Electronic Supplementary Material (ESI) for Chemical Communications.

s-block Carbodicarbene Chemistry: C(sp^3)–H Activation and Cyclization Mediated by a Beryllium Center

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Supporting Information

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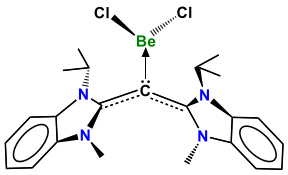
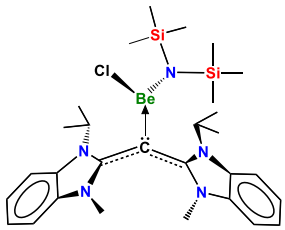
General Procedures

All manipulations were carried out under an atmosphere of purified argon using standard Schlenk techniques or in a MBRAUN LABmaster glovebox equipped with a −37 °C freezer. Dichloromethane was purified by distillation over calcium hydride. All other solvents were distilled over sodium/benzophenone. Glassware was oven-dried at 190 °C overnight. The NMR spectra were recorded at room temperature on a Varian Inova 500 MHz (^{1}H: 500.13 MHz), a Bruker Avance 600 MHz (^{1}H: 600.13 MHz, ^{13}C: 150.90 MHz, and ^{9}Be: 84.28 MHz), and an 800 MHz spectrometer (^{1}H: 800.13 MHz and ^{13}C: 201.193 MHz). Proton and carbon chemical shifts are reported in ppm and are referenced using the residual proton and carbon signals of the deuterated solvent (^{1}H; C_6D_6, δ 7.16, ^{13}C; C_6D_6, δ 128.06; ^{1}H; CD_2Cl_2, δ 5.32, ^{13}C; CD_2Cl_2, δ 53.84). All ^{9}Be NMR spectra were referenced to the reported diethyl ether beryllium dichloride $BeCl_2(Et_2O)_2$, δ 1.15.[1] Reference samples were sealed in a capillary tube and placed in the NMR sample tube. IR spectra were recorded on an Agilent Cary 630 FT-IR equipped with a diamond ATR unit in an argon filled glovebox. Single crystal X-ray diffraction data were collected on a Bruker Kappa APEXII Duo diffractometer running the APEX3 software suite using the Mo K_α fine-focus sealed tube (λ = 0.71073 Å) for **1-3**. The structures were solved and refined using the Bruker SHELXTL Software Package within OLEX2.[2-4] Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in geometrically calculated positions with U_{iso} = 1.2U_{equiv} of the parent atom (U_{iso} = 1.5U_{equiv} for methyl). The crystal data is summarized in Table S9. Deuterated solvents were purchased from Acros Organics and Cambridge Isotope Laboratories dried the same way as their protic analogues. Due to the toxicity of the beryllium compounds no combustion analysis was performed. Instead, purity was accessed by IR, ^{1}H, ^{13}C, and ^{9}Be NMR. **CATUTION!** Beryllium and its compounds are regarded as HIGHLY TOXIC and carcinogenic. Please adhere to protocols outlined in safety data sheets including using a respirator/mask and working in a well-ventilated fume hood.

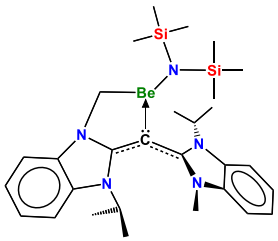
Experimental Procedures



Synthesis of Compound 1 To a 100 mL Schlenk flask bis(1-isopropyl-3-methyl-benzimidazol-2-ylidene)methane (1.00 grams, 2.77 mmol) was stirred in dry benzene (25 mL). A solution of $(Et_2O)_2BeCl_2$ (633 mg, 2.77 mmol) dissolved in benzene (10 mL) was added dropwise to the stirring solution, which formed a yellow precipitate immediately upon addition. After filtration and drying *in vacuo*, compound **1** was isolated as an air- and moisture-sensitive yellow solid (1.18 g, 97% yield). Yellow block-shaped crystals suitable for a single crystal X-Ray diffraction were obtained from a DCM/hexane mixture (1:1) at −37 °C. ^{1}H NMR (500.13 MHz, CD_2Cl_2, 298K) δ 7.45-7.44 (m, 2H, H_{ortho}-Ph-N-ipr), 7.24-7.15 (m, 6H, Aryl), 4.73-4.68 (septet, J_{HH} = 7.0 Hz, 2H, C*H*$(CH_3)_2$), 3.24 (s, 6H, N-C*H*$_3$), 1.63 (d, J_{HH} = 7.0 Hz, 2H, CH(C*H*$_3)_2$), 1.56 (d, J_{HH} = 7.0 Hz, 2H, CH(C*H*$_3)_2$); ^{13}C NMR (800.13 MHz, CD_2Cl_2) δ 160.34 (Carbone), 134.59, 131.40, 122.98, 112.03, 109.56, 51.68, 32.82, 20.55, 20.21; ^{9}Be NMR (600 MHz, ,CD_2Cl_2) δ 11.39. m.p.: decomposes at 170 °C.



Synthesis of Compound 2 A suspension of compound **1** (200 mg, 0.454 mmol) was stirred in dry toluene (5 mL). A solution of potassium bis(trimethylsilyl)amide (75.4 mg, 0.378 mmol) in dry toluene (5 mL) was added dropwise to the stirring suspension. Upon addition, a yellow product went into solution. The reaction mixture was stirred for 15 minutes. After filtering and drying *in vacuo*, compound **2** was obtained as an air- and moisture-sensitive yellow solid (161 mg, 75.3 % yield). Yellow block-shaped crystals suitable for X-ray diffraction were obtained from a hexane/toluene (3:1) mixture at room temperature. ^{1}H NMR (500.13 MHz, C_6D_6, 298K) δ 6.97-6.95 (m, 2H, Aryl), 6.92-6.86 (m, 4H, Aryl), 6.53-6.52 (m, 2H, Aryl), 4.80 (br, 2H, C*H*$(CH_3)_2$), 2.75 (s, 6H, N-C*H*$_3$), 1.40 (d, 6H, J_{HH} = 6.9 Hz, C(C*H*$_3)_2$), 1.25 (d, 6H, J_{HH} = 6.2 Hz, C(C*H*$_3)_2$), 0.57 (d, 18H, N[Si(C*H*$_3)_3]_2$); ^{13}C NMR (800.13 MHz, C_6D_6) δ 160.81 (Carbone), 134.24, 131.09, 128.19, 122.15, 111.10, 108.66, 50.15, 32.23, 20.12, 19.60, 6.53; ^{9}Be NMR (600 MHz, C_6D_6) δ 10.41. m.p.: 65-69 °C.



Synthesis of Compound 3 Compound **1** (178 mg, 0.404 mmol) was suspended in dry toluene (5 mL) and stirred vigorously. A dry toluene (5 mL) solution of potassium bis(trimethylsilyl)amide (161 mg, 0.808 mmol) was added dropwise to the stirring suspension, a product was formed in solution upon addition. Free CDC ligand is produced during the reaction and cannot be removed by washing or extraction due to the solubility of compound **3.** Therefore, CDC ligand was removed by complexing with $(Et_2O)_2BeCl_2$ (19.4 mg, 0.085 mmol) to form compound **1**, which is insoluble in toluene. After filtering to remove compound **1** and drying the filtrate *in vacuo*, compound **3** was produced as an air- and moisture-sensitive yellow solid (109.8 mg, 51.4% yield). Yellow rod-shaped crystals suitable for X-ray diffraction were obtained from a hexane/toluene (10:1) solution from the reaction mixture at −37 °C prior to purification. ^{1}H NMR (800.13 MHz, C_6D_6, 298K) δ 7.15-7.14 (m, 1H, Aryl), 7.08-7.06 (m, 2H, Aryl), 6.92-6.89 (m, 4H, Aryl), 6.58 (m, 1H, Aryl), 5.57 (septet, 1H, J_{HH} = 6.9 Hz, C*H*$(CH_3)_2$), 3.35 (septet, 1H, J_{HH} = 6.9 Hz, C*H*$(CH_3)_2$), 2.85 (s, 3H, N-C*H*$_3$), 2.76 (d, 1H, J_{HH} = 14.3 Hz, Be-C*H*H-N), 2.61 (d, 1H, J_{HH} = 14.4 Hz, Be-CH*H*-N), 1.79 (d, 3H, J_{HH} = 6.9 Hz, CH(C*H*$_3)_2$), 1.18 (d, 3H, J_{HH} = 6.9 Hz, CH(C*H*$_3)_2$), 1.03 (d, 3H, J_{HH} = 6.9 Hz, CH(C*H*$_3)_2$), 0.68 (d, 3H, J_{HH} = 6.9 Hz, CH(C*H*$_3)_2$), 0.33 (s, 18H, N[Si(C*H*$_3)_3]_2$); ^{13}C NMR (800.13 MHz, C_6D_6) δ 164.38, 160.14, 138.58, 133.77, 133.47, 131.38, 122.78, 122.38, 122.22, 119.14, 111.41, 110.33, 108.96, 108.42, 49.69, 49.02, 33.71, 31.56, 21.42, 21.29, 20.20,19.12, 5.31, 1.46; ^{9}Be NMR (600 MHz, C_6D_6) δ 17.73. m.p.: 183-185 °C.

NMR Spectra: ^{1}H, ^{13}C, and ^{9}Be NMR Spectra

Figure S1. ^{1}H NMR of compound **1**.

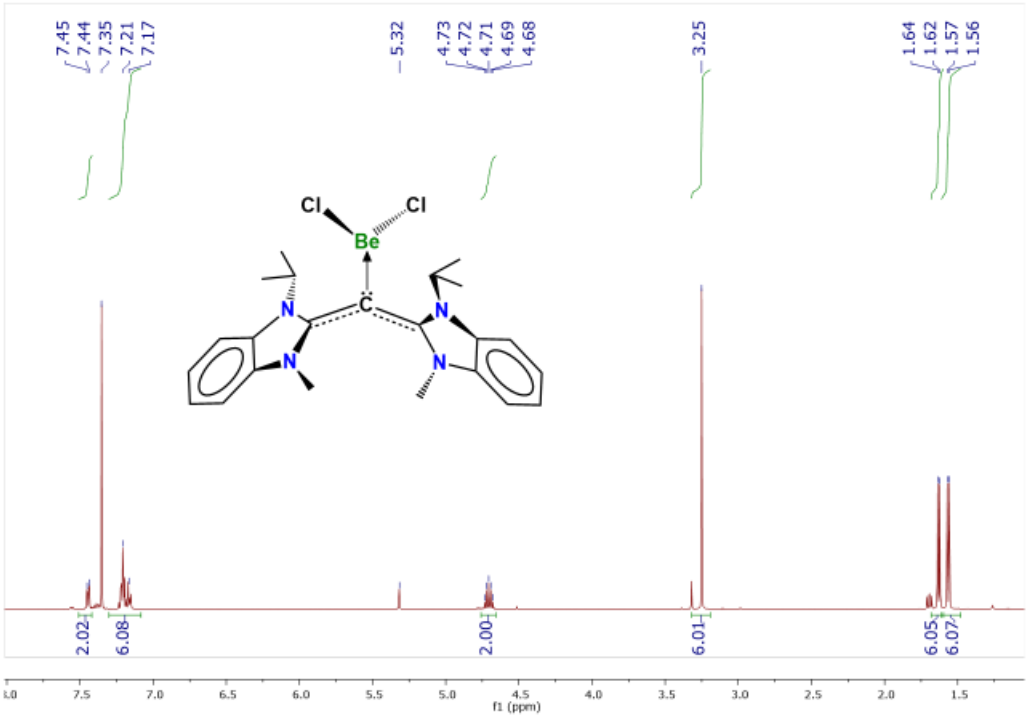


Figure S2. ^{13}C NMR of compound **1**.

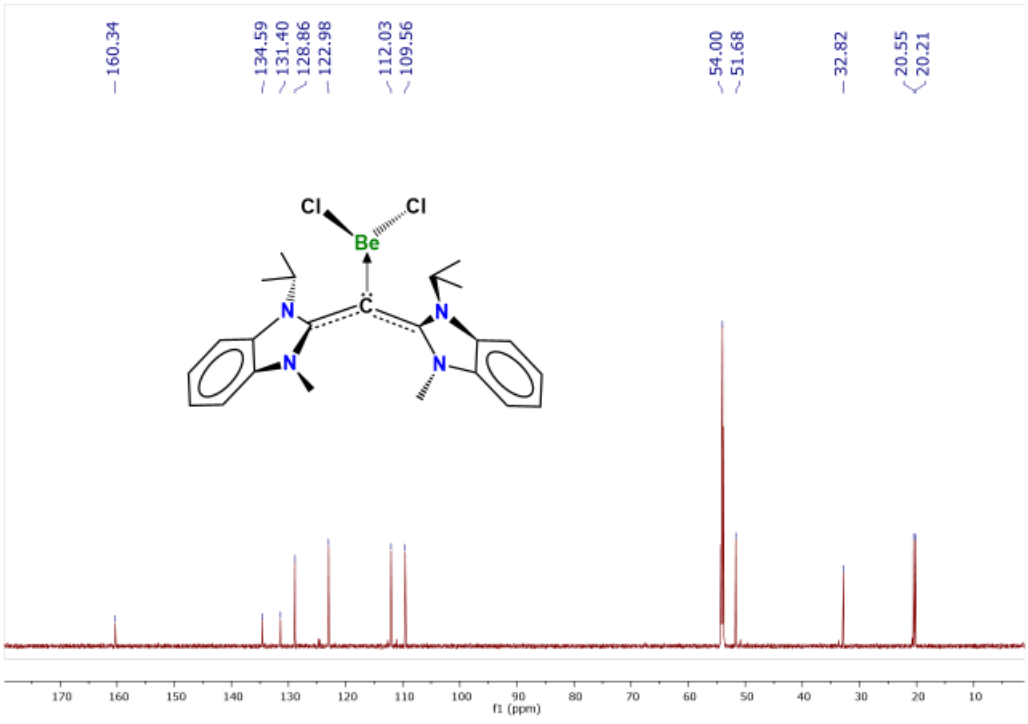


Figure S3. ^{9}Be NMR of compound **1**.

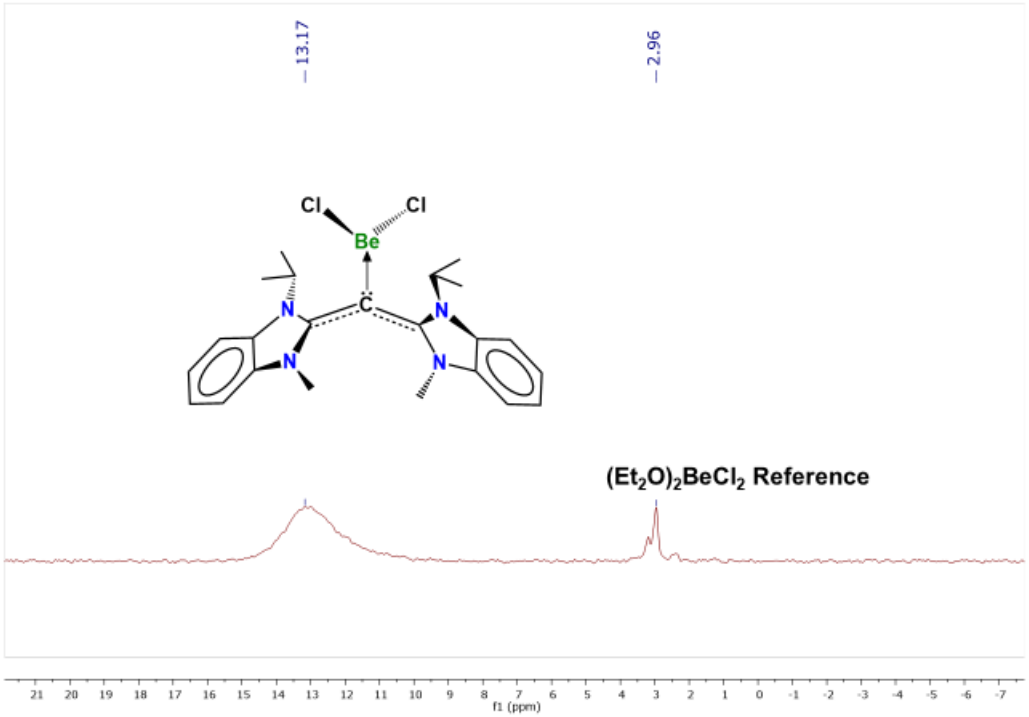


Figure S4. ^{1}H NMR of compound **2**.

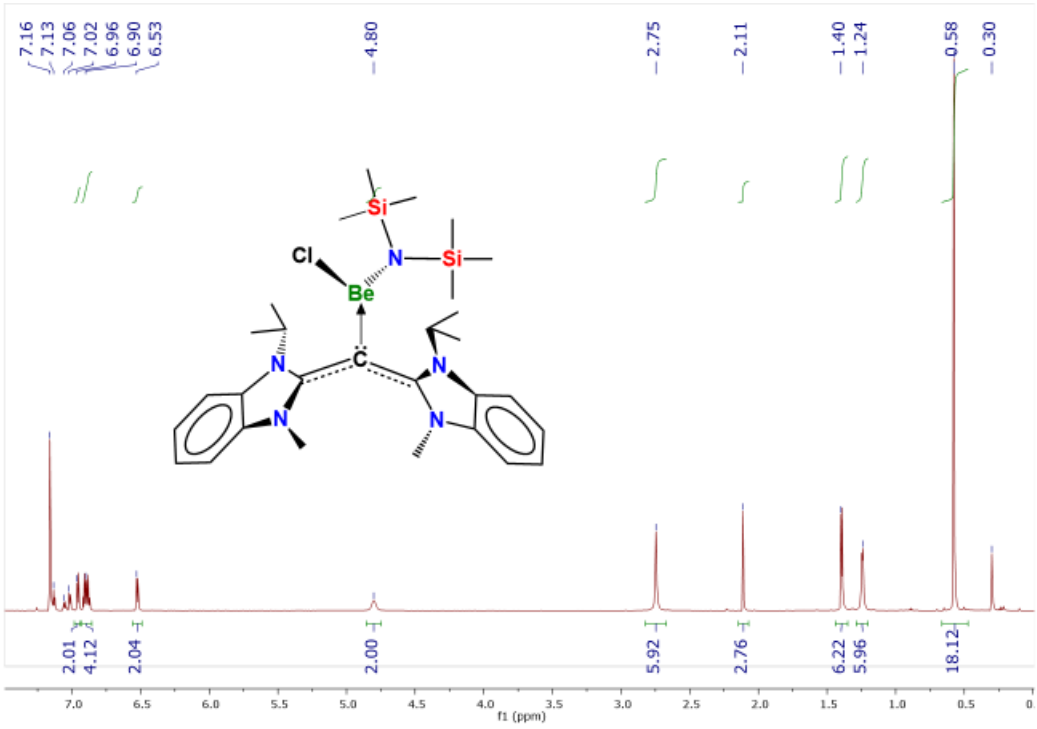


Figure S5. ^{13}C NMR of compound **2**.

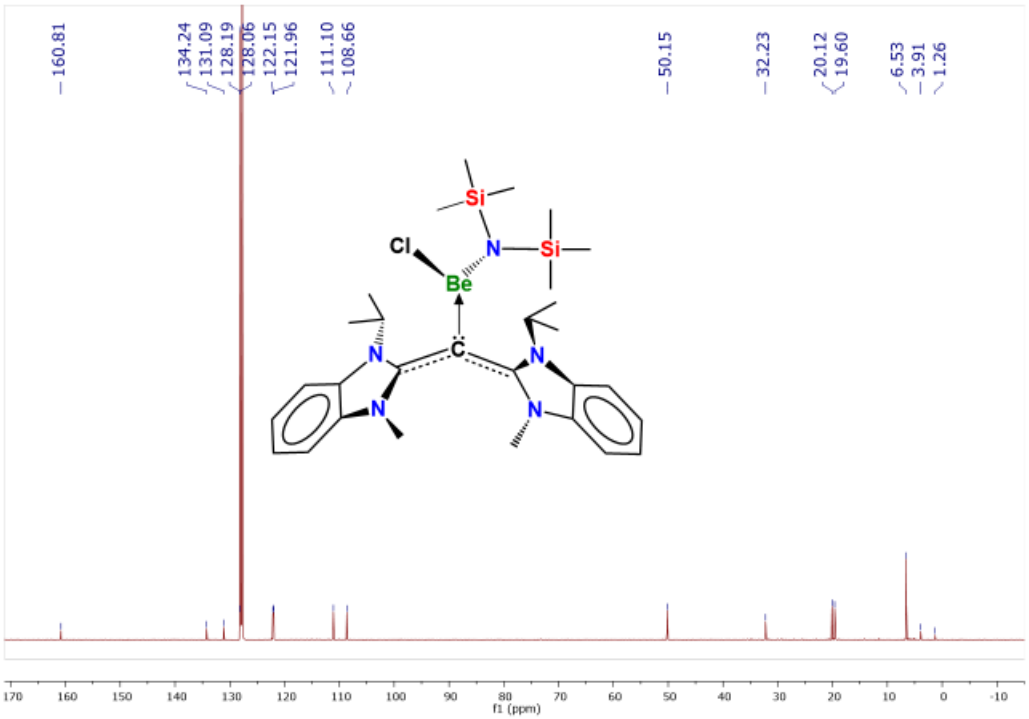


Figure S6. ^{9}Be NMR of compound **2**.

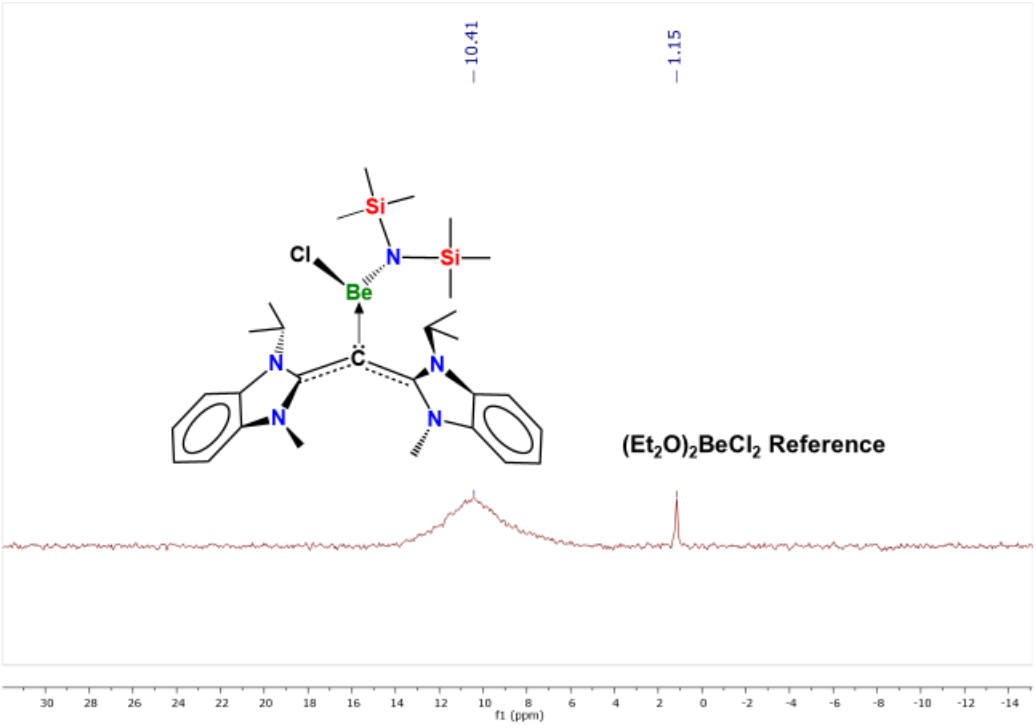


Figure S7. ^{1}H NMR of compound **3**.

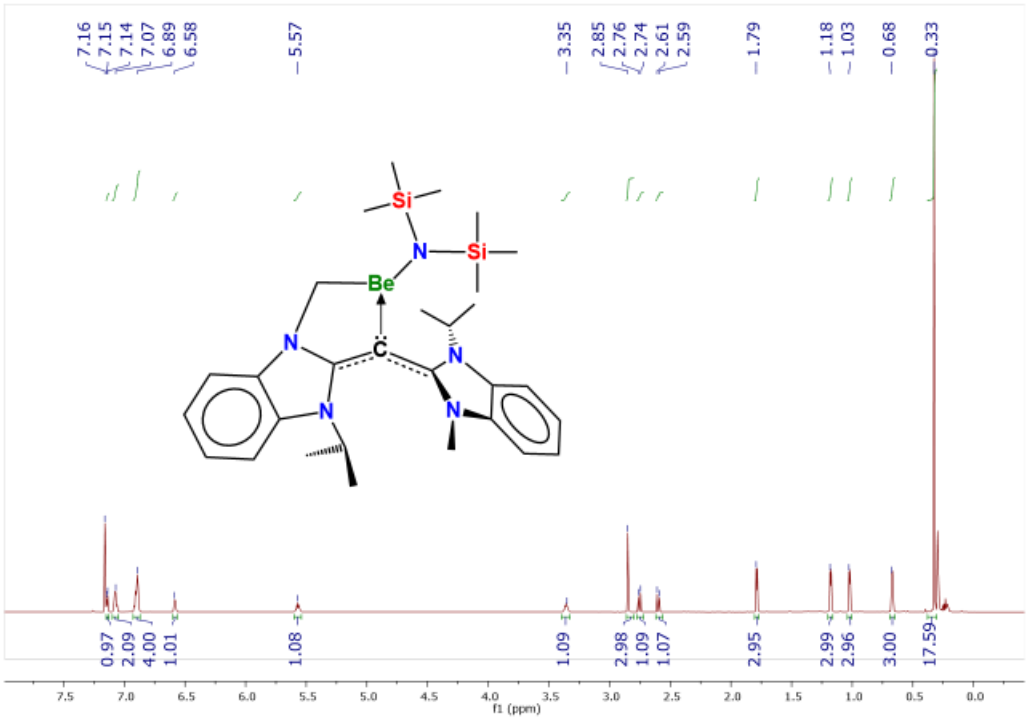


Figure S8. ^{13}C NMR of compound **3**.

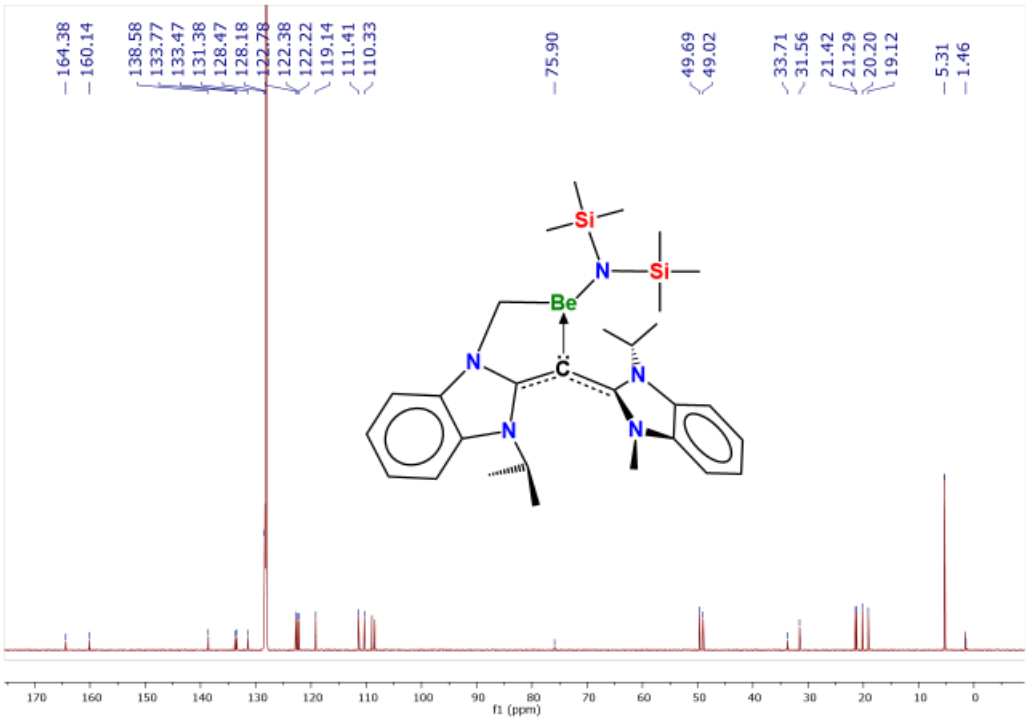
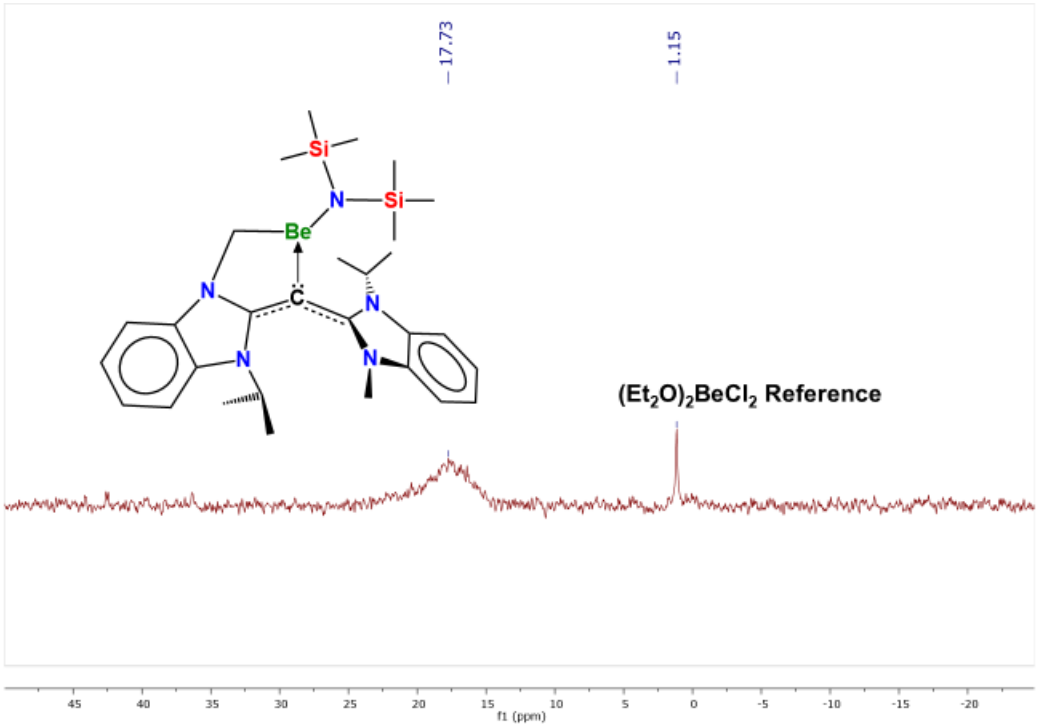
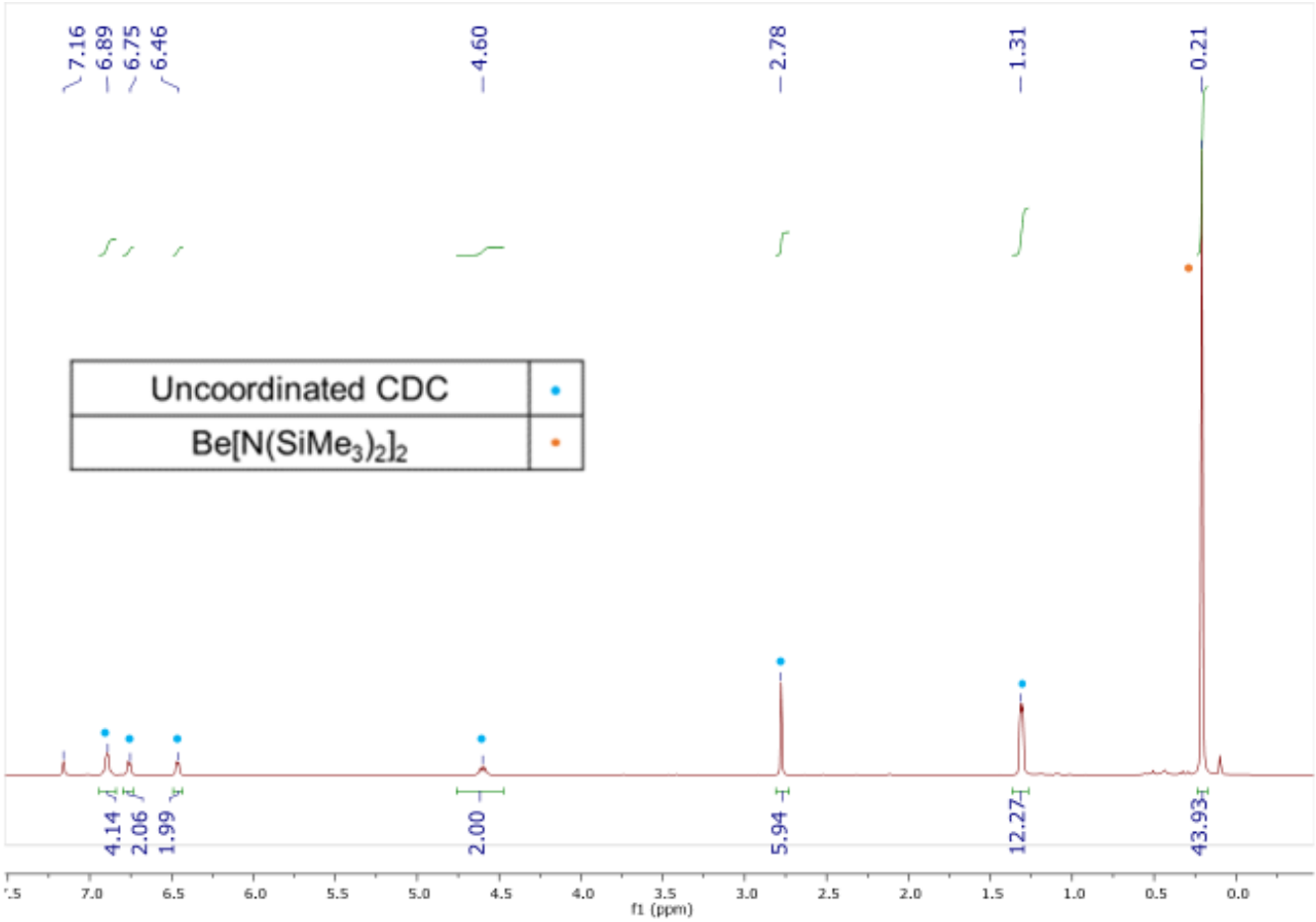


Figure S9. ^{9}Be NMR of compound **3**.



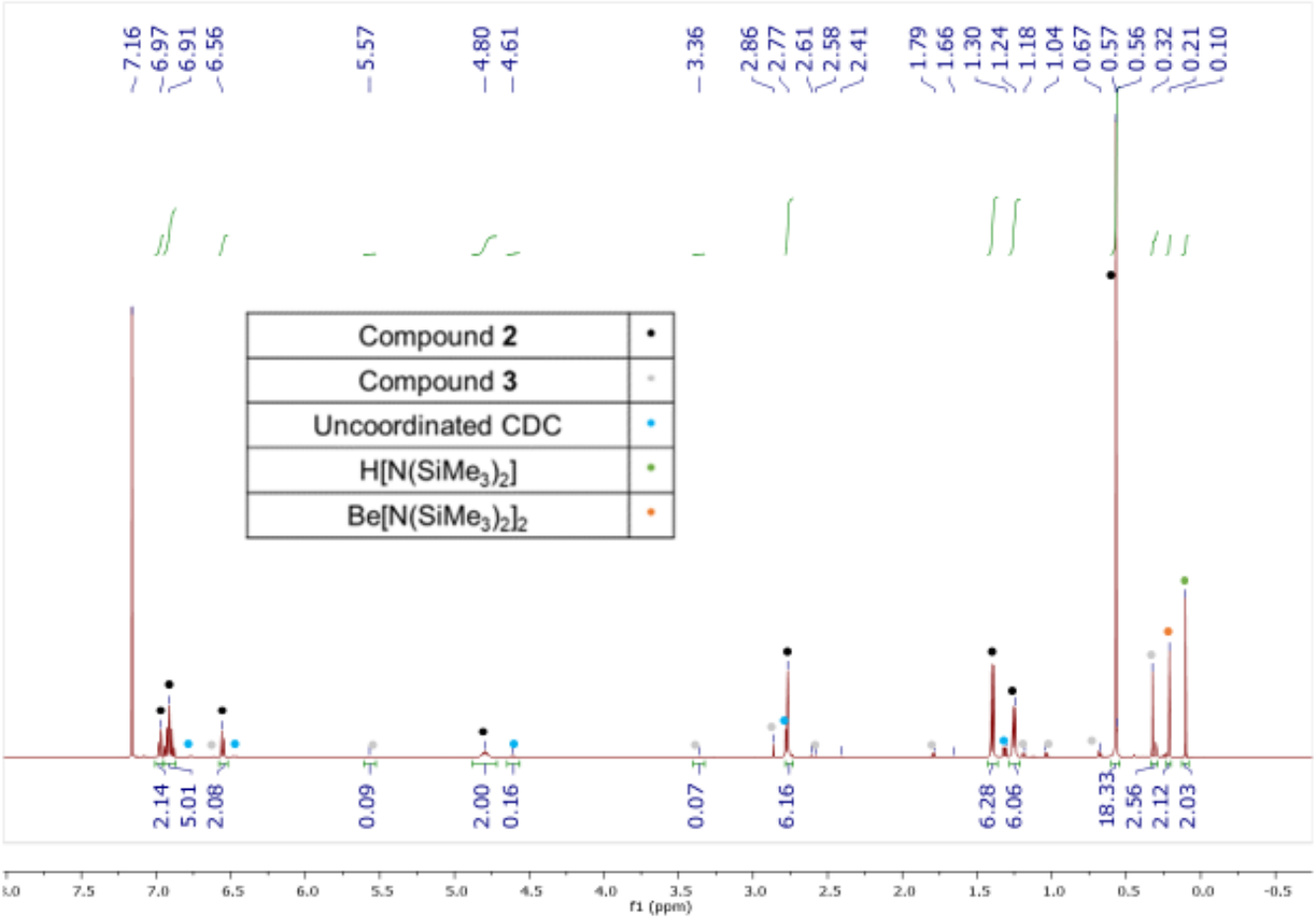
^{1}H NMR Reaction Studies

Figure S10. Reaction of CDC with $Be[N(SiMe_3)_2]_2$.



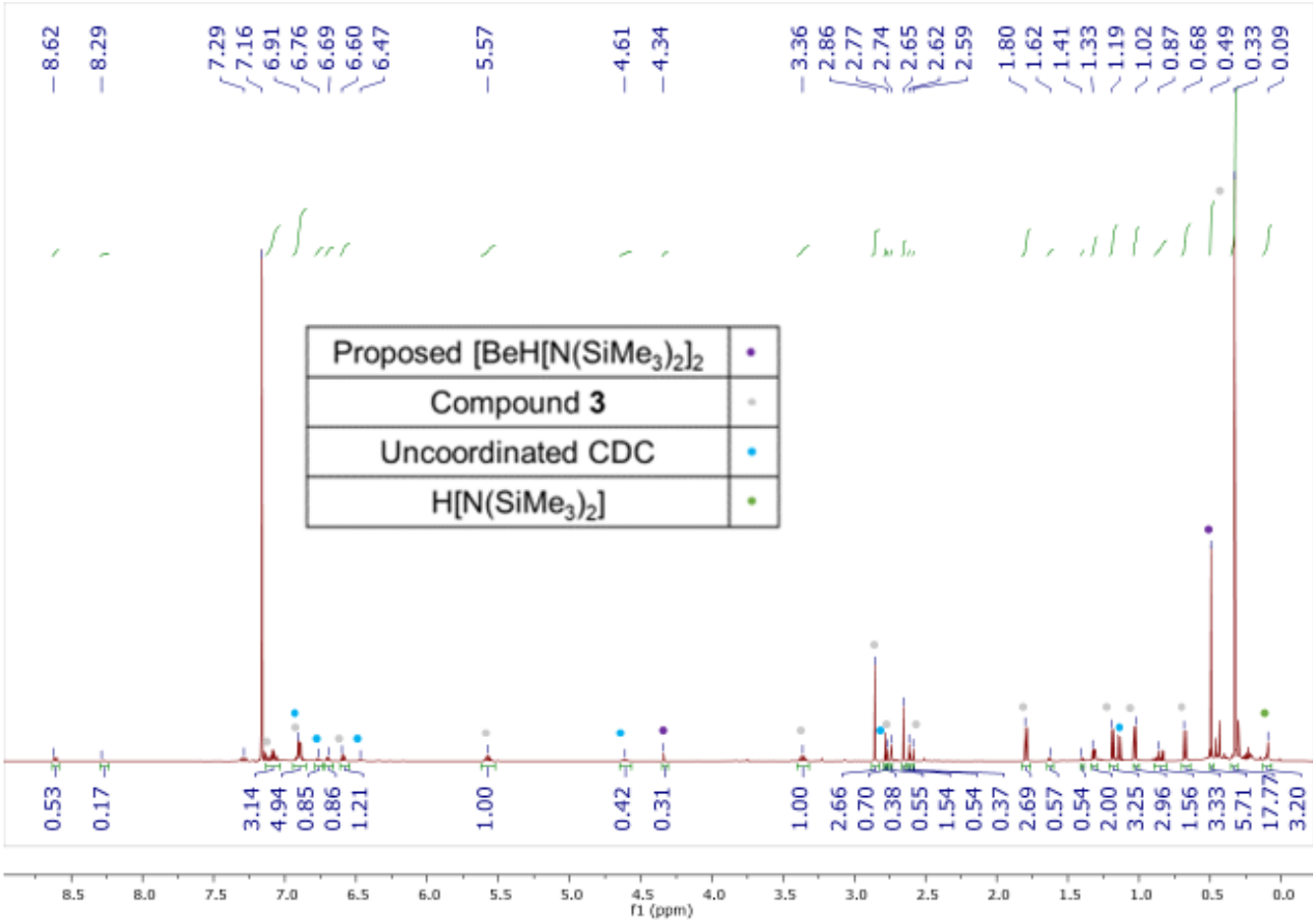
In the reaction of **2** with $K[N(SiMe_3)_2]$, $Be[N(SiMe_3)_2]_2$ is a side product. Therefore, we synthesized $Be[N(SiMe_3)_2]_2$ independently and confirmed that it does not react with CDC, there was no reaction even at elevated temperatures.

Figure S11. Reaction of compound **1** with 1.1 equivalents of $K[N(SiMe_3)_2]$.



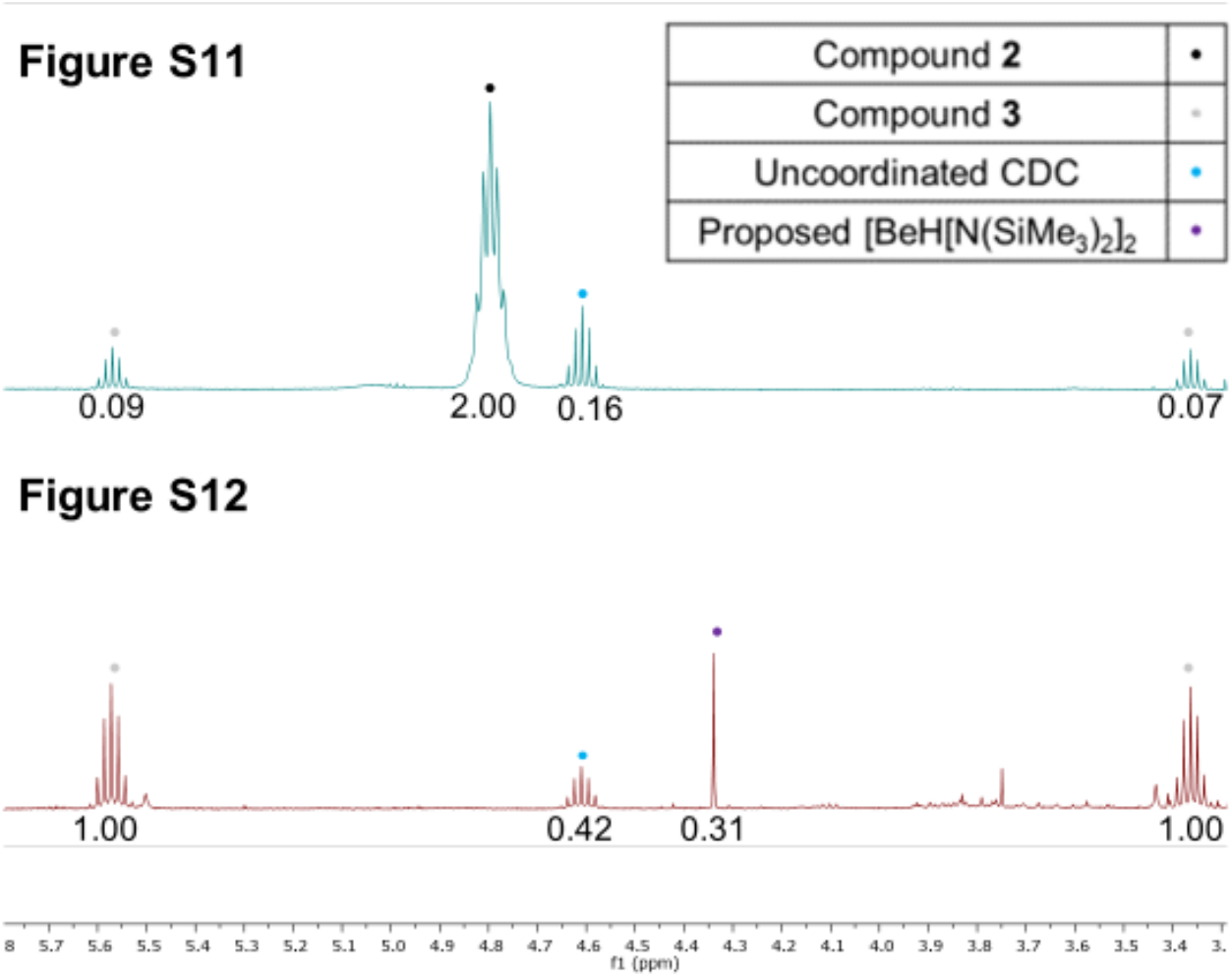
1.1 equivalents of $K[N(SiMe_3)_2]$ was added to compound **1**. This generated approximately 8% of compound **3** with respect to compound **2** (major product). The uncoordinated CDC was approximately 8%.

Figure S12. Reaction from Figure S11 with 1 equivalent of KC_8.



The reaction mixture from **Figure S11** was combined with KC_8 and stirred overnight. The ratio of metallocycle to free CDC increased.

Figure S13. Stacked spectra, comparison of the methine region from Figure S11 and S12.



With the reaction from **Figure S11**, we added a slight excess (1.1 eq) of $K[N(SiMe_3)_2]$, which partially converted to compound **3**. We then want to see if KC_8 could make the same compound (Reaction 3). Relative to free ligand, compound **3** increased substantially in the reaction from **Figure S12**, confirming that KC_8 results in the formation of the same compounds.

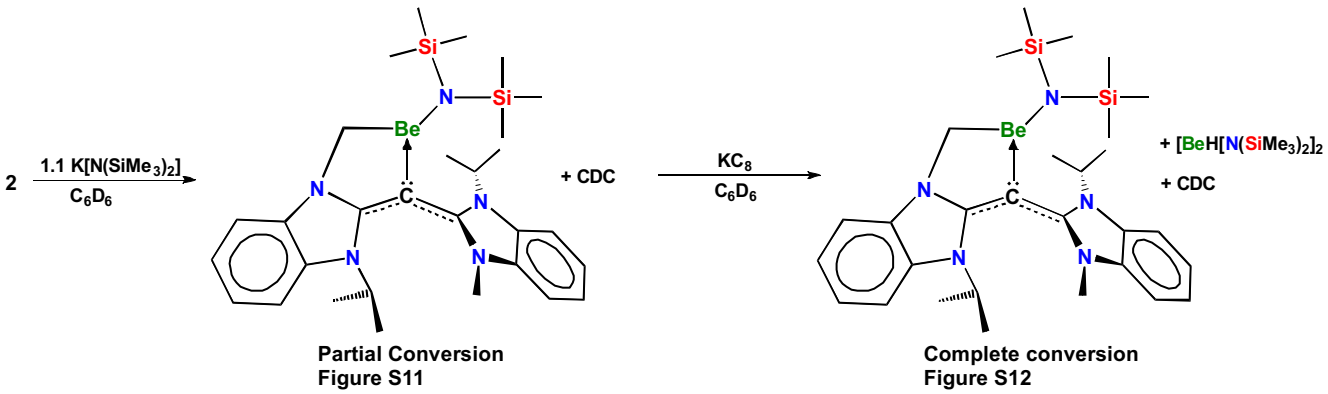
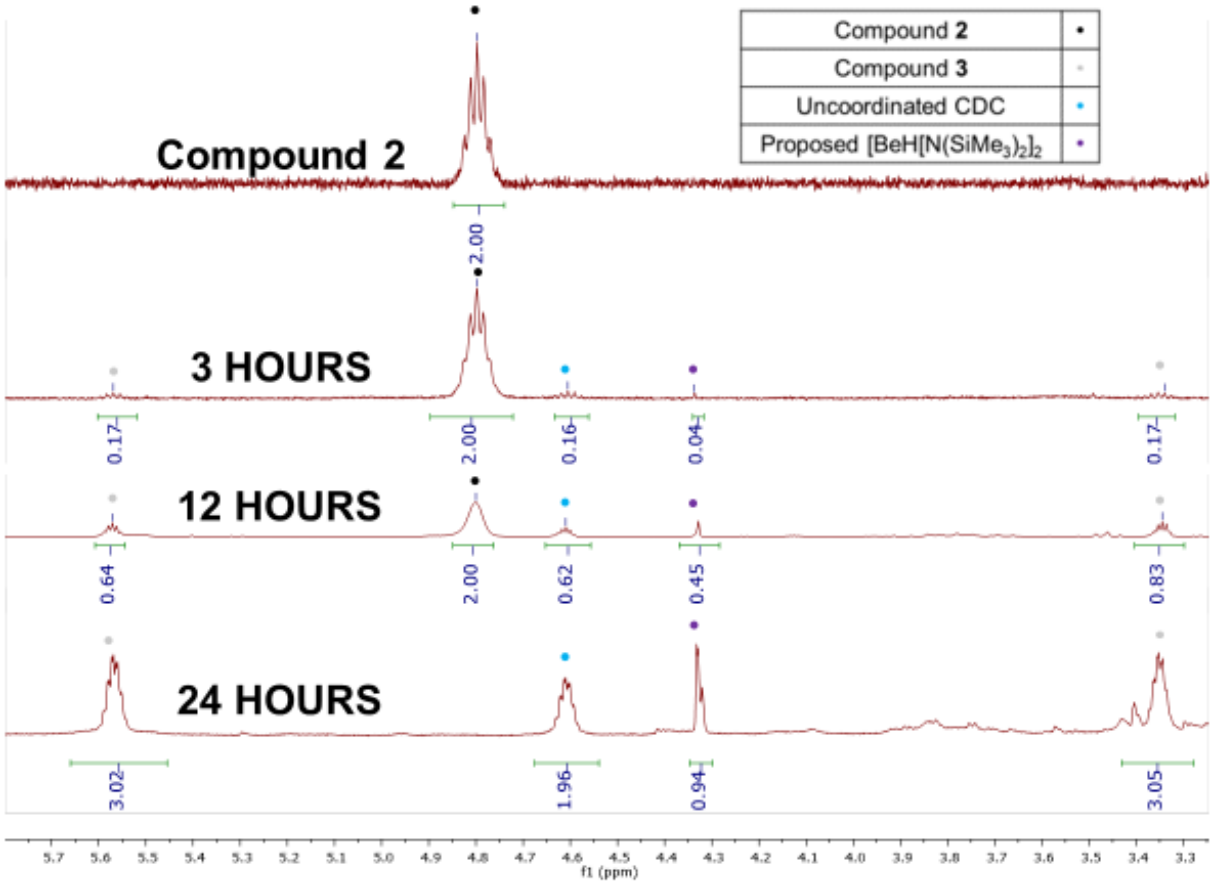
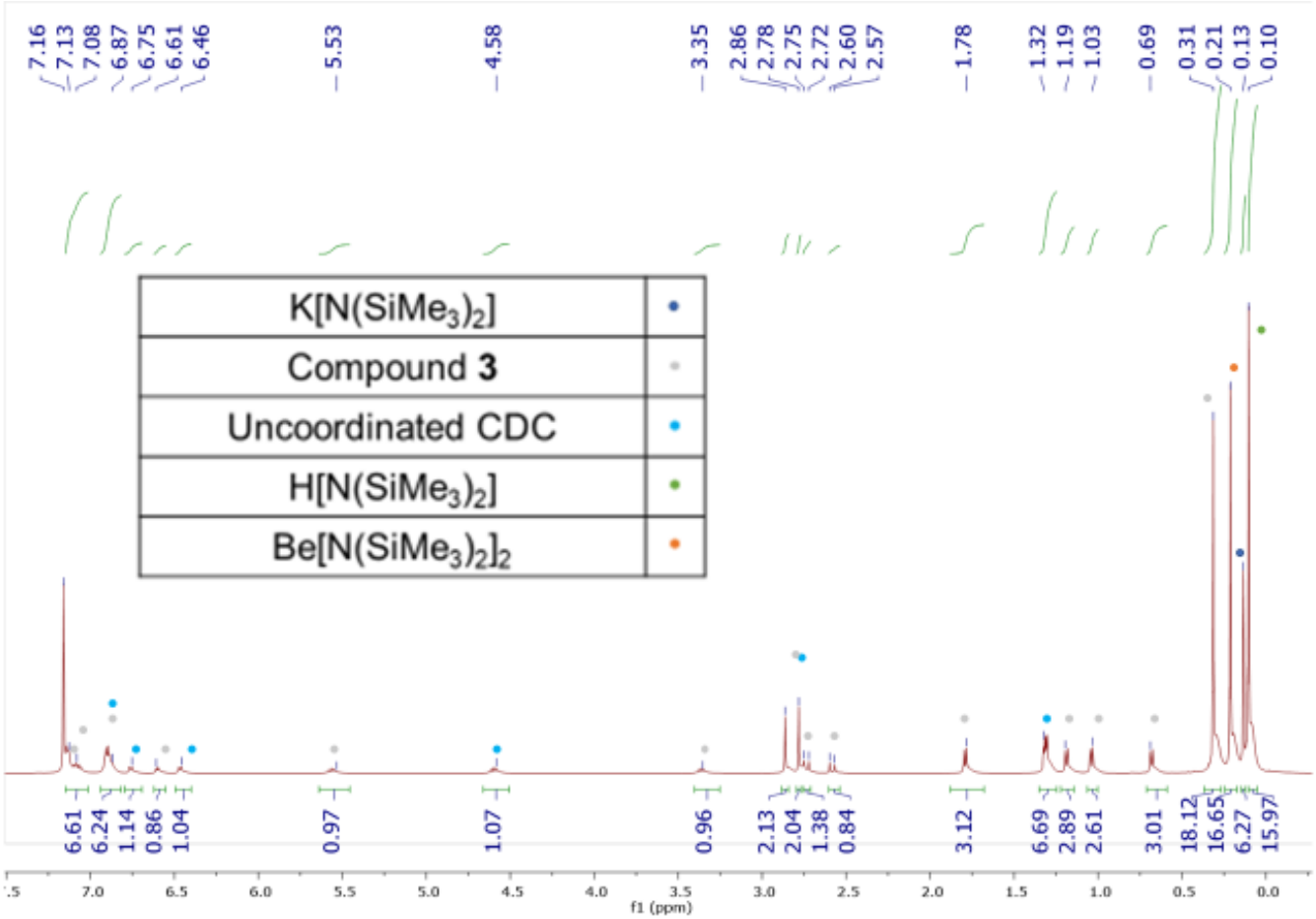


Figure S14. Reaction of pure compound **2** reaction with 1 equivalent of KC_8 at different time intervals.



Reaction of purified compound **2** with KC_8 at different time intervals. The ratio of compound **3** to free CDC is (3:1).

Figure S15. Reaction of compound **2** with 1 equivalents of $K[N(SiMe_3)_2]$.



The reaction of **2** with 1 equivalent of $K[N(SiMe_3)_2]$ shows a smaller ratio of **3** to free CDC (2:1) than with the reaction of **2** with KC_8 (3:1). The crystal structure for **3** was obtained from a similar reaction mixture with toluene as the solvent. Therefore, **3** co-crystallized as a 1:1 mixture with a toluene adduct of $K[N(SiMe_3)_2]$.

IR Spectra

Figure S16. IR spectra of (CDC)$BeCl_2$ (Compound **1**).

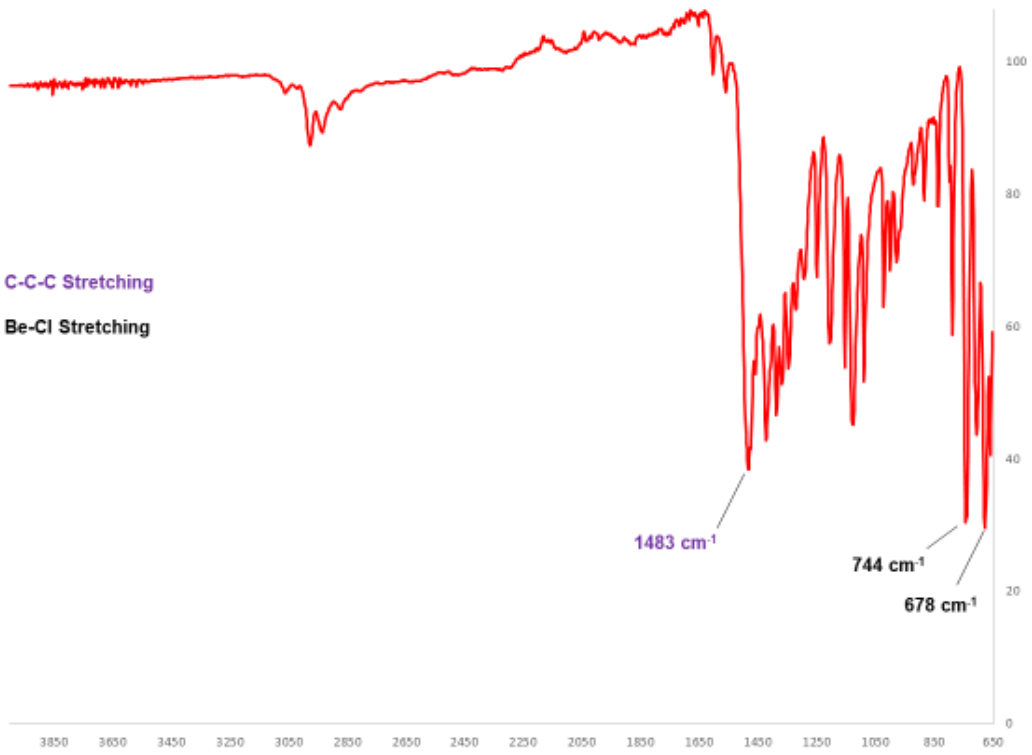


Table S1: Computed B3LYP-D3(BJ)/def2-TZVP vibrational frequencies of (CDC)$BeCl_2$.

Scaled Freq	Intensity	Vib.
17.142	198.572	Cl-Be-Cl Rock
119.044	135.798	Cl-Be-Cl Scissoring
259.009	44.623	Cl-Be-Cl Scissoring
360.747	8.411	Cl-Be-Cl Wag
414.980	116.761	Cl-Be-Cl Wag
423.330	58.261	Cl-Be-Cl Wag
517.331	111.678	Cl-Be-Cl Symm. Stretch
653.308	227.178	Cl-Be-Cl Symm. Stretch
720.740	165.501	Cl-Be-Cl Symm. Stretch
653.308	227.178	Cl-Be-Cl Symm. Stretch
720.740	165.501	Cl-Be-Cl Symm. Stretch
1480.226	401.498	C-C-C Symm. Stretch
1507.253	6186.954	C-C-C Asymm. Stretch

Figure S17. IR spectra of (CDC)BeCl[N(SiMe$_3$)$_2$] **(**Compound **2).**

Table S2: Computed B3LYP-D3(BJ)/def2-TZVP vibrational frequencies of (CDC)BeCl[N(SiMe3)2].

Scaled Freq	Intensity	Vib.
336.452	95.634	Si-N-Si Scissoring
357.526	47.096	Si-N-Si Scissoring
447.280	13.560	CDC-Be Wag
452.749	22.654	CDC-Be Wag
476.508	270.573	CDC-Be Wag
509.633	37.481	CDC-Be Symm. Stretch
525.891	15.104	CDC-Be Symm. Stretch
566.745	87.099	CDC-Be Asymm. Stretch
570.847	72.355	CDC-Be Asymm. Stretch
635.501	199.827	CDC-Be Symm. Stretch
684.955	43.350	CDC-Be Symm. Stretch
767.718	53.978	CDC-Be Symm. Stretch
906.936	1104.208	N-Be Asymm. Stretch
939.083	1261.513	N-Be Asymm. Stretch
996.322	1830.127	N-Be Asymm. Stretch
1365.075	388.692	C-C-C Symm. Stretch
1479.911	619.670	C-C-C Symm. Stretch
1509.380	5469.159	C-C-C Asymm. Stretch

Figure S18. IR spectra of (CDC)Be[N(SiMe$_3$)$_2$] (Compound **3**).

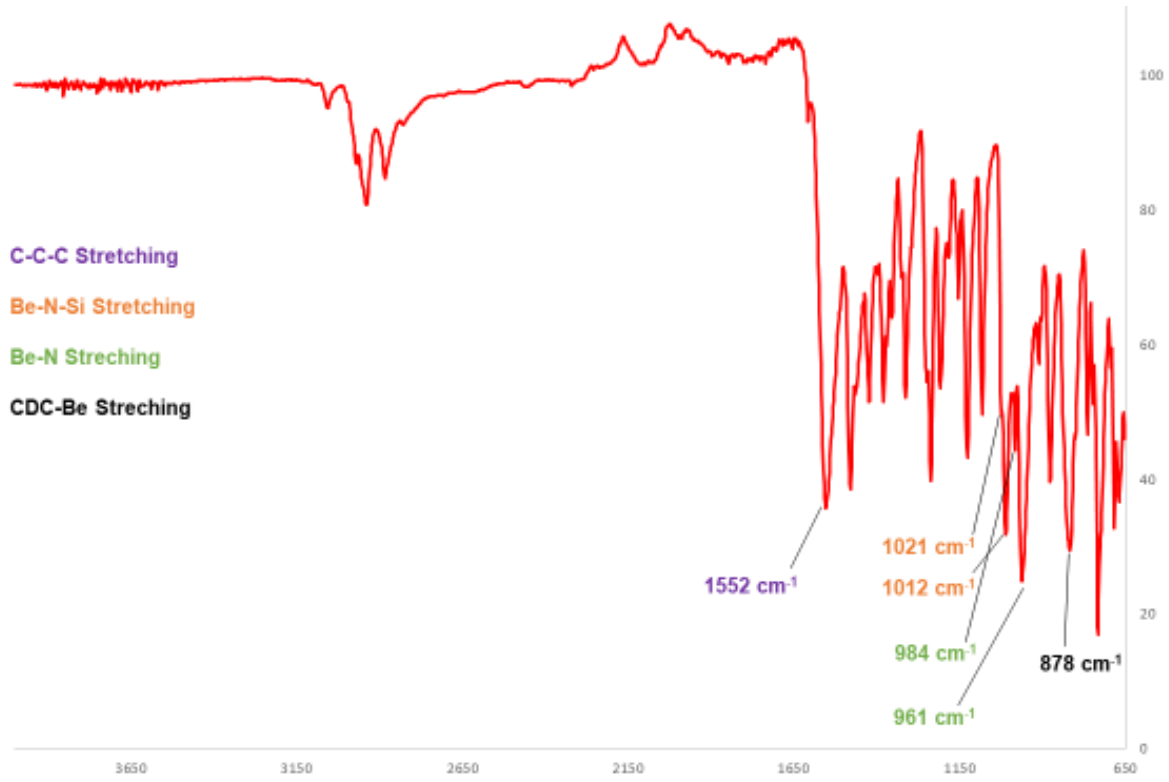


Table S3: Computed B3LYP-D3(BJ)/def2-TZVP vibrational frequencies of (CDC)Be[N(SiMe$_3$)$_2$].

Scaled Freq	Intensity	Vib.
342.226	7.204	Si-N-Si Symm. Stretch
352.362	37.572	Si-N-Si Scissoring
497.421	17.125	CDC-Be Wag
544.246	46.720	CDC-Be Wag
577.181	15.376	CDC-Be Wag
586.575	25.151	CH^2-Be-C Twist
593.636	35.019	CH^2-Be-C Symm. Stretch
646.027	66.287	CH^2-Be-C Asymm. Stretch
664.223	71.288	C-Be-N Scissoring
685.161	27.049	C-Be-N Scissoring
709.169	232.907	CH^2-Be-N Scissoring
756.578	243.886	CH^2-Be-CDC Asymm. Stretch
900.849	68.548	Be-CDC Stretch
968.822	715.072	Be-N Stretch
972.870	218.745	Be-N Stretch
978.599	1491.082	Be-N-Si Symm. Stretch
993.115	1254.196	Be-N-Si Symm. Stretch
1363.470	355.180	C-C-C Symm. Stretch
1559.873	5685.994	C-C-C Asymm. Stretch

Computational Methods. All calculations were performed in the gas phase using Gaussian 16 revision A.03 unless noted.[5] Geometry optimizations were performed using the B3LYP and M06-2X density functionals utilizing both def2-SVP and def2-TZVP basis sets.[6] Grimme's D3 dispersion with Becke-Johnson damping was included with B3LYP, labelled B3LYP-D3(BJ).[7] Harmonic vibrational frequencies were computed analytically at the same level of theory in order to characterise the stationary points as minima. NPA charge analysis was performed using NBO 6.0 integrated with Gaussian 16.[9] QTAIM calculations were performed using the AIMAll software package using the Proaim atomic integration algorithm.[10] EDA analysis was conducted within the ADF package[11] at the BP86-D3(BJ)/TZ2P level of theory. Scalar relativistic effects were incorporated by applying the zeroth-order regular approximation (ZORA) in all ADF calculations.

Cartesian Coordinates of B3LYP-D3BJ/def2-TZVP Optimized Geometries.

CDC-BeCl2

E_e = -2048.26036625 (Hartrees)

0 1

Be	0.00003900	2.28866000	0.00008600
Cl	0.74329800	3.20950700	-1.51840900
N	-1.39602700	-1.36190200	0.80359900
N	-2.43607500	0.23519200	-0.31913600
C	0.00001200	0.52509900	0.00008800
C	-1.19502300	-0.16965400	0.12796500
C	-0.43012500	-1.97983500	1.68472600
H	0.15060700	-2.75582900	1.18294400
H	-0.95497300	-2.41967900	2.53089600
H	0.25189400	-1.21400500	2.04862900
C	-2.63855800	1.34841300	-1.25996400
H	-1.65329500	1.79351800	-1.38725300
C	-3.57137100	2.41065300	-0.69202600
H	-4.59660900	2.05211000	-0.60230900
H	-3.57342000	3.27442700	-1.35735700
H	-3.22115600	2.73834800	0.28492200
C	-3.06185000	0.83051600	-2.63293200
H	-2.33772300	0.10852900	-3.01293100
H	-3.10639200	1.66427300	-3.33361400
H	-4.04118600	0.35320900	-2.60907200
C	-3.40252000	-0.68996100	0.06116200
C	-4.77421900	-0.75513100	-0.13955900
H	-5.30698700	0.01301800	-0.67667800
C	-5.45733700	-1.85105600	0.38459600
H	-6.52690000	-1.92047500	0.23946800
C	-4.79435700	-2.85262700	1.09015000
H	-5.35395900	-3.68878400	1.48665400
C	-3.41653600	-2.79448800	1.29092600
H	-2.89823600	-3.57617500	1.82870900
C	-2.74069000	-1.70536600	0.76808900
N	1.39601200	-1.36186700	-0.80354400
N	2.43611500	0.23518000	0.31920400
C	1.19504200	-0.16965800	-0.12783900
C	0.43005500	-1.97975600	-1.68464200
H	-0.15064000	-2.75577900	-1.18286100
H	0.95484900	-2.41955300	-2.53087100
H	-0.25199100	-1.21390800	-2.04845700
C	2.63864300	1.34838500	1.26004200
H	1.65335500	1.79337100	1.38753500
C	3.57120500	2.41078000	0.69197800
H	4.59647700	2.05239300	0.60206000
H	3.57325000	3.27452600	1.35734400
H	3.22076200	2.73846400	-0.28489200
C	3.06226100	0.83047200	2.63290200
H	2.33829100	0.10838600	3.01301000
H	3.10684800	1.66420100	3.33361400
H	4.04164800	0.35327500	2.60882200
C	3.40254100	-0.68996300	-0.06117200
C	4.77424600	-0.75516000	0.13950200
H	5.30703900	0.01294900	0.67665400
C	5.45733500	-1.85106300	-0.38473600
H	6.52690300	-1.92050100	-0.23964500
C	4.79432400	-2.85258800	-1.09032400
H	5.35390500	-3.68872900	-1.48689100
C	3.41649500	-2.79443000	-1.29104400
H	2.89816900	-3.57608800	-1.82884300
C	2.74067700	-1.70533200	-0.76812000
Cl	-0.74343800	3.20956000	1.51844400

CDC-BeCl[N(SiMe3)2]

E_e = -2461.59088108 (Hartrees)

0 1

Cl	-0.11274900	-1.76650200	-2.38073400
Si	2.69700800	-2.91082500	-0.73776000
Si	2.15399800	-1.35797700	1.77388800
N	-2.81261500	0.93571700	-0.68397700
N	-2.46688100	-1.02599600	0.27291500
N	-0.48232600	2.61561000	0.76848900
N	1.19928300	2.13265400	-0.58919300
N	1.83486700	-1.64212600	0.10016600
C	-0.45429500	0.33476400	-0.20652600
C	-1.82633400	0.11026900	-0.17444200
C	-2.56276400	2.07361300	-1.54208700
H	-2.52841100	3.01196400	-0.98611300
H	-3.35217000	2.13026400	-2.28912800
H	-1.60858900	1.92697900	-2.04409100
C	-1.79586400	-2.10423400	1.01311900
H	-0.74226000	-1.83485500	0.99346100
C	-2.24030500	-2.12114600	2.47359500
H	-2.07568400	-1.15049300	2.94253500
H	-1.65963900	-2.86287000	3.02194900
H	-3.29523800	-2.37472000	2.57487600
C	-1.94272700	-3.45292200	0.31875200
H	-2.96148500	-3.83538700	0.37319200
H	-1.28578300	-4.17537100	0.80336700
H	-1.64834900	-3.37324300	-0.72563200
C	-3.83636800	-0.91464300	0.06154700
C	-4.90384200	-1.75820600	0.33594900
H	-4.76242900	-2.72305000	0.79577300
C	-6.18166800	-1.32381500	-0.01063400
H	-7.02732200	-1.96651200	0.19353500
C	-6.39096500	-0.08556900	-0.61415100
H	-7.39516400	0.22075700	-0.87358600
C	-5.32350000	0.76731400	-0.88693100
H	-5.48468200	1.73285000	-1.34584400
C	-4.05515800	0.33366800	-0.54068000
C	0.03401800	1.61787200	-0.04719300
C	-1.53192800	2.43027800	1.74460500
H	-2.50633500	2.74501600	1.36624000
H	-1.29183900	3.00686600	2.63630300
H	-1.58416900	1.37821800	2.01112200
C	1.91174600	1.51462900	-1.71846300
H	1.40347800	0.56859400	-1.89249200
C	1.73702300	2.33911800	-2.99218100
H	0.67903300	2.49908200	-3.20359200
H	2.17007000	1.79620800	-3.83223300
H	2.22412900	3.31149500	-2.92665300
C	3.36461300	1.21842300	-1.37499700

H	3.92355500	2.12133800	-1.13204300
H	3.84529100	0.74164200	-2.22852400
H	3.41588300	0.53061000	-0.53463900
C	1.40979300	3.42691800	-0.12225800
C	2.40792000	4.36184800	-0.35681100
H	3.23952400	4.15402500	-1.01081900
C	2.31136300	5.59471200	0.28771100
H	3.07996700	6.33653600	0.11795200
C	1.25158000	5.88747800	1.14190700
H	1.20636500	6.85198200	1.62899900
C	0.24274600	4.95415400	1.37633000
H	-0.58773300	5.18362400	2.02933800
C	0.34124300	3.73193700	0.73424300
C	1.11412400	-0.00048700	2.57146000
H	1.33505100	0.98294400	2.15597500
H	1.37617900	0.02644600	3.63299500
H	0.04284900	-0.16967900	2.49485500
C	3.91756000	-0.79692200	2.14445700
H	4.67145000	-1.55187900	1.93334100
H	3.99585200	-0.53647200	3.20372500
H	4.17072100	0.09840400	1.57163400
C	1.79253700	-2.90709000	2.79454900
H	0.74028800	-3.18681700	2.70075000
H	1.99761600	-2.73854300	3.85498800
H	2.38337700	-3.76553700	2.47366300
C	4.29212500	-3.45879900	0.12036000
H	5.05211600	-2.67627200	0.11215800
H	4.68938200	-4.30187800	-0.45232700
H	4.16522500	-3.79815600	1.14831300
C	1.64821400	-4.46654700	-0.87469000
H	1.35553800	-4.81228200	0.12024200
H	2.20801500	-5.27309300	-1.35558500
H	0.74457600	-4.28446600	-1.45436700
C	3.29502300	-2.36440800	-2.43624200
H	2.49251200	-1.97552600	-3.05934200
H	3.74645100	-3.21406800	-2.95599700
H	4.06675700	-1.59811900	-2.33361300
Be	0.57922800	-1.03676700	-0.67213900

CDC-Be-Cyc

E_e = -2000.67595188 (Hartrees)

0 1

Si	2.73297400	-1.40748400	-1.55917600
Si	2.26209100	-3.13227100	0.90294900
N	-2.25941100	-1.53187900	-0.40883500
N	-3.06671800	0.49951200	-0.00067100
N	-0.08084000	2.26958000	-0.97859400
N	1.13992100	1.65640200	0.75824300
N	1.82326100	-1.88246700	-0.18781200
C	-0.55427600	0.04397100	0.03198500
C	-1.89769200	-0.23627800	-0.14820800
C	-1.19052400	-2.52461500	-0.51188800
H	-1.18340200	-2.94796400	-1.52199400
H	-1.40967000	-3.34520000	0.17796000
C	-3.08860800	1.81960700	0.63660400
H	-2.07436000	2.19516000	0.53699600
C	-3.39684900	1.69570100	2.12816400
H	-4.39430900	1.28681800	2.29165300
H	-3.34598900	2.67506000	2.60664000
H	-2.67358300	1.03725300	2.61030700
C	-4.01293800	2.80416800	-0.07699000
H	-3.87248200	2.76174500	-1.15661300
H	-3.79180800	3.81745600	0.26094800
H	-5.06312400	2.61113400	0.13395600
C	-4.15836100	-0.37662500	-0.10488500
C	-5.52671300	-0.19352500	0.01176400
H	-5.95932900	0.76915800	0.23347100
C	-6.35309300	-1.30619000	-0.16290200
H	-7.42422500	-1.18297400	-0.07554200
C	-5.82505600	-2.56318300	-0.44644700
H	-6.49223700	-3.40439000	-0.57972100
C	-4.44944700	-2.75621900	-0.55845100
H	-4.02622900	-3.72805700	-0.77093500
C	-3.63001200	-1.65397300	-0.37921200
C	0.08600200	1.26534600	-0.04262200
C	-0.92296300	2.17415500	-2.14974400
H	-1.27098200	1.14967200	-2.24233400
H	-0.34473400	2.43467500	-3.03631000
H	-1.78265900	2.84097800	-2.07578600
C	1.42670500	0.99269100	2.03978900
H	0.83080600	0.08386200	1.99243300
C	0.91970700	1.84602800	3.20036400
H	1.45654500	2.79250100	3.27427100
H	1.05378500	1.30706900	4.13889600
H	-0.14281300	2.06336400	3.08083500
C	2.88721500	0.58921500	2.17420700
H	3.17171700	-0.05273300	1.34651800
H	3.01689500	0.02920400	3.10099900
H	3.56010200	1.44523000	2.20900400
C	1.62496400	2.89038000	0.33753000
C	2.64235000	3.71281600	0.79950900
H	3.24632200	3.44581300	1.65181300
C	2.87109500	4.90853500	0.12018800
H	3.66127900	5.56291000	0.46271000
C	2.11029700	5.27434000	-0.98813100
H	2.31851100	6.20608000	-1.49619300
C	1.08027600	4.45749400	-1.45092500
H	0.48037300	4.74156800	-2.30434900
C	0.85219100	3.27388100	-0.77055300
C	1.65386700	-0.43263400	-2.76328800
H	0.72005300	-0.95022600	-2.99458000
H	2.19143200	-0.27924400	-3.70261400
H	1.40620600	0.55078800	-2.36358400
C	4.19599800	-0.28606100	-1.15605100
H	3.86320200	0.67267000	-0.75262500
H	4.77464300	-0.07931100	-2.06064700
H	4.87131100	-0.74027000	-0.42832400
C	3.41537500	-2.88650000	-2.51085800
H	4.09917500	-3.48370200	-1.90397700
H	3.96321700	-2.56079300	-3.39909200
H	2.60540100	-3.54325500	-2.83644500
C	4.10106400	-3.11335800	1.31870400
H	4.72035000	-3.27013300	0.43315800
H	4.33784700	-3.91011000	2.02872400
H	4.40090900	-2.16543500	1.76961700
C	1.30958000	-2.90906400	2.51783600
H	1.59431800	-1.98595000	3.02653500
H	1.50445600	-3.73806800	3.20291100
H	0.23098800	-2.87515700	2.34392900
C	1.84013200	-4.84740000	0.24713600
H	0.77578900	-4.91411800	0.01017500
H	2.07179000	-5.62700100	0.97794800
H	2.39565000	-5.06808500	-0.66641000
Be	0.26068500	-1.53142300	-0.16980500

CDP-BeCl2

E_e = -3046.86231824 (Hartrees)

0 1

C	-0.00437500	-0.72437400	-0.34776200
P	-1.45015400	0.09041100	-0.03470500
P	1.51035400	-0.02076800	-0.10477700
C	2.77853200	-0.91800200	-1.03112400
C	1.64587900	1.71248200	-0.65720400
C	2.12819800	0.01425100	1.61215700
C	-2.84171200	-1.06313600	-0.14569100
C	-1.55931300	0.85769900	1.61625800
C	-1.91659000	1.37099100	-1.24525700
C	-3.77067800	-1.22360400	0.87977800
C	-4.81537400	-2.12647500	0.73391300
C	-4.93627000	-2.87225200	-0.43191500
C	-4.01765500	-2.70546900	-1.46151100
C	-2.97914000	-1.79726800	-1.32619900
C	-1.80871600	2.21065700	1.84514000
C	-1.76662000	2.72226400	3.13685900
C	-1.48069400	1.88693100	4.20956100

C	-1.23638800	0.53572400	3.98814800
C	-1.27055400	0.02223700	2.70073800
C	-3.11703800	2.07456200	-1.11297300
C	-3.48767200	3.00922100	-2.06804400
C	-2.67020700	3.24091300	-3.17078800
C	-1.49374000	2.51949900	-3.32350100
C	-1.12405600	1.58107700	-2.36847700
C	1.82181000	-1.06635900	2.44045100
C	2.29848600	-1.10402200	3.74308700
C	3.07859900	-0.06334600	4.23410100
C	3.39310500	1.01226800	3.41201100
C	2.92561400	1.04936200	2.10415900
C	4.07072200	-1.08010200	-0.52830400
C	5.03916100	-1.71540200	-1.29301000
C	4.72436500	-2.19123100	-2.56133600
C	3.43811400	-2.03537600	-3.06297500
C	2.46615000	-1.40061400	-2.30260900
C	1.03516000	2.72445200	0.08585300
C	0.99756100	4.02539900	-0.39287000
C	1.58126800	4.33519700	-1.61574400
C	2.21563100	3.33957100	-2.34829900
C	2.24971200	2.03482200	-1.87254200
Be	-0.18853300	-2.48841900	-0.35979200
Cl	-0.63616200	-3.40409900	1.29918100
Cl	-0.01695600	-3.53249300	-1.97134400
H	-3.67346800	-0.66121600	1.79674800
H	-5.52656400	-2.25688800	1.53910100
H	-5.74255000	-3.58667600	-0.53632500
H	-4.09876400	-3.29108600	-2.36727800
H	0.58601800	2.49669400	1.04075000
H	0.51100900	4.79692700	0.18979300
H	1.54829700	5.34932000	-1.99207200
H	2.68518500	3.57661000	-3.29423500
H	2.73935300	1.26559300	-2.45287300
H	4.31733600	-0.72210100	0.46111600
H	6.03673300	-1.84704100	-0.89467400
H	5.47874200	-2.69473300	-3.15224200
H	3.18085300	-2.42657900	-4.03817200
H	1.45699400	-1.31047500	-2.67447000
H	1.20020100	-1.87289600	2.07492700
H	2.05267100	-1.94785100	4.37474000
H	3.44288200	-0.09083800	5.25315200
H	4.00380200	1.82359300	3.78682300
H	3.18400700	1.88557600	1.47018400
H	-3.77047500	1.88054000	-0.27255000
H	-4.41845900	3.55057100	-1.95837900
H	-2.96046300	3.97115600	-3.91515600
H	-0.86264300	2.68172400	-4.18734900
H	-0.22463100	0.99827900	-2.49167100
H	-2.01276600	2.87384800	1.01753600
H	-1.95343100	3.77556500	3.30244900
H	-1.44337800	2.28799500	5.21418000
H	-1.00464700	-0.11933500	4.81747100
H	-1.06539000	-1.02677400	2.52717700
H	-2.25996700	-1.68368100	-2.12503200

CDP

E_e = -2111.42109678 (Hartrees)

0 1

C	0.00332500	0.10428600	1.07492400
P	-1.48958900	0.02849700	0.41533600
P	1.47978600	0.06221300	0.37971800
C	2.76137800	-0.31748600	1.62155100
C	1.75865200	-1.17662300	-0.93797200
C	2.05457300	1.63981500	-0.36440000
C	-2.64090000	1.21547800	1.18661500
C	-1.65279900	0.37363600	-1.37543500
C	-2.30719500	-1.60028300	0.60728700
C	-3.78453600	1.68166200	0.53790700
C	-4.63466200	2.57908800	1.17298400
C	-4.34857600	3.01583400	2.46127200
C	-3.20529400	2.55986700	3.10957600
C	-2.35248000	1.66766900	2.47351800
C	-1.97500400	-0.61271300	-2.30524300
C	-1.91957600	-0.34030900	-3.66833000
C	-1.54023900	0.91809900	-4.11478800
C	-1.22329500	1.91240300	-3.19151600
C	-1.28108100	1.64199600	-1.83359100
C	-3.68936300	-1.77739400	0.54208500
C	-4.23882100	-3.04875400	0.64706600
C	-3.41150200	-4.15460100	0.81352600
C	-2.03377500	-3.98362500	0.88298600
C	-1.48540000	-2.71085400	0.78605700
C	1.46941400	2.81307200	0.11073400
C	1.85482500	4.04807600	-0.39256500
C	2.82709900	4.12314900	-1.38442400
C	3.41556700	2.95871500	-1.86399400
C	3.03450400	1.72346000	-1.35360900
C	4.12156600	-0.30236200	1.31186400
C	5.06372500	-0.61357300	2.28221200
C	4.65366000	-0.93970500	3.57161300
C	3.29994700	-0.95266700	3.88548600
C	2.35608600	-0.64248000	2.91304000
C	1.36401900	-0.91617500	-2.25200900
C	1.41035100	-1.91708400	-3.21265400
C	1.84840100	-3.19228100	-2.87476700
C	2.24116300	-3.46194800	-1.56823000
C	2.19652500	-2.46119500	-0.60683900
H	-4.00218900	1.36027400	-0.47227200
H	-5.51588900	2.94210600	0.65942100
H	-5.00985600	3.71645000	2.95511700
H	-2.97505300	2.90575500	4.10936100
H	1.00839500	0.06697900	-2.52593100
H	1.09484800	-1.69925800	-4.22480300
H	1.88306700	-3.97216300	-3.62467700
H	2.58529400	-4.45224000	-1.29785800
H	2.50432300	-2.67771900	0.40771700
H	4.44919900	-0.04847200	0.31265600
H	6.11759000	-0.59984100	2.03493700
H	5.38938400	-1.18062700	4.32847700
H	2.97800100	-1.20403800	4.88821300
H	1.29454500	-0.64239900	3.12746600
H	0.69987900	2.73453100	0.86896500
H	1.39376900	4.95204100	-0.01486900
H	3.12335100	5.08477500	-1.78381800
H	4.16893000	3.01110400	-2.63986000
H	3.48929000	0.82336800	-1.74447100
H	-4.34141300	-0.92396500	0.41671300
H	-5.31296700	-3.17663500	0.60223000
H	-3.84115600	-5.14494600	0.89538600
H	-1.38589800	-4.84059400	1.01706200
H	-0.41666400	-2.55679800	0.85569900
H	-2.25284600	-1.60138400	-1.96840200
H	-2.16412900	-1.11842700	-4.38017500
H	-1.49110300	1.12740400	-5.17572600
H	-0.92484800	2.89579800	-3.53146200
H	-1.01669600	2.41201200	-1.12196000
H	-1.44382500	1.32110200	2.94942100

CDC

E_e = -1112.81955939 (Hartrees)

0 1

N	-1.64281700	-0.95567800	0.84396200
N	-2.41182400	0.70124900	-0.41839000
N	1.64249300	-0.95550300	-0.84381400
N	2.41211600	0.70112900	0.41856800
C	0.00005100	0.69059600	0.00049100
C	-1.23035100	0.16432500	0.10764000
C	-0.76675200	-1.75273000	1.66111700
H	-0.49833400	-2.69620400	1.17809600
H	-1.24996000	-1.97454400	2.61405100
H	0.14278600	-1.18554700	1.84725500
C	-2.39824000	1.89659300	-1.25344900
H	-1.34109900	2.16743700	-1.28498600
C	-2.86246600	1.59168500	-2.67564700
H	-2.25453200	0.79837000	-3.11239400

H	-2.76316600	2.48131800	-3.29964700
H	-3.90543900	1.27433500	-2.70544600
C	-3.16375200	3.04543000	-0.60081400
H	-4.22977100	2.83411000	-0.51464900
H	-3.04837700	3.95250400	-1.19629400
H	-2.77295000	3.23915600	0.39842800
C	-3.50713100	-0.04541700	-0.01828400
C	-4.86556800	0.06680200	-0.26780300
H	-5.26532800	0.86001300	-0.88068200
C	-5.72116700	-0.88256800	0.30189300
H	-6.78447300	-0.80851900	0.11646900
C	-5.23219100	-1.91275700	1.09432600
H	-5.91615100	-2.63460400	1.52007600
C	-3.86153200	-2.03443600	1.34674200
H	-3.47736700	-2.84228700	1.95451500
C	-3.01696100	-1.09503700	0.78490000
C	1.23041100	0.16435300	-0.10709800
C	0.76554400	-1.75227400	-1.66029900
H	0.49153500	-2.69262600	-1.17433600
H	1.25086500	-1.97992100	-2.61071000
H	-0.14109800	-1.18209600	-1.85164900
C	2.39893100	1.89650800	1.25358200
H	1.34184000	2.16752800	1.28534400
C	2.86340900	1.59151300	2.67568200
H	2.25524500	0.79848500	3.11262900
H	2.76466700	2.48122200	3.29966200
H	3.90625500	1.27370900	2.70519400
C	3.16448700	3.04521700	0.60077600
H	4.23048900	2.83384200	0.51456400
H	3.04919700	3.95235900	1.19616900
H	2.77364200	3.23886800	-0.39846500
C	3.50718200	-0.04567000	0.01805300
C	4.86569100	0.06631200	0.26729500
H	5.26568500	0.85942300	0.88015300
C	5.72103200	-0.88315800	-0.30259900
H	6.78438700	-0.80928400	-0.11739300
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C	3.86097300	-2.03474900	-1.34700300
H	3.47660100	-2.84265100	-1.95457600
C	3.01663600	-1.09518300	-0.78507500

BeCl2

E_e = -935.359726606 (Hartrees)

0 1

Be	0.00000000	0.00000000	0.00000000
Cl	0.00000000	0.00000000	1.80403200
Cl	0.00000000	0.00000000	-1.80403200

BeCl[N(SiMe3)2]

E_e = -1348.69998457 (Hartrees)

0 1

Cl	-3.48181100	0.00027900	0.00000300
Si	0.63040100	-1.55461700	0.00375200
Si	0.63065400	1.55451900	-0.00375600
N	-0.15853100	0.00001500	-0.00001400
C	-0.65120400	2.84023600	-0.48941200
H	-1.04141600	2.66191600	-1.49426100
H	-0.21064000	3.84008900	-0.47974500
H	-1.50002300	2.85776700	0.19998700
C	2.04544400	1.59268900	-1.23473100
H	2.83426300	0.88622600	-0.96849400
H	2.49485600	2.58833600	-1.26494500
H	1.70197800	1.34795800	-2.24165900
C	1.28885800	1.97654200	1.70128600
H	0.48536000	1.96393900	2.44131600
H	1.73606700	2.97384000	1.71007400
H	2.05094600	1.26680500	2.02662900
C	2.04498900	-1.59308400	1.23494800
H	2.83396000	-0.88673300	0.96887100
H	2.49423900	-2.58880400	1.26519200
H	1.70139700	-1.34834100	2.24182900
C	-0.65174500	-2.84015100	0.48913800
H	-1.04209200	-2.66183100	1.49393500
H	-0.21133000	-3.84007100	0.47948800
H	-1.50045600	-2.85752100	-0.20039800
C	1.28878300	-1.97666200	-1.70121400
H	0.48538600	-1.96391300	-2.44135200
H	1.73584600	-2.97402500	-1.70997900
H	2.05101900	-1.26702300	-2.02642700
Be	-1.66109700	0.00012100	-0.00001000

Quantum Theory of Atoms in Molecules (QTAIM)

CDC-BeCl[N(SiMe$_3$)$_2$]

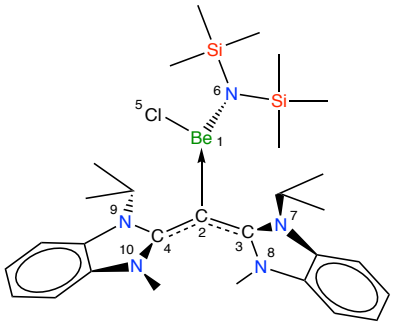

Table S4: QTAIM calculated properties for CDC-BeCl[N(SiMe$_3$)$_2$]. All values are reported at the bond critical point (BCP).

Bond	Bond ρ	$\nabla^2\rho$	Delocalization Index	Bond Ellipticity
Be(1)-C(2)	0.077	0.277	0.175	0.089
Be(1)-Cl(5)	0.060	0.252	0.180	0.148
Be(1)-N(6)	0.098	0.589	0.239	0.041
C(2)-C(4)	0.304	-0.822	1.284	0.192
C(2)-C(3)	0.308	-0.842	1.324	0.219
C(4)-N(10)	0.311	-0.949	0.994	0.171
C(4)-N(9)	0.316	-0.992	1.014	0.197
C(3)-N(7)	0.313	-0.993	1.006	0.193
C(3)-N(8)	0.308	-0.940	0.985	0.172

CDC-Be-Cyc

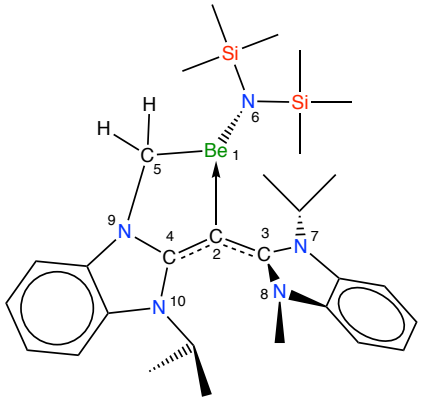

Table S5: QTAIM calculated properties for CDC-Be-Cyc. All values are reported at the bond critical point (BCP).

Bond	Bond ρ	$\nabla^2\rho$	Delocalization Index	Bond Ellipticity
Be(1)-C(5)	0.776	0.287	0.193	0.148
Be(1)-C(2)	0.070	0.296	0.173	0.170
Be(1)-N(6)	0.094	0.558	0.228	0.107
C(2)-C(3)	0.314	-0.910	1.313	0.152
C(2)-C(4)	0.311	-0.872	1.343	0.198
N(9)-C(5)	0.244	-0.519	0.951	0.186
C(4)-N(9)	0.332	-1.093	1.061	0.212
C(4)-N(10)	0.312	-0.964	1.021	0.175
C(3)-N(8)	0.315	-0.975	1.021	0.185
C(3)-N(7)	0.319	-1.006	1.043	0.199

Geometry and NBO analysis: Natural Population Analysis (NPA) and Wiberg Bond Indices (WBI)

CDC-BeCl[N(SiMe$_3$)$_2$]

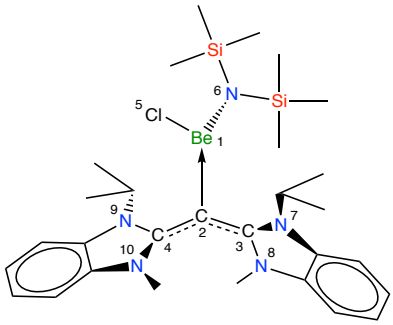

Table S6: CDC-BeCl[N(SiMe$_3$)$_2$] bond distances (Å), angles (˚), WBI in brackets, and NPA charges.

	Be(1)-C(2)	Be(1)-Cl(5)	Be(1)-N(6)	C(2)-C(3)	C(2)-C(4)	C(4)-C(2)-C(3)
B3LYP-D3(BJ)/def2-TZVP	1.779(0.196)	1.983(0.312)	1.594(0.164)	1.382(1.415)	1.391(1.369)	119.72
B3LYP-D3(BJ)/def2-SVP	1.772(0.190)	1.998(0.290)	1.594(0.177)	1.390(1.407)	1.397(1.367)	119.63
M06-2X/def2-SVP	1.776(0.181)	1.994(0.289)	1.599(0.170)	1.390(1.399)	1.398(1.353)	118.63
			NPA Charges			
	Be(1)	C(2)	C(3)	C(4)	N(6)	Cl(5)
B3LYP-D3(BJ)/def2-SVP	1.577	-0.851	0.476	0.496	-1.914	-0.734
M06-2X/def2-SVP	1.590	-0.885	0.502	0.524	-1.937	-0.748

CDC-Be-Cyc

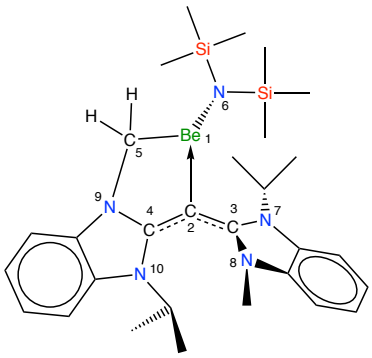

Table S7: CDC-Be-Cyc bond distances (Å), angles (˚), WBI in brackets, and NPA charges.

	Be(1)-C(2)	Be(1)-C(5)	Be(1)-N(6)	C(2)-C(3)	C(2)-C(4)	C(4)-C(2)-C(3)
B3LYP(D3)/def2-TZVP	1.785(0.184)	1.792(0.254)	1.602(0.165)	1.381(1.380)	1.384(1.418)	128.46
B3LYP(D3)/def2-SVP	1.786(0.179)	1.794(0.255)	1.599(0.174)	1.389(1.337)	1.392(1.424)	129.33
M06-2X/def2-SVP	1.789(0.174)	1.804(0.248)	1.607(0.168)	1.390(1.374)	1.394(1.405)	130.07
			NPA Charges			
	Be(1)	C(5)	C(2)	C(3)	C(4)	N(6)
B3LYP(D3)/def2-SVP	1.612	-0.889	-0.864	0.491	0.467	-1.905
M06-2X/def2-SVP	1.624	-0.900	-0.899	0.517	0.494	-1.926

Binding Energies

Table S8: Ligand binding energies (ΔG) kJ mol^{-1}computed at the B3LYP-D3(BJ)/def2-TZVP level of theory.

	Binding Energy
CDP-$BeCl_2$	151.3
CDC-$BeCl_2$	145.1
CDC-BeCl[$N(SiMe_3)_2$]	93.2

Vibrational Frequencies

Figure S19: Calculated vibrational frequencies at the B3LYP-D3(BJ)/def2-TZVP level of theory.

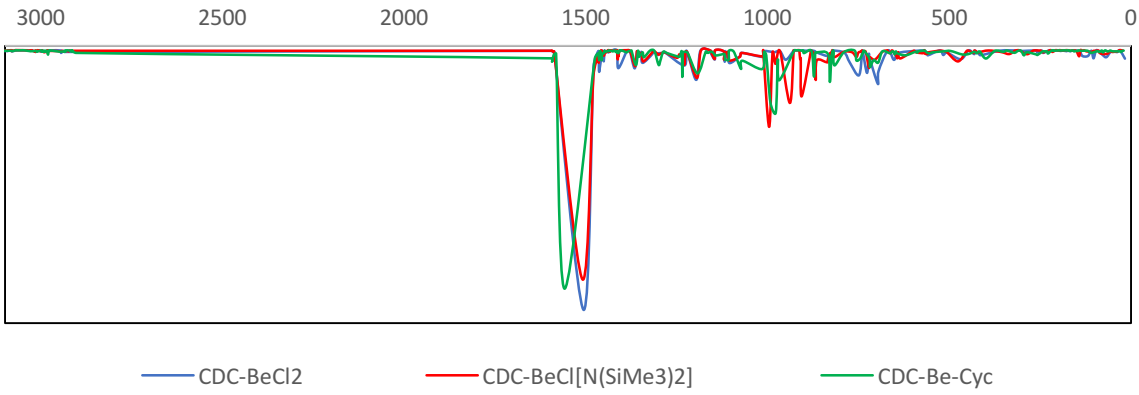

Table S9. Crystallographic details for **1-3**.

	1	**2**	**3**
CCDC code	1880508	1880509	1880510
Chemical formula	$C_{23}H_{28}BeCl_2N_4$	$C_{36}H_{54}BeClN_5Si_2$	$C_{77}H_{133}Be_2K_2N_{12}Si_8$
Formula weight (g/mol)	440.40	657.48	1547.89
Temperature (K)	100(2)	100(2)	100(2)
Crystal size (mm)	0.089 x 0.099 x 0.183	0.228 x 0.281 x 0.304	0.067 x 0.103 x 0.492
Crystal system	monoclinic	monoclinic	triclinic
Space group	C2/c	$P2_1/n$	P-1
a (Å)	15.654(2)	9.0264(6)	9.7119(12)
b (Å)	8.9806(13)	24.8747(19)	13.7589(18)
c (Å)	16.425(3)	16.8657(12)	17.563(2)
α (°)			102.983(3)
β (°)	106.399(5)	90.557(2)	90.576(3)
γ (°)			90.238(4)
V ($Å^3$)	2215.1(6)	3786.7(5)	2286.7(5)
Z	4	4	1
Density (g/cm^3)	1.321	1.153	1.124
μ (mm^{-1})	0.311	0.195	0.253
Theta range (°)	2.58 to 26.39	1.46 to 28.39	1.52 to 26.45
Reflections collected	8525	45014	33877
Independent reflections	2278 [R_{int} = 0.0520]	9419 [R_{int} = 0.0506]	9381 [R_{int} = 0.1300]
Goodness of fit on F^2	1.005	1.018	0.957
R1 [I>2σ(I)]	0.0503	0.0346	0.0561
wR2 [all data]	0.1204	0.1061	0.1472

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