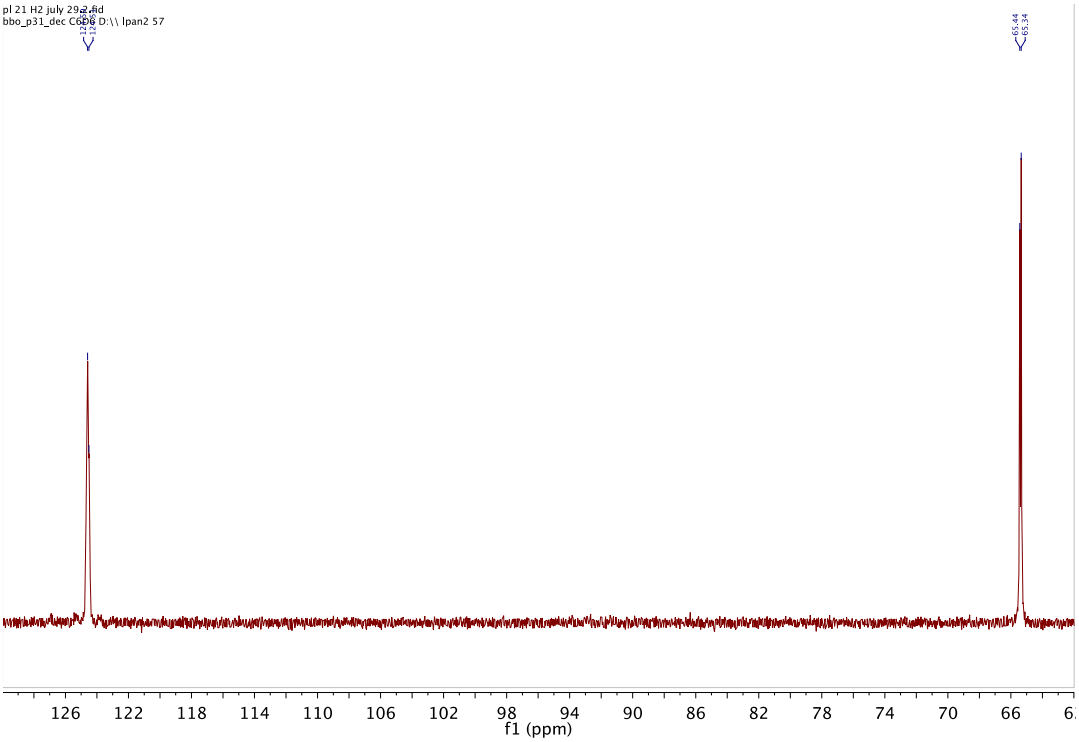


Figure S15: ^{31}P{^{1}H} NMR spectrum of complex **4** in C_6D_6.

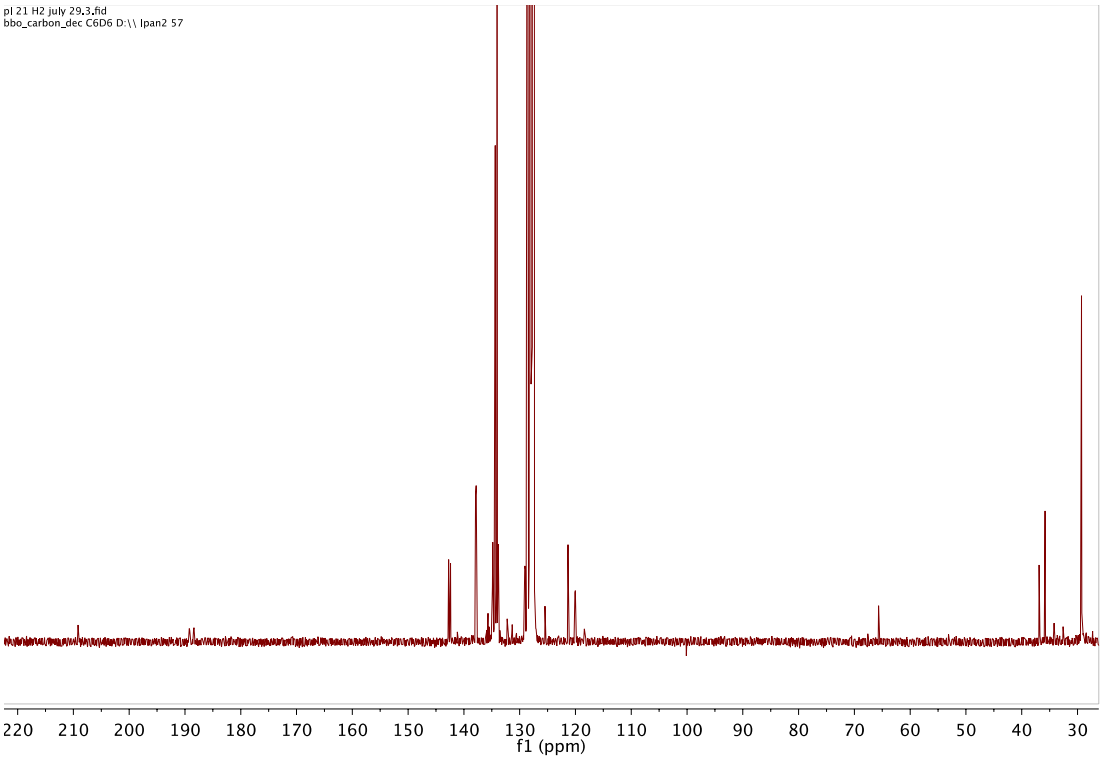
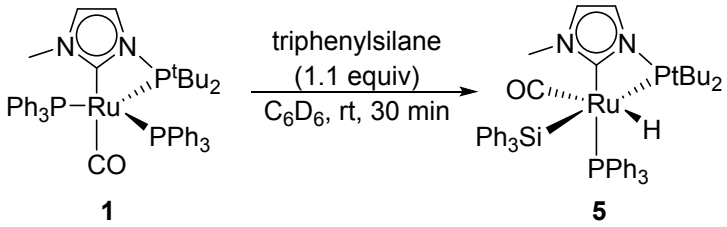


Figure S16: $^{13}C\{^{1}H\}$ NMR spectrum of complex **4** in C_6D_6.

8. Synthesis of complex 5.



Complex **1** (0.0440 g, 0.0500 mmol) was dissolved in benzene (8 mL) in a vial. To the orange benzene solution was added Ph_3SiH (0.0145 g, 0.0557 mmol). The orange color changed to pale yellow in 10 minutes. The reaction was allowed to proceed for 30 minutes before being evacuated to dryness. Pentane (8 mL) was added to the residue and stirred vigorously for another 10 minutes. The suspension was filtered over celite and dissolved in benzene (5 mL). The filtrate was concentrated to dryness to afford complex **5** as a pale yellow solid (0.0350 g, 80%). X-ray quallity crystals were grown by layering a saturated benzene solution of the product with pentane.

^{1}H NMR (C_6D_6): -4.20 (dd, $^{2}J_{P-H}$= 19 Hz, $^{2}J_{P-H}$= 15 Hz, 1 H, Ru-*H*), 0.78 (d, $^{3}J_{P-H}$= 13 Hz, 9 H, C(C*H*$_3$)$_3$), 1.38 (d, $^{3}J_{P-H}$= 13 Hz, 9 H, C(C*H*$_3$)$_3$), 2.56 (s, 3 H, N-C*H*$_3$), 5.43 (bs, 1 H, C*H* on carbene backbone), 6.06 (m, 1 H, C*H* on carbene backbone), 7.37 – 7.73 (m, 30 H, Ph). **^{31}P{^{1}H} NMR (C_6D_6):** 55.7 (d, $^{2}J_{P-P}$ = 18 Hz, PPh_3), 103.4 (d, $^{2}J_{P-P}$ = 18 Hz, N-P*t*Bu$_2$). **^{13}C{^{1}H} NMR (C_6D_6):** 29.1 (d, $^{2}J_{C-P}$=10 Hz, C(*C*H$_3$)$_3$), 29.2 (d, $^{2}J_{C-P}$=8 Hz, C(*C*H$_3$)$_3$), 36.0 (s, N-*C*H$_3$), 37.0 (d, $^{1}J_{C-P}$=10 Hz, *C*(CH$_3$)$_3$), 37.5 (d, $^{1}J_{C-P}$=15 Hz, *C*(CH$_3$)$_3$), 120.6 (s, *C*H on carbene), 122.5 (d, $^{2}J_{C-P}$=2 Hz, *C*H on carbene), 128.0 (s, *m*-SiPh), 128.3 (s, *m*-PPh_3), 129.7 (s, *p*-SiPh), 133.7 (s, *p*-PPh_3), 133.9 (s, *ipso*-SiPh), 135.3 (s, *o*-SiPh), 135.9 (s, *o*-PPh_3), 137.7 (d, $^{1}J_{C-P}$=12 Hz, *ipso*-PPh_3), 182.9 (dd, $^{2}J_{C-P}$ = 81 Hz, 6 Hz, N-*C*-N*),* 211.7 (dd, $^{2}J_{C-P}$=13 Hz, 2 Hz, *C*O). ν_{CO}= 1918 cm^{-1}. **Elemental Analysis:** Calcd C: 67.03, H: 6.20, N: 3.19. Found C: 66.87, H: 5.94, N: 2.89;

*Despite long acquisition times ^{29}Si spectra were not able to be obtained

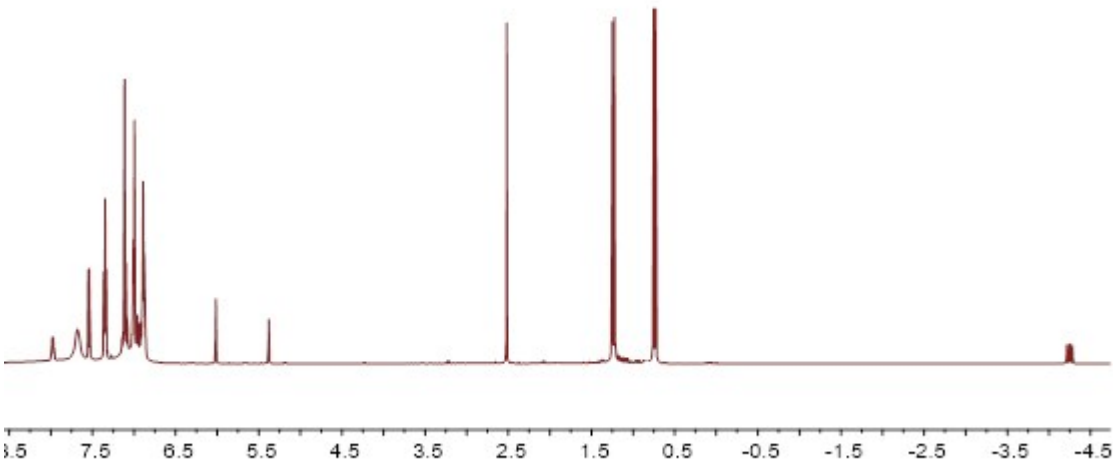


Figure S17: ^{1}H NMR spectrum of complex **5** in C_6D_6.

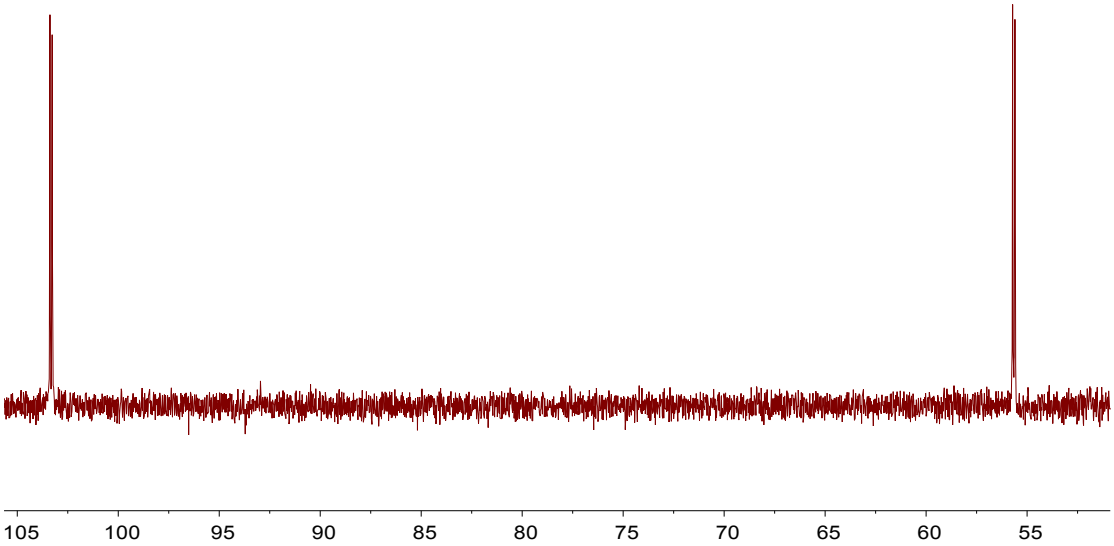


Figure S18: $^{31}P\{^{1}H\}$ NMR spectrum of complex **5** in C_6D_6.

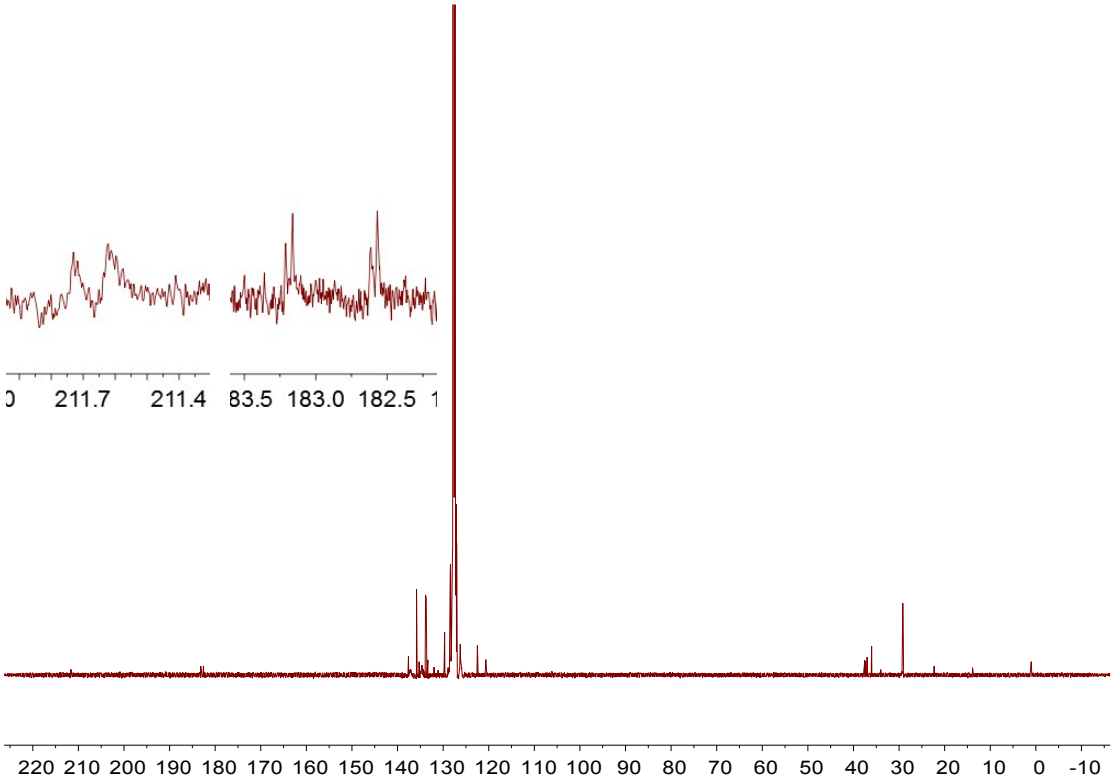
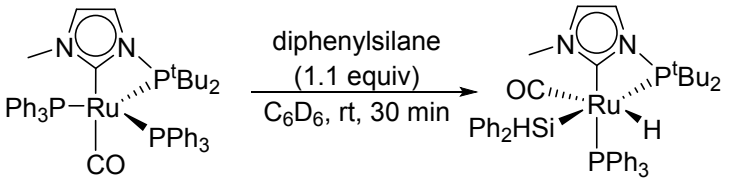


Figure S19: $^{13}C\{^{1}H\}$ NMR spectrum of complex **5** in C_6D_6.

9. Synthesis of complex 6.



1 **6**

Complex **6** was obtained in a similar fashion to complex **5** (0.0280 g, 71%). X-ray quality crystals were grown by layering a saturated benzene solution of the product with pentane.

^{1}H NMR (C_6D_6): -4.61 (td, $^{2}J_{H\text{-}P}$ = 18 Hz, $^{3}J_{H\text{-}H}$ = 4 Hz, 1 H, Ru-*H*), 0.99 (d, $^{3}J_{P\text{-}H}$= 13 Hz, 9 H, C(C*H*$_3$)$_3$), 1.17 (d, $^{3}J_{P\text{-}H}$= 13 Hz, 9 H, C(C*H*$_3$)$_3$), 2.70 (s, 3 H, N-C*H*$_3$), 5.51 (s, 1 H, C*H* on carbene backbone), 5.80 (m, 1 H, Si-*H*), 6.05 (dd, $^{3}J_{P\text{-}H}$= 2 Hz, 1 H, C*H* on carbene backbone), 6.99 – 8.19 (m, 25 H, Ph). **^{31}P{^{1}H} NMR (C_6D_6):** 58.5 (d, $^{2}J_{P\text{-}P}$ = 17 Hz, PPh_3), 104.5 (d, $^{2}J_{P\text{-}P}$ = 18 Hz, N-P(^{t}Bu)$_2$). **^{13}C{^{1}H} NMR (C_6D_6):** 29.1 (d, $^{2}J_{C\text{-}P}$=6 Hz, C(*C*H$_3$)$_3$), 29.2 (d, $^{2}J_{C\text{-}P}$=4 Hz, C(*C*H$_3$)$_3$), 36.3 (d, $^{1}J_{C\text{-}P}$=9 Hz, *C*(CH$_3$)$_3$), 36.4 (s, N-*C*H$_3$), 37.0 (d, $^{1}J_{C\text{-}P}$=14 Hz, *C*(CH$_3$)$_3$), 188.2 (s, *C*H on carbene), 123.5 (d, $^{2}J_{C\text{-}P}$=3 Hz, *C*H on carbene), 127.9 (s, *m*-Si(C$_6$H$_5$)), 128.2 (s, *m*-PPh_3), 128.8 (s, *p*-Si(C$_6$H$_5$)), 133.7 (s, *p*-PPh_3), 134.3 (s, *o*-Si(C$_6$H$_5$)), 135.8 (s, *o*-PPh_3), 136.2 (s, *ipso*-Si(C$_6$H$_5$)), 137.7 (d, $^{1}J_{C\text{-}P}$=12 Hz, *ipso*-PPh_3). **^{29}Si{^{1}H} DEPT-135 (C_6D_6):** 19.6 (dd, $^{2}J_{Si\text{-}P\text{-}trans}$ = 96 Hz, $^{2}J_{Si\text{-}P\text{-}cis}$ = 19 Hz) ν_{CO}= 1931 cm^{-1}. **Elemental Analysis:** Calcd C: 64.40, H: 6.28, N: 3.49. Found C: 64.00, H: 5.88, N: 3.11;

* Peaks corresponding to the carbene and CO carbons were not found despite long acquisition times.

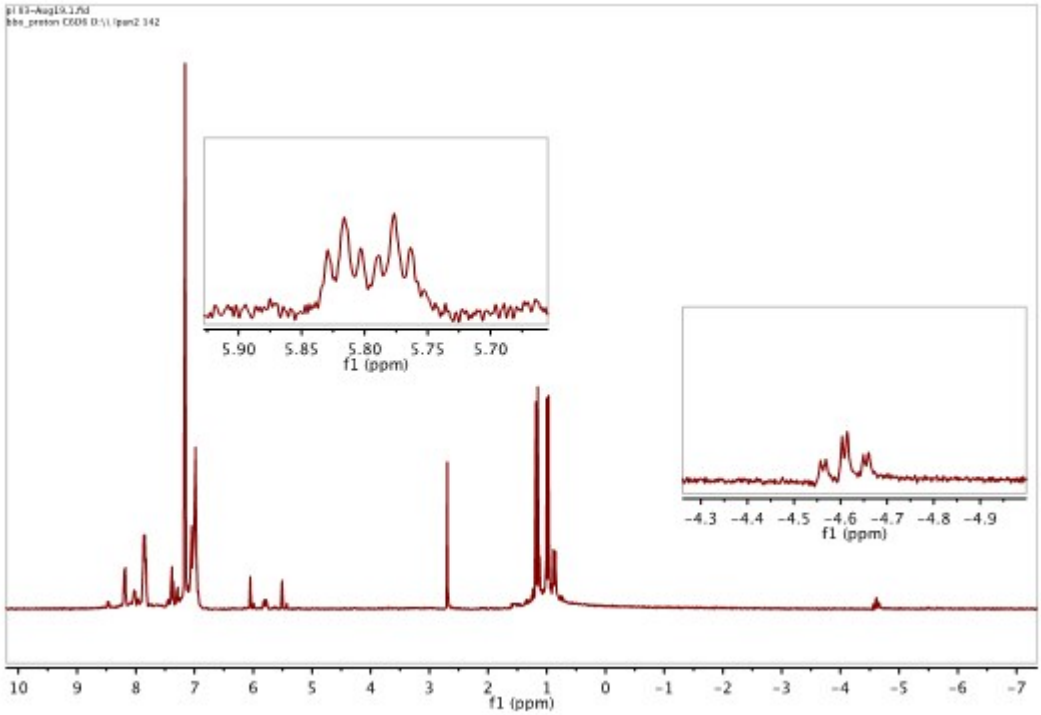


Figure S20: ^{1}H NMR spectrum of complex **6** in C_6D_6.

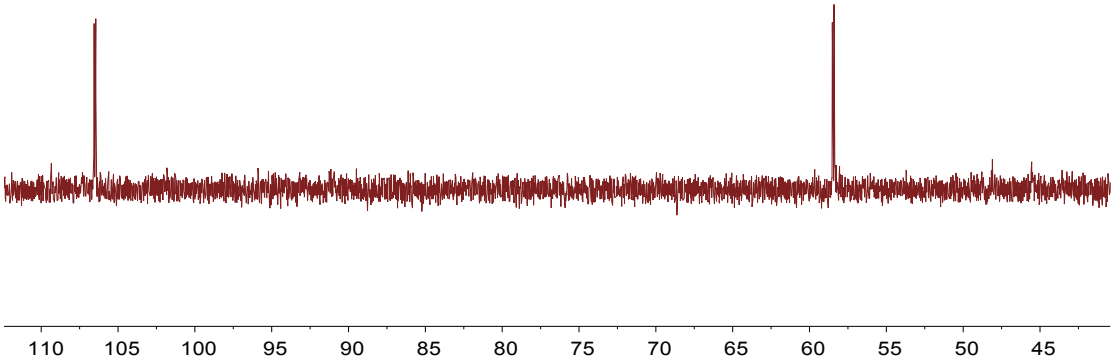


Figure S21: $^{31}P\{^{1}H\}$ NMR spectrum of complex **6** in C_6D_6.

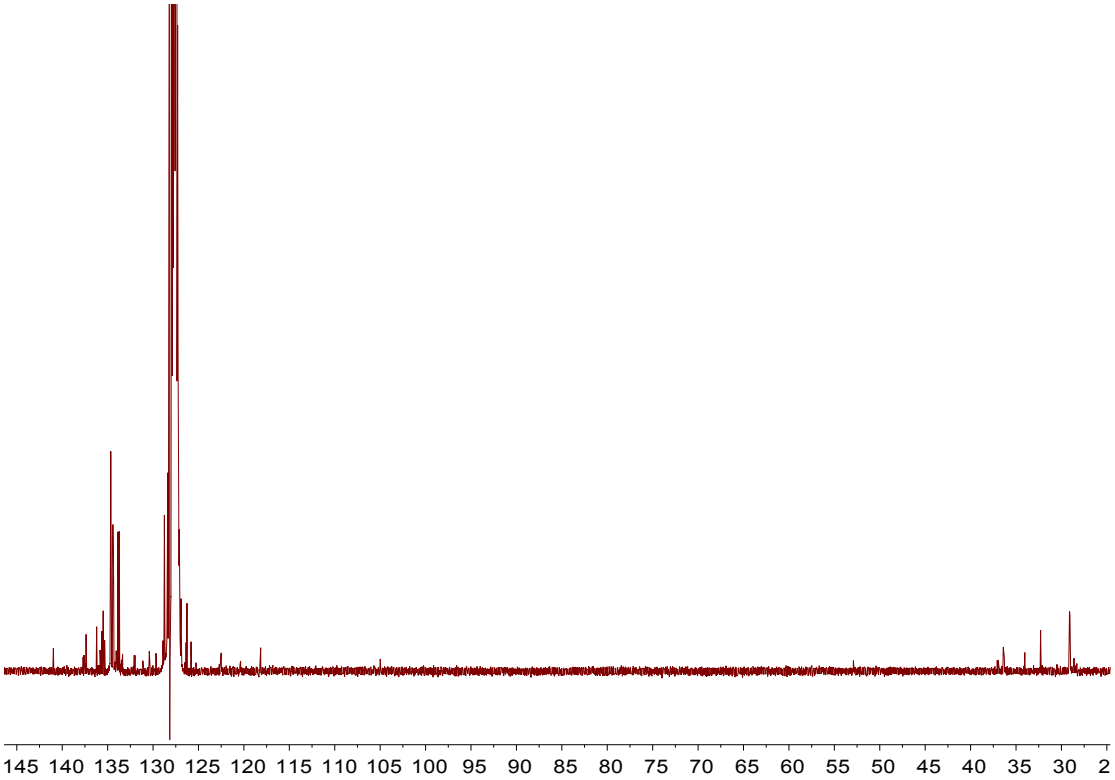


Figure S22: $^{13}C\{^{1}H\}$ NMR spectrum of complex **6** in C_6D_6.

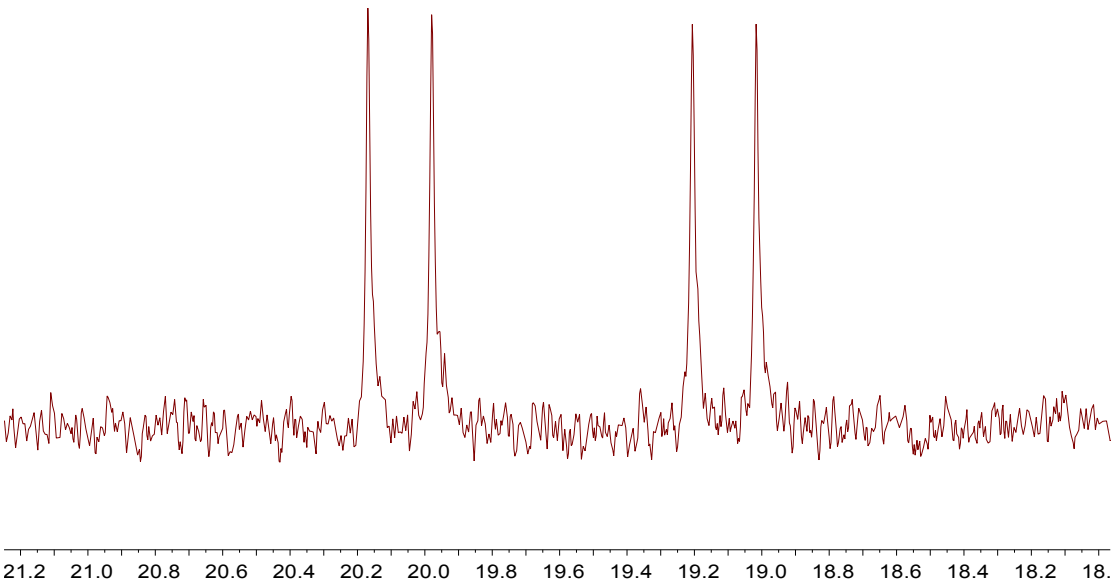
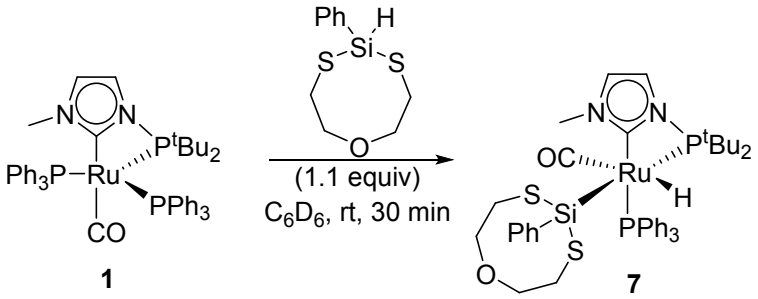


Figure S23: $^{29}Si\{^{1}H\}$ DEPT-135 NMR spectrum of complex **6** in C_6D_6

10. Synthesis of complex 7.



To solution of complex **1** (0.0440 g, 0.0500 mmol) in benzene (10 mL) was added $PhHSi(SCH_2CH_2)_2O$ (0.0130 g, 0.0537 mmol). The orange solution turned pale yellow in 5 minutes. Pentane (10 mL) was added to the solution to precipitate the pale yellow product which was washed with pentane (3 x 5 mL). The residue was dried under vacuum to afford complex **7** as a pale yellow solid (0.0370 mg, 86%).

^{1}H NMR (C_6D_6): -4.50 (dd, $^2J_{P-H}$= 22 Hz, $^2J_{P-H}$= 17 Hz, 1 H, Ru-*H*), 0.77 (d, $^3J_{P-H}$= 14 Hz, 9 H, C(C*H*$_3$)$_3$), 1.23 (d, $^3J_{P-H}$= 13 Hz, 9 H, C(C*H*$_3$)$_3$), 2.11-2.18 (m, 1H CH_2), 2.42-2.53 (m, 2H, CH_2), 2.77 (td, $^2J_{H-H}$ = 14 Hz, $^3J_{H-H}$ = 4 Hz, 1H, CH_2), 3.19 (ddd, $^2J_{H-H}$ = 16 Hz, $^3J_{H-H}$ = 13 Hz, $^3J_{H-H}$ = 4 Hz, 2 H, CH_2), 3.78 (td, $^2J_{H-H}$ = 13 Hz, $^3J_{H-H}$ = 4 Hz, 1H, CH_2), 3.94 (td, $^2J_{H-H}$ = 12 Hz, $^3J_{H-H}$ = 4 Hz, 1H, CH_2), 4.54 (s, 3 H, N-CH_3), 5.96 (s, 1 H, imidazole C-H), 6.08 (ws, 1 H, imidazole C-H), 6.88 – 8.20 (m, 20 H, Ph). **^{31}P{^{1}H} NMR (C_6D_6):** 54.9 (d, $^2J_{P-P}$ = 20 Hz, PPh_3), 102.2 (d, $^2J_{P-P}$ = 20 Hz, N-P*t*Bu$_2$). **^{13}C{^{1}H} NMR (C_6D_6):** 28.7 (d, $^2J_{C-P}$=5 Hz, C(*C*H$_3$)$_3$), 28.8 (d, $^2J_{C-P}$=5 Hz, C(*C*H$_3$)$_3$), 29.1 (s, S*C*H$_2$), 36.0 (d, $^1J_{C-P}$=15 Hz, *C*(CH$_3$)$_3$), 36.3 (d, $^1J_{C-P}$=8 Hz, *C*(CH$_3$)$_3$), 70.6 (s, O*C*H$_2$), 120.1 (s, *C*H on carbene backbone), 123.9 (d, $^2J_{C-P}$=2 Hz, *C*H on carbene backbone), 127.9 (s, *m*-SiPh), 128.4 (s, *m*-PPh_3), 129.9 (s, *p*-SiPh), 133.7 (s, *p*-PPh_3), 134.3 (s, *o*-SiPh), 136.1 (s, *o*-PPh_3), 136.2 (s, *ipso*-SiPh), 137.7 (d, $^1J_{C-P}$=12 Hz, *ipso*-PPh_3). ν_{CO}= 1918 cm^{-1}. **Elemental Analysis:** Calcd C: 57.25, H: 6.09, N: 3.26. Found C: 55.26, H: 5.26, N: 2.54;

*Despite long acquisition times ^{29}Si spectra were not able to be obtained.

* Peaks corresponding to the carbene and CO carbons were not found despite long acquisition times.

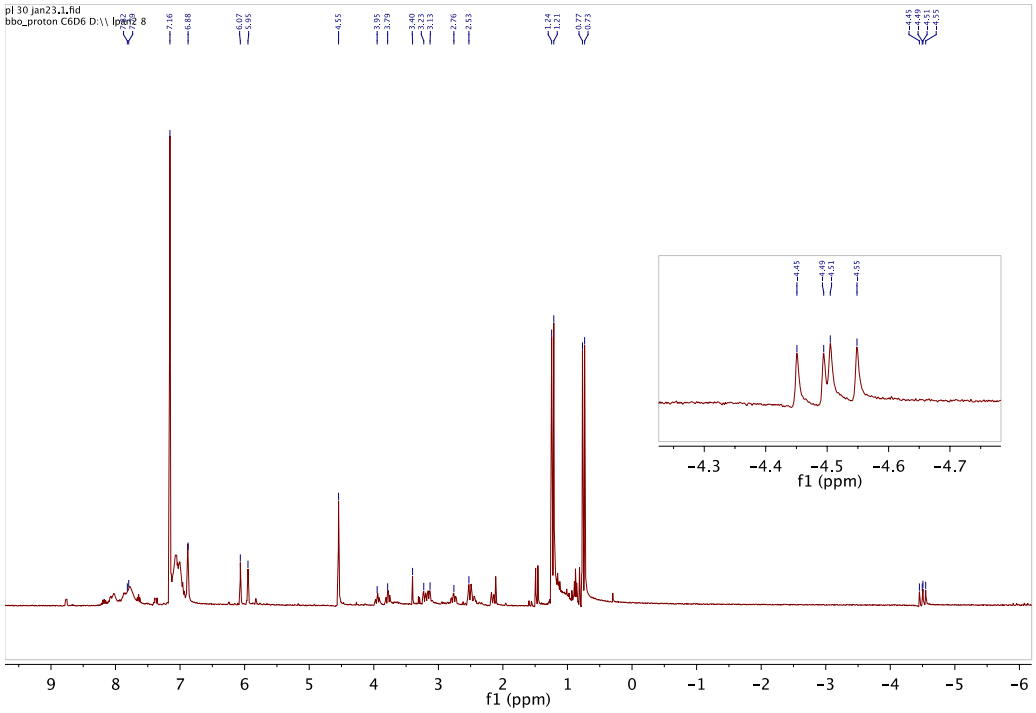


Figure S24: ^{1}H NMR spectrum of complex **7** in C_6D_6.

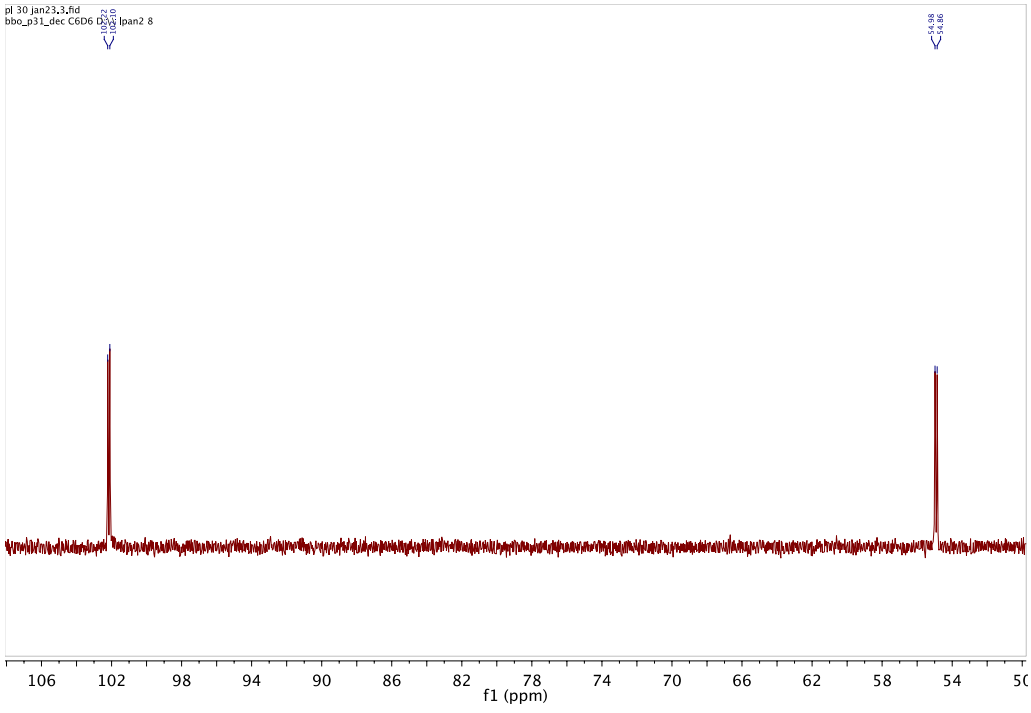


Figure S25: $^{31}P\{^{1}H\}$ NMR spectrum of complex **7** in C_6D_6.

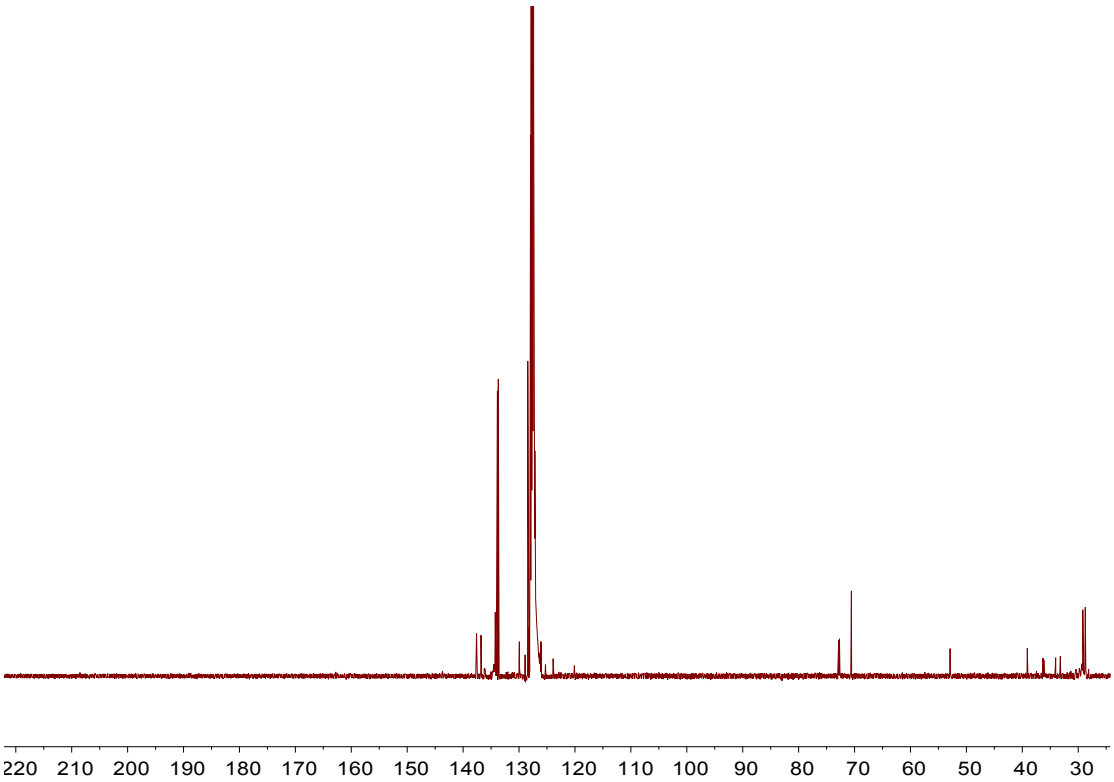
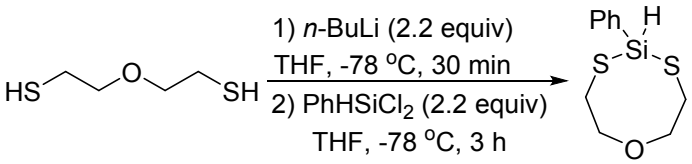


Figure S26: $^{13}C\{^1H\}$ NMR spectrum of complex **7** in C_6D_6.

11. Synthesis of $PhHSi(SCH_2CH_2)_2O$.



Dithiosilyl acetal was prepared according to a literature procedure with modifications[3]. To a solution of $O(CH_2CH_2SH)_2$ (0.0950 g, 0.6872 mmol) in THF (15 mL) in a 50 mL flask, *n*-BuLi (0.5 mL, 1.6mol/L in hexane) was added drop-wise at -78 ºC. The solution was stirred for thirty minutes before $PhHSiCl_2$ (0.1316 g, 0.7431 mmol) was slowly added to the reaction mixture. The reaction was stirred at -78 ºC for 30 minutes and then allowed to continue for 3 hours at room temperature. Upon completion of reaction hexane (30 mL) was added to the mixture to precipitate LiCl. The suspension was filtered and the filtrate was evaporated under vacuum. The product was washed with pentane (5 x 30 mL), dried under vacuum, and obtained as colorless crystals (0.1449 g, 87%).

^{1}H NMR (CD_2Cl_2): 2.90-2.93 (m, 4H, SCH_2), 3.63-3.68 (m, 2H, CH_2), 3.85-3.90 (m, 2H, CH_2), 5.80 (s, 1H, Si-H), 7.35-7.41 (m, 3H, Ph), 7.69-7.72 (m, 2H, Ph). **^{13}C{^{1}H} NMR (CD_2Cl_2):** 29.1 (s, SCH_2), 71.0 (s, OCH_2), 127. 9 (s, *m*-C_6H_5), 130.0 (s, *p*-C_6H_5), 133.9 (s, *o*-C_6H_5), 136.2 (s, *ipso*-C_6H_5). **^{29}Si{^{1}H} DEPT-135 (C_6D_6):** -2.8 (s, *Si*-H). **Elemental Analysis:** Calcd C: 49.55 H: 5.82. Found C: 49.46 H: 5.80.

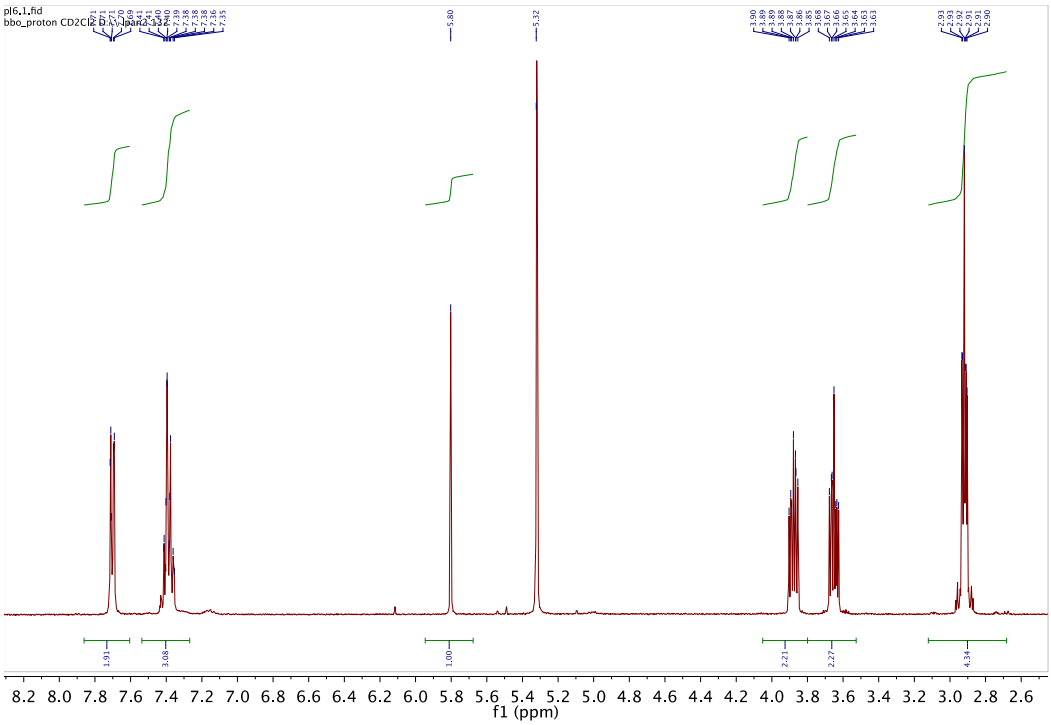


Figure S27: ^{1}H NMR spectrum of $PhHSi(SCH_2CH_2)_2O$ in CD_2Cl_2.

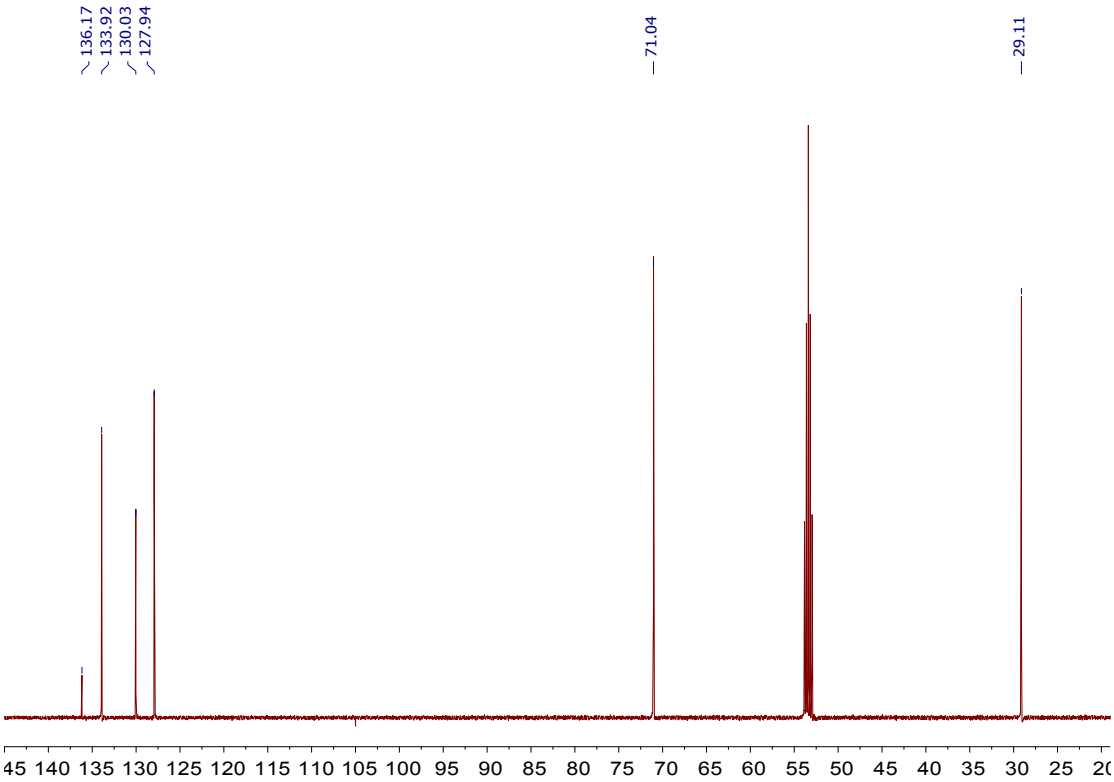


Figure S28: $^{13}C\{^{1}H\}$ NMR spectrum of $PhHSi(SCH_2CH_2)_2O$ in CD_2Cl_2.

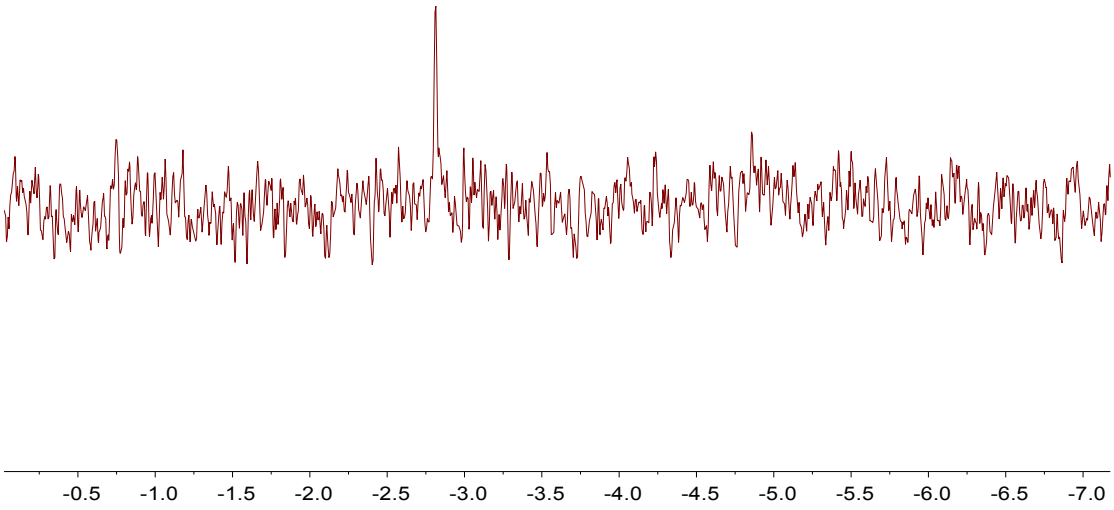


Figure S29: $^{29}Si\{^{1}H\}$ NMR spectrum of $PhHSi(SCH_2CH_2)_2O$ in CD_2Cl_2.

References:

1. Marchenko, A. P.; Koidan, H. N.; Huryeva, A. N.; Zarudnitskii, E. V.; Yurchenko, A. A.; Kostyuk, A. N. *J. Org. Chem.* **2010,** *75* (21), 7141.
2. Nägele, P.; Herrlich, U.; Rominger, F.; Hofmann, P. *Organometallics* **2013,** *32* (1), 181-191.
3. McKinty, A. M.; Stephan, D. W. *Dalton T.* **2014,** *43* (7), 2710-2.