CHEMISTRY
A European Journal

Supporting Information

Isolation of Cyclic(Alkyl)(Amino) Carbene–Bismuthinidene Mediated by a Beryllium(0) Complex

Guocang Wang,[a] Lucas A. Freeman,[a] Diane A. Dickie,[a] Réka Mokrai,[b] Zoltán Benkő,*[b] and Robert J. Gilliard, Jr.*[a]

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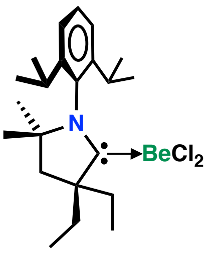
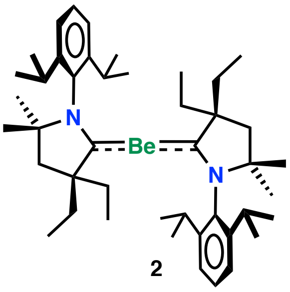
General Procedures: All manipulations were carried out under an atmosphere of purified nitrogen or argon using standard Schlenk techniques or in a MBRAUN LABmaster glovebox equipped with a −37 °C freezer. All reaction solvents (toluene and hexane) were distilled over sodium/benzophenone. Deuterated solvents were purchased from Acros Organics and Cambridge Isotope Laboratories and dried over sodium/benzophenone or Na/K alloy. Glassware was oven-dried at 190 °C overnight. The NMR spectra were recorded at the room temperature on a Bruker Echo 600 MHz (^{1}H: 600.13 MHz and ^{9}Be: 64.476 MHz) and 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, Toluene-d_8, δ 2.08; ^{13}C; C_6D_6, δ 128.07, Toluene-d_8, δ 20.43). ^{9}Be NMR signals were referenced to beryllium chloride diethyl ether [$BeCl_2(OEt_2)$ - δ 1.15 ppm].[1] Single crystal X-ray diffraction data were collected on a Bruker Kappa APEXII Duo system equipped with a fine-focus sealed tube (Mo K_α, $\lambda = 0.71073$ Å) and a graphite monochromator for **1-3**. The structures were solved and refined using the Bruker SHELXTL Software Package[2] within OLEX2.[3] Elemental analyses were performed at Robertson Microlit Laboratories, Ledgewood, NJ, USA. $[PhBiCl_2(THF)]_n$ and ^{Et2}CAACBi(Ph)Cl_2 were prepared using literature procedure.[4-5] Note: 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



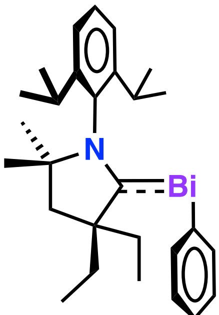
1

Synthesis of ^{Et2}CAACBeCl$_2$ (1). A suspension of $BeCl_2(Et_2O)_2$ (1.47 g, 6.45 mmol) in toluene (30 mL) was added a solution of ^{Et2}CAAC (1.91 g, 6.1 mmol) in toluene (30 mL) and stirred overnight at room temperature. The reaction mixture was filtered and the filtrate dried *in vacuo*. The resulting white solid was washed with hexane (20 mL) and recrystallized from toluene at –37 °C, affording ^{Et2}CAACBeCl$_2$ as a colorless crystalline solid (2.30 g, 84.5% yield). Block-like single crystals suitable for X-ray diffraction studies were obtained from a saturated toluene solution at –37 °C. ^{9}Be NMR (C_6D_6, 84.329 MHz): δ = 13.74 (s). ^{1}H NMR (C_6D_6, 600.13 MHz): δ = 7.09 (t, J_{HH} = 7.7 Hz, 1H, ***CH****para*), 6.99 (d, J_{HH} = 7.7 Hz, 2H, ***CH****para*), 2.73 (sept., J_{HH} = 6.6 Hz, 2H, ***CH****(CH$_3$)$_2$*), 2.07 (m, 2H, ***CH$_2$****CH$_3$*), 1.86 (m, 2H, ***CH$_2$****CH$_3$*), 1.51 (d, J_{HH} = 6.6 Hz, 6H, *CH(**CH$_3$**)$_2$*), 1.39 (s, 2H, ***CH$_2$***), 1.33 (s, 2H, ***CH$_2$***), 1.08 (d, J_{HH} = 6.6 Hz, 6H, *CH(**CH$_3$**)$_2$*), 0.87 (t, 6H, J_{HH} = 7.4 Hz, *CH$_2$**CH$_3$***), 0.87 (s, 6H, *C(**CH$_3$**)$_2$*). ^{13}C{^{1}H} NMR (C_6D_6, 201.193 MHz): δ = 241.8 (***C****q, carbene*), 145.5 (***C****q*), 133.5 (***C****q*), 130.3 (***C****Hpara*), 128.3 (***C****q*), 125.6 (***C****Hmeta*), 82.3 (***C****q*), 63.7 (***C****q*), 41.4 (***CH$_2$***), 30.8 (***CH$_2$****CH$_3$*), 29.2 (***CH****(CH$_3$)$_2$*), 27.2 (*CH(**CH$_3$**)$_2$*), 24.8 (***CH$_3$***), 10.0 (*CH$_2$**CH$_3$***). Compound **1** is not soluble in hexane but soluble in benzene and toluene.



2

Synthesis of Be(^{Et2}CAAC)$_2$ (2). A suspension of ^{Et2}CAACBeCl$_2$ (1.556 g, 3.95 mmol) in toluene (30 mL) was added to one equivalent of ^{Et2}CAAC (1.24 g, 3.95 mmol) and KC_8 (1.18 g, 8.7 mmol) and was stirred for 5 h at room temperature. The suspension was filtered over a pad of Celite and the pad was washed with toluene until the filtrate became colorless. The purple filtrate was reduced *in vacuo*. Compound **2** was isolated as a purple solid after filtration (1.99 g, 79% yield). Purple single crystals suitable for X-ray diffraction studies were obtained from a saturated toluene solution at –37 °C. ^{1}H NMR (C_6D_6, 600.13 MHz): δ = 7.18 (t, J_{HH} = 9.6 Hz, 2H, ***CH****para*), 7.12 (d, J_{HH} = 9.6 Hz, 4H, ***CH****para*), 3.40 (sept., J_{HH} = 6.8 Hz, 4H, ***CH****(CH$_3$)$_2$*), 1.77 (br s, 4H, ***CH$_2$***), 1.55 (d, J_{HH} = 6.8 Hz, 12H, *CH(**CH$_3$**)$_2$*), 1.30 (s, 4H, ***CH$_2$****CH$_3$*), 1.22 (d, J_{HH} = 6.8 Hz, 12H, *CH(**CH$_3$**)$_2$*), 1.22 (s, 12H, *C(**CH$_3$**)$_2$*), 0.93 (t, 12H, J_{HH} = 7.1 Hz, *CH$_2$**CH$_3$***), 0.88 (br s, 4H, ***CH$_2$****CH$_3$*). ^{13}C{^{1}H} NMR (C_6D_6, 201.193 MHz): δ = 190.8 (***C****q, carbene*), 150.1 (***C****q*), 139.9 (***C****q*), 128.3 (***C****Hpara*), 127.5 (***C****q*), 125.8 (***C****Hmeta*), 69.7 (***C****q*), 54.9 (***C****q*), 46.7 (***CH***$_2$), 36.3 (***CH***$_2$*CH*$_3$), 30.5 (***CH***$_3$), 28.5 (***CH***(*CH*$_3$)$_2$), 25.8 (*CH*(***CH***$_3$)$_2$), 11.4 (*CH*$_2$***CH***$_3$). UV-vis: λ_{max}: 576 nm. Compound **2** is soluble in hexane, diethyl ether, benzene and toluene.



3

Synthesis of ^{Et2}CAACBiPh (3). To a purple solution of Be(^{Et2}CAAC)$_2$ (322 mg, 0.506 mmol) in toluene (10 mL) was added a yellow suspension of ^{Et2}CAACBi(Ph)Cl$_2$ (339 mg, 0.506 mmol) in toluene (5 mL) or a solution PhBiCl$_2$(THF) (217 mg, 0.506 mmol) in THF (2 mL) at –37 °C. The reaction mixture was stirred at –37 °C for 30 min. The black solid was filtered off at –37 °C to give a dark-red solution. The solvent was removed and the red residue was extracted with hexane (3 mL) at 0 °C. Dark red crystals suitable for X-ray diffraction studies were obtained from a saturated hexanes solution at –37 °C (30.0 mg, 10% yield). In some cases, a crop of colorless ^{Et2}CAAC crystals were isolated first and the solution was transferred back to the freezer before isolating **3**. m.p.: decomposed at 100 °C. UV-vis: λ_{max}: 516 nm. ^{1}H NMR (Toluene-*d*$_8$, 800.13 MHz, 273 K): δ = 8.91 (d, J = 8Hz, 2H), 7.20-7.10 (m, 6H), 3.11 (br s, 2H, ***CH***(*CH*$_3$)$_2$), 1.75 (br s, 2H, ***CH***$_2$*CH*$_3$), 1.63 (br s, 2H, ***CH***$_2$*CH*$_3$), 1.52 (br s, 2H, ***CH***$_2$), 1.24 (d, 6H, *CH*(***CH***$_3$)$_2$), 1.07 (br s, 12H, *CH*(***CH***$_3$)$_2$ and *C*(***CH***$_3$)$_2$), 1.0 (br t, 6H, *CH*$_2$***CH***$_3$). ^{13}C{^{1}H} NMR (Toluene-*d*$_8$, 201.193 MHz, 273 K): δ = 190 (***C****q, carbene*). Compound **3** is highly soluble in hexane, benzene and toluene. It is stable for weeks in the solid-state but not in solution, decomposing to form free ligand and bismuth metal. However, it may be handled at low temperature. Due to the thermal instability of **3** in solution, even at 0 °C, it is currently impossible to acquire pure NMR data. Therefore, ^{1}H and ^{13}C data contain free ^{Et2}CAAC. For ^{1}H NMR, a sample was prepared at –37 °C using pure crystals of compound **3**, and the data were collected immediately at 0 °C (Figure S6). Due to the time required for ^{13}C NMR, the peaks were assigned by essentially running the reaction in the NMR tube and immediately collecting the data (Figure S7). Anal. Calcd. for $C_{28}H_{40}BiN$ crystals: C, 56.09; H, 6.72; N, 2.34%. Found: C, 56.97; H, 6.71; N, 2.33%.

Figure S1. ^{1}H NMR spectrum (600.13 MHz, C_6D_6, 298 K) of complex **1**.

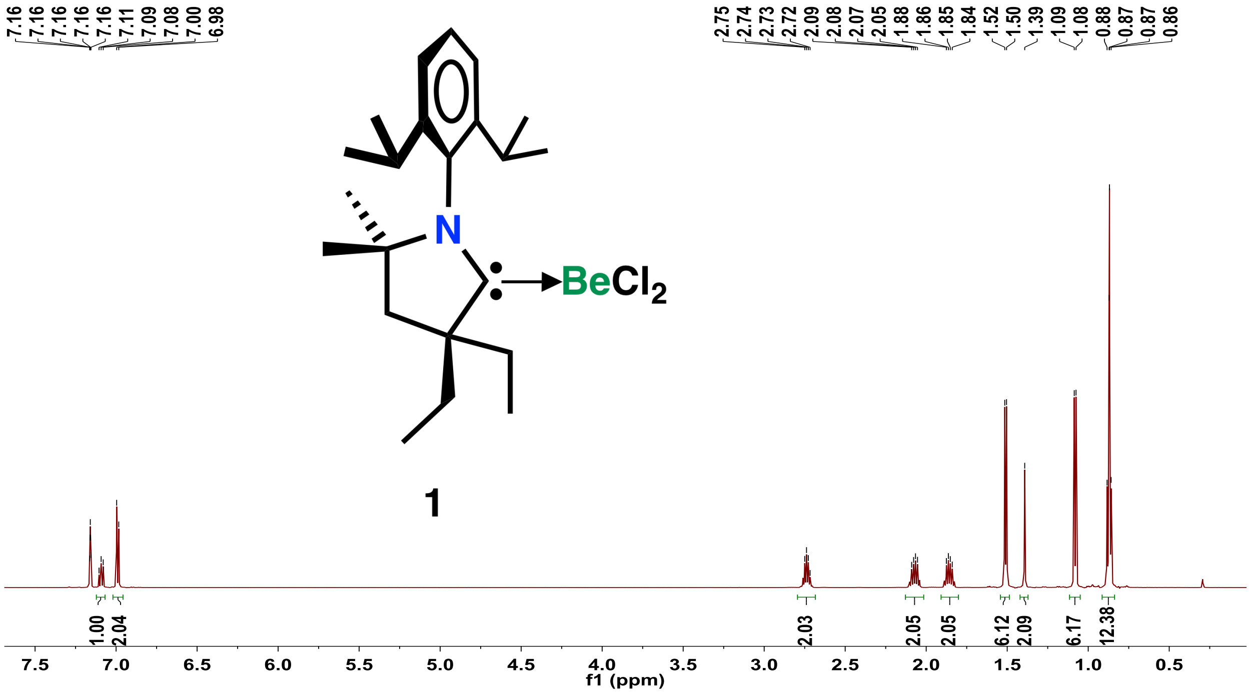


Figure S2. $^{13}C\{^1H\}$ NMR spectrum (201.193 MHz, C_6D_6, 298 K) of complex **1**.

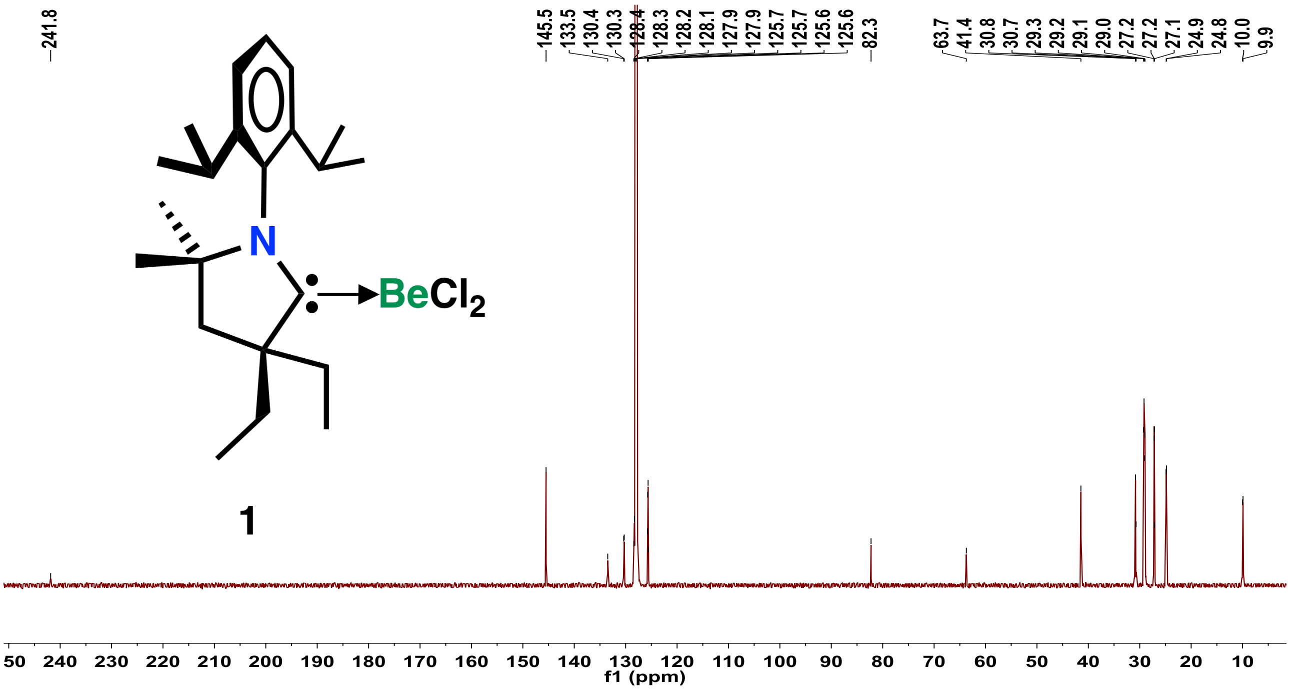


Figure S3. ^{9}Be NMR spectrum (64.476 MHz, C_6D_6, 298 K) of complex **1**.

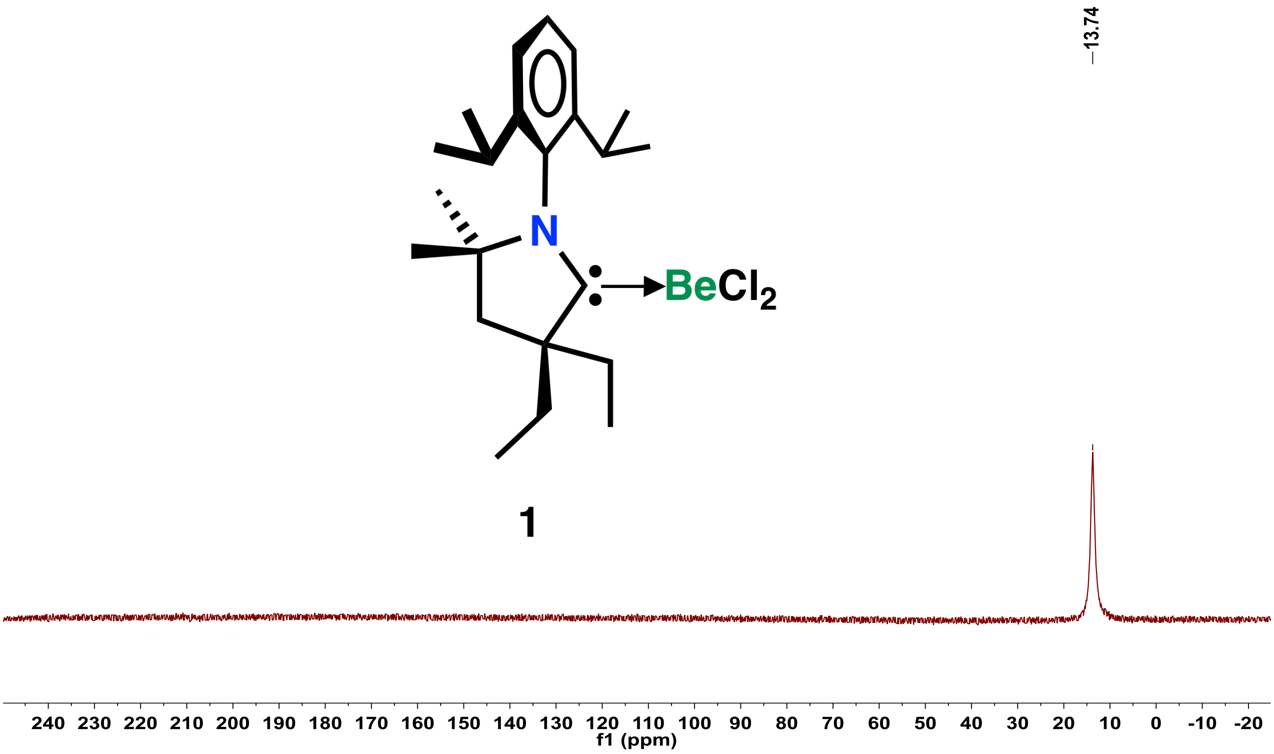


Figure S4. ^{1}H NMR spectrum (800.13 MHz, C_6D_6, 298 K) of complex **2**.

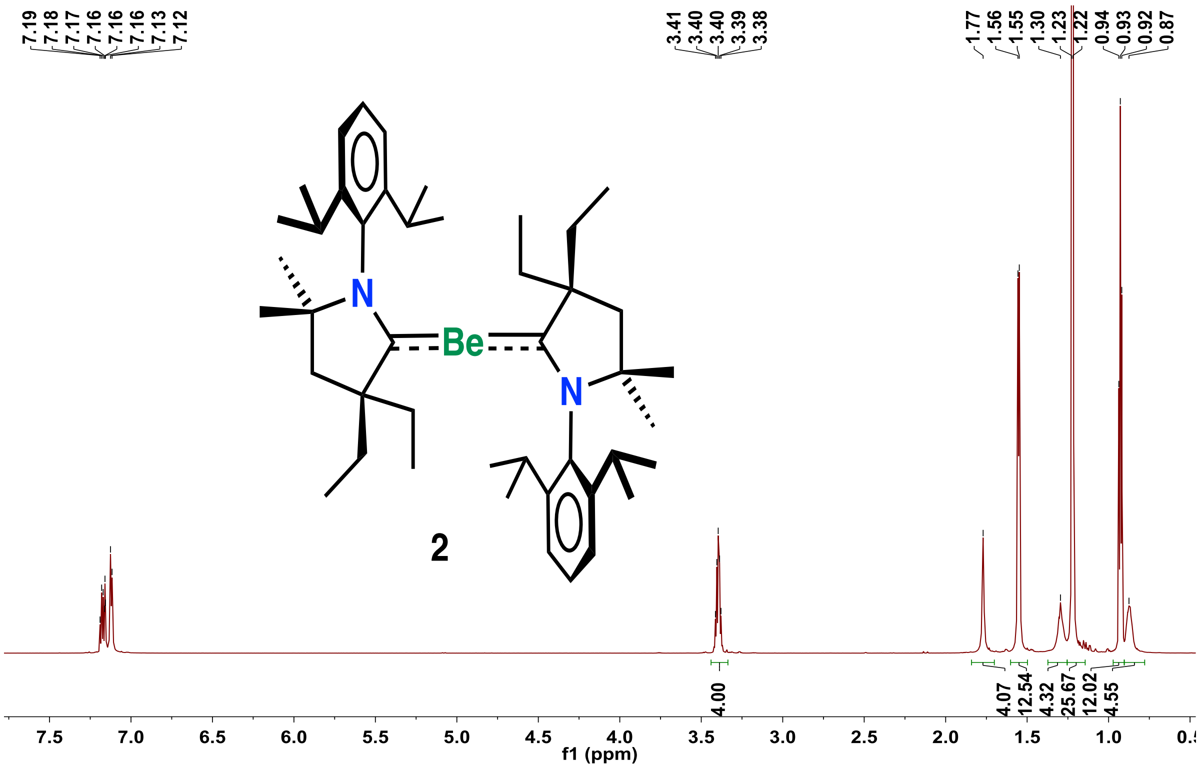


Figure S5. $^{13}C\{^{1}H\}$ NMR spectrum (201.193 MHz, C_6D_6, 298 K) of complex **2**.

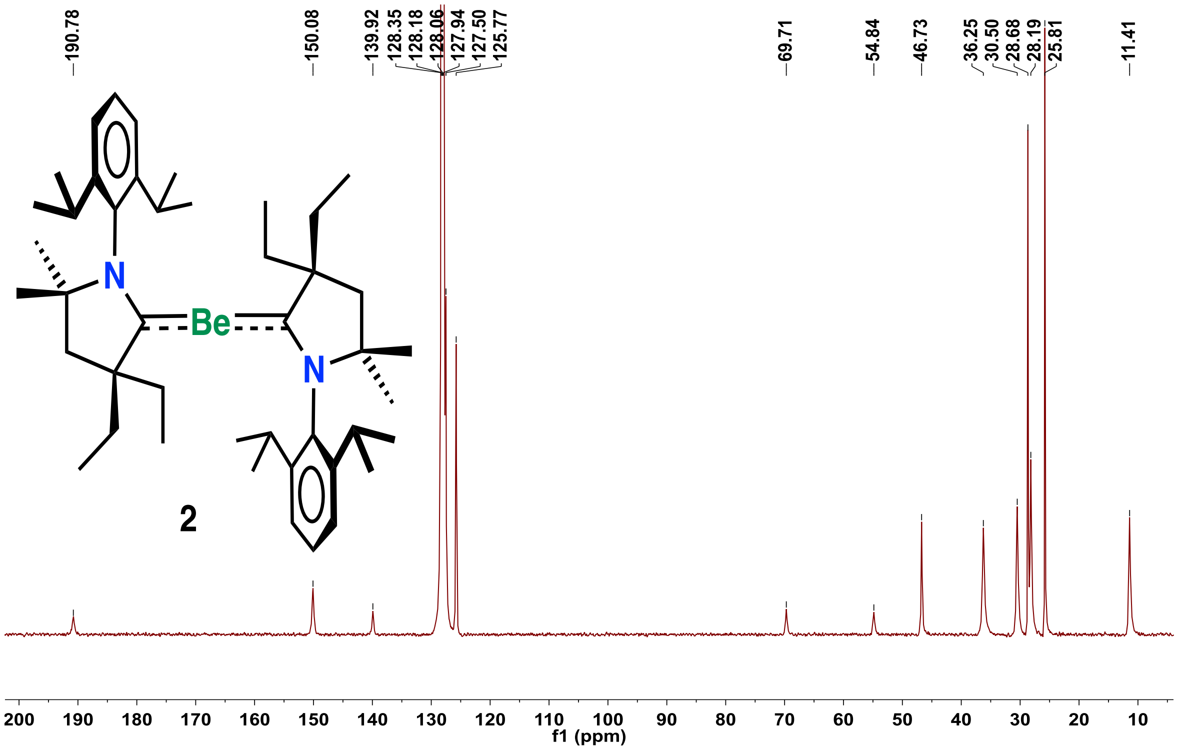


Figure S6. ^{1}H NMR spectrum (800.13 MHz, Toluene-d_8, 273 K) of complex **3**.

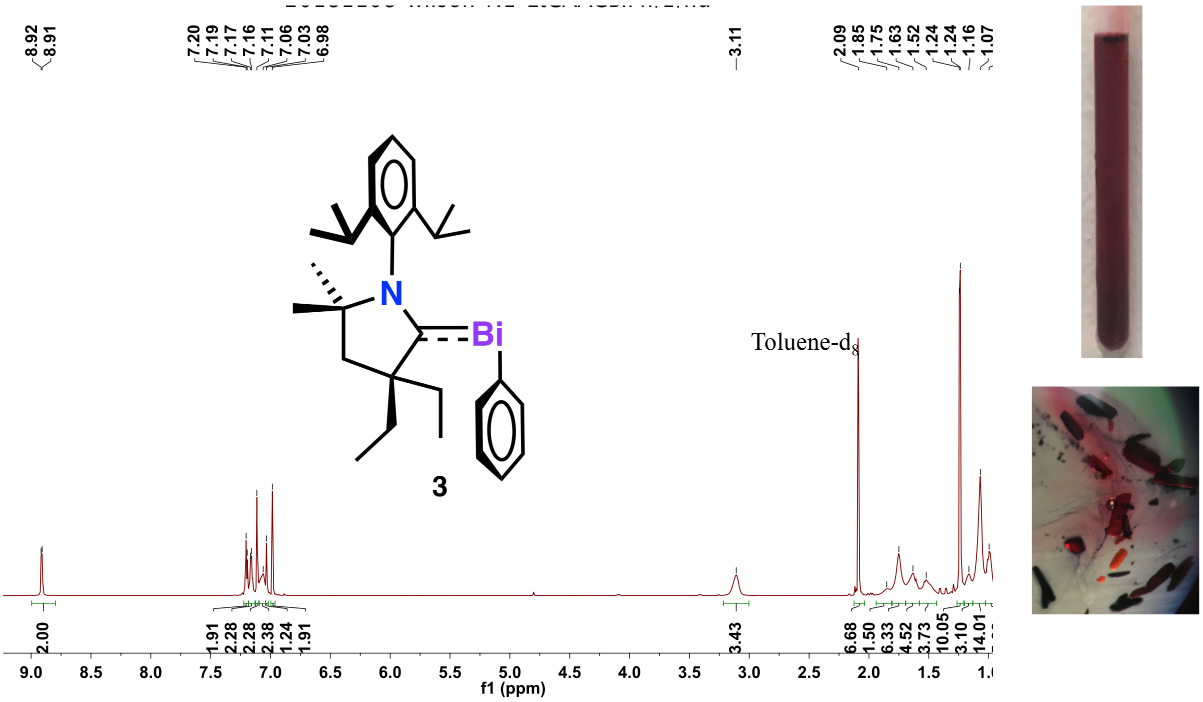


Figure S6a. ^{1}H NMR spectrum (800.13 MHz, Toluene-d_8, 273 K) of complex **3** (expanded to show selected peaks).

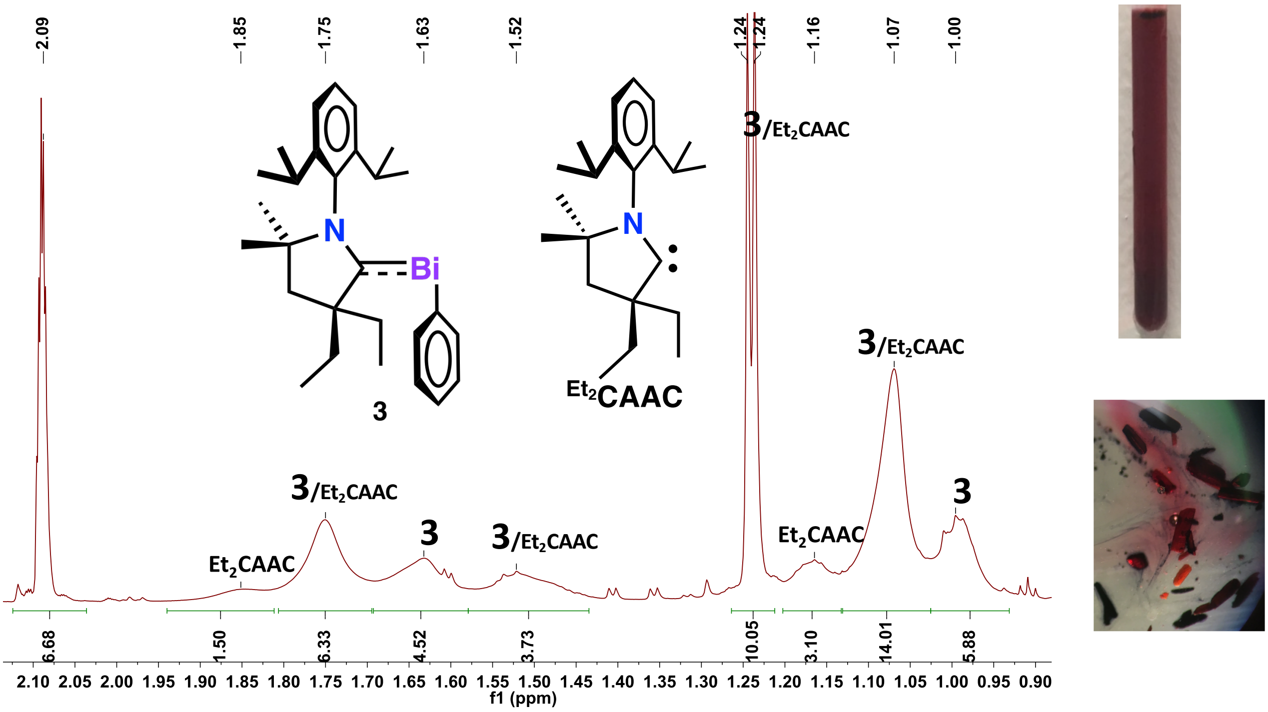


Figure S6b. ^{1}H NMR spectrum (800.13 MHz, 273 K, Toluene-d_8) of complex **3** showing decomposition to pure free ^{Et2}CAAC over time.

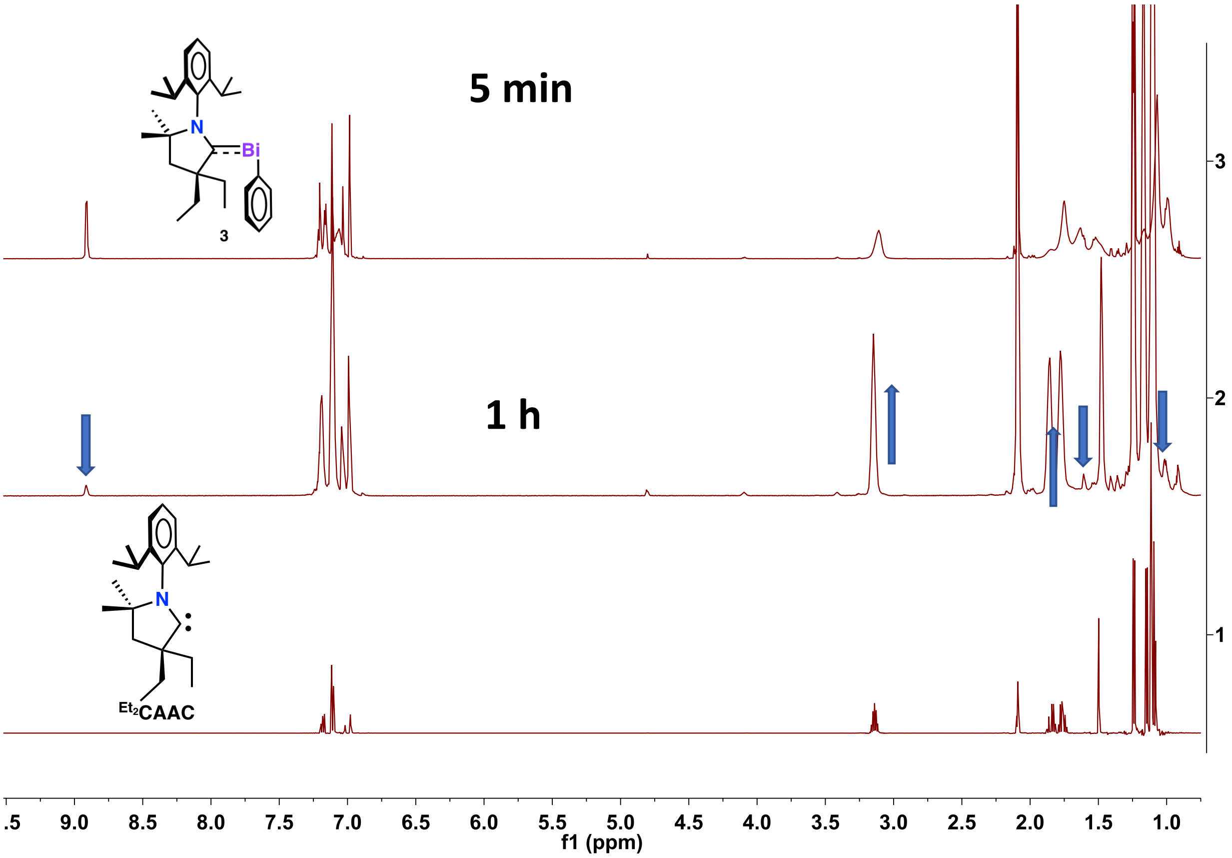
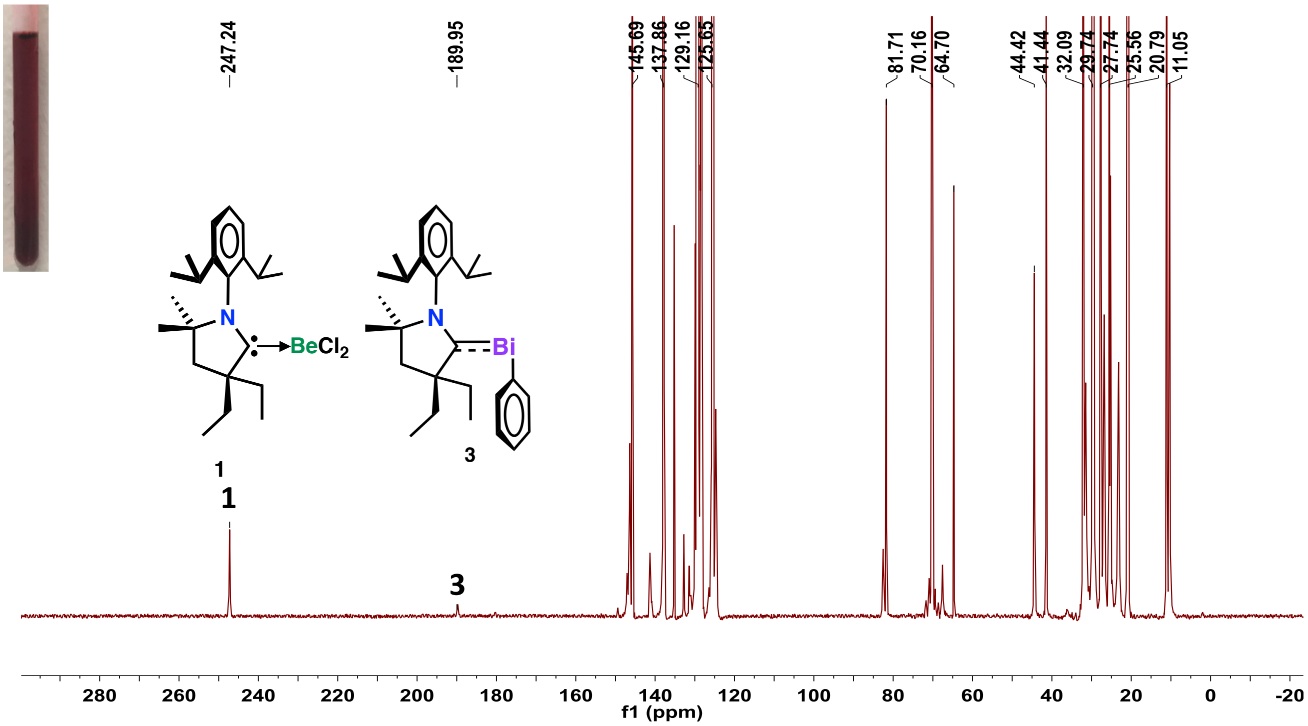


Figure S7. ^{13}C NMR spectrum (201.193MHz, Toluene-d_8, 273 K) of the reaction of **2** with PhBiCl$_2$(THF) in Toluene-d_8.



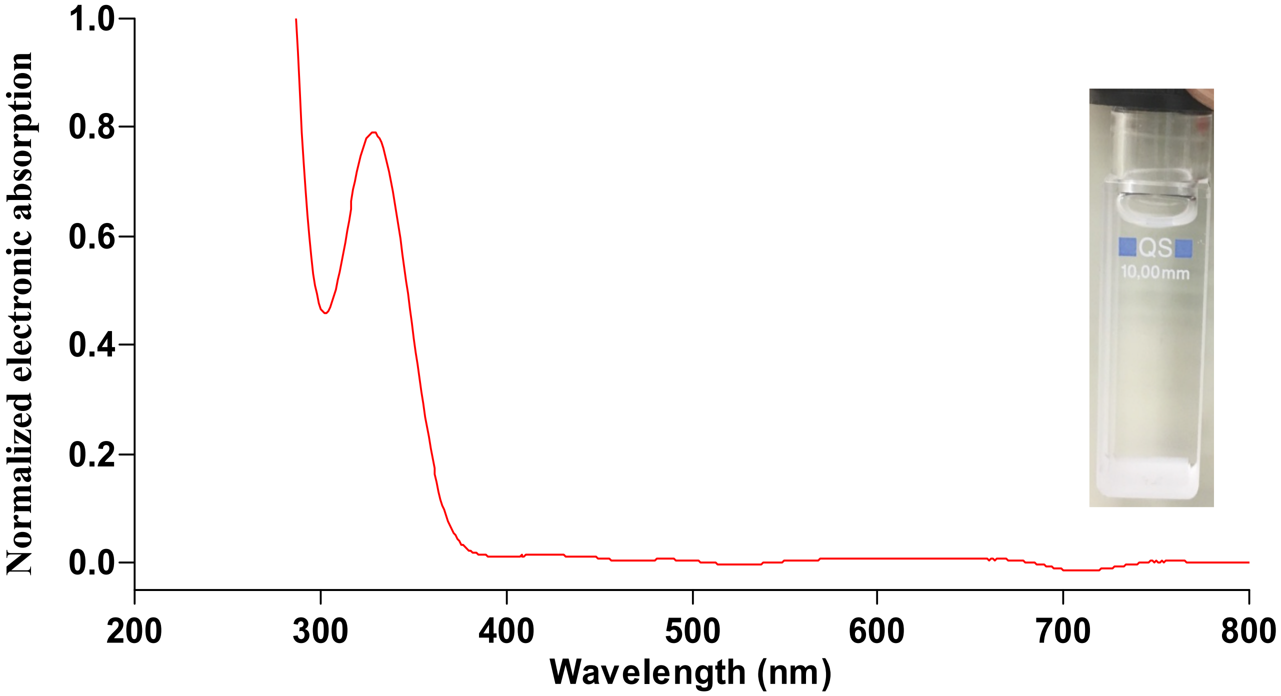


Figure S8. Normalized electronic absorption spectrum of free ^{Et2}CAAC in hexane. λ = 329 nm.

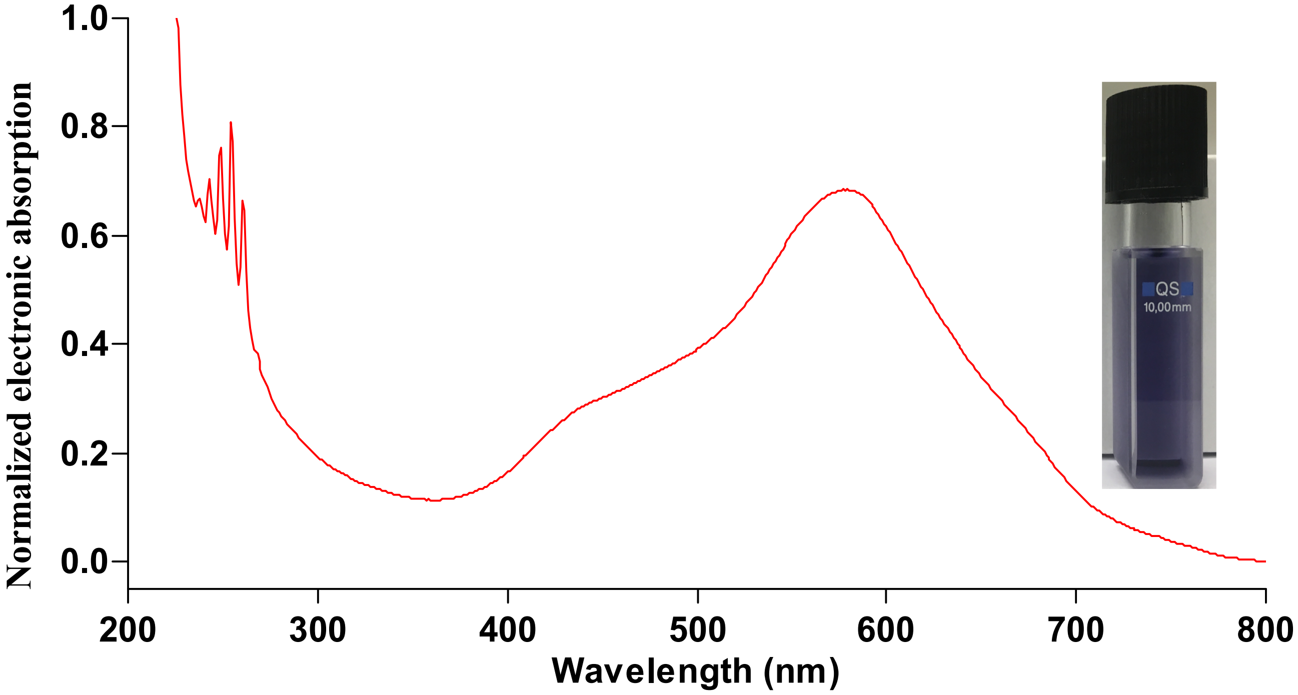


Figure S9. Normalized electronic absorption spectrum of compound **2** in hexane. λ = 576 nm.

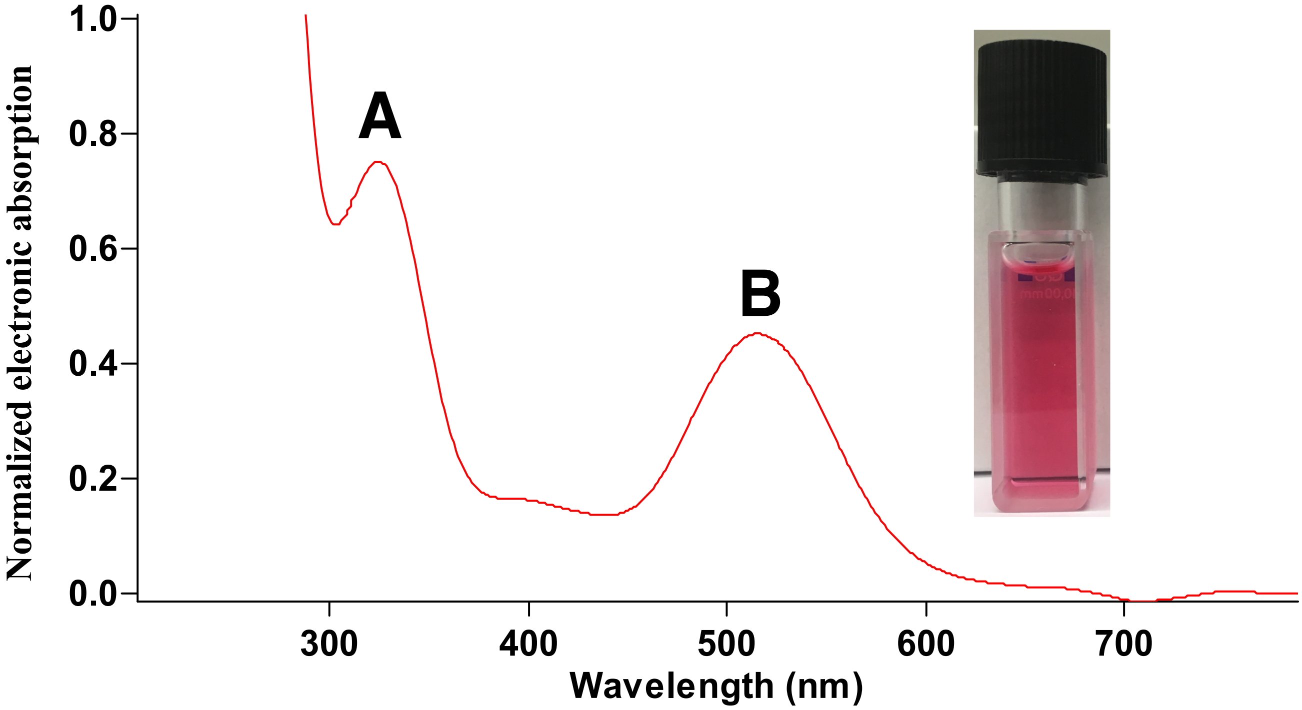


Figure S10. Normalized electronic absorption spectrum of compound **3** in hexane. Transition **A**, λ = 324 nm. Transition **B**, λ = 516 nm.

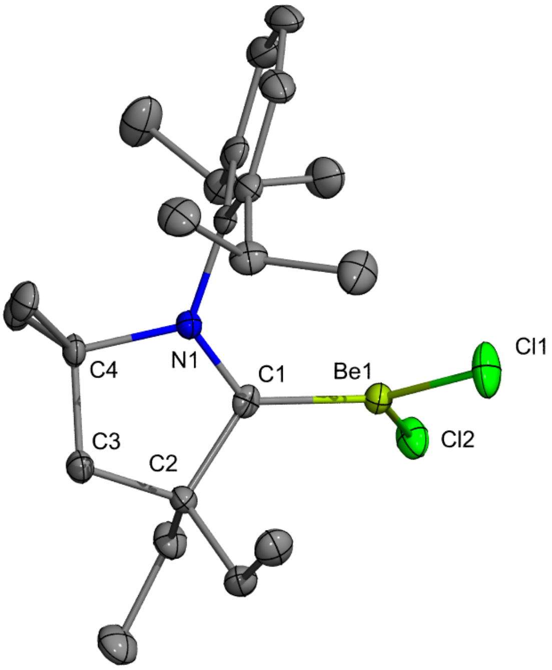


Figure S11. X-ray crystal structure of [Be(^{Et2}CAAC)Cl2] (**1**). Ellipsoids represent 50% probability and all hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°) in Table S2

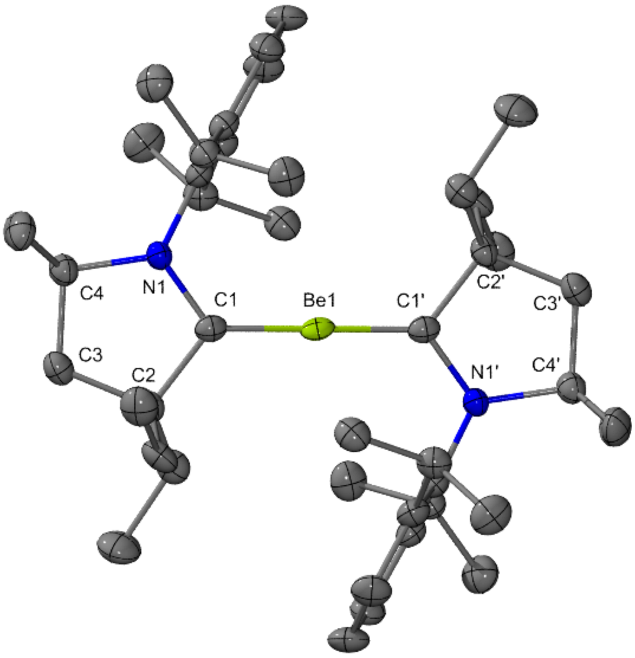


Figure S12. X-ray crystal structure of **[**Be(^{Et2}CAAC)$_2$**]** (**2**). Only one of the two chemically identical but crystallographically distinct molecules in the asymmetric unit is shown. Ellipsoids represent 50% probability and all hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°) in Table S2

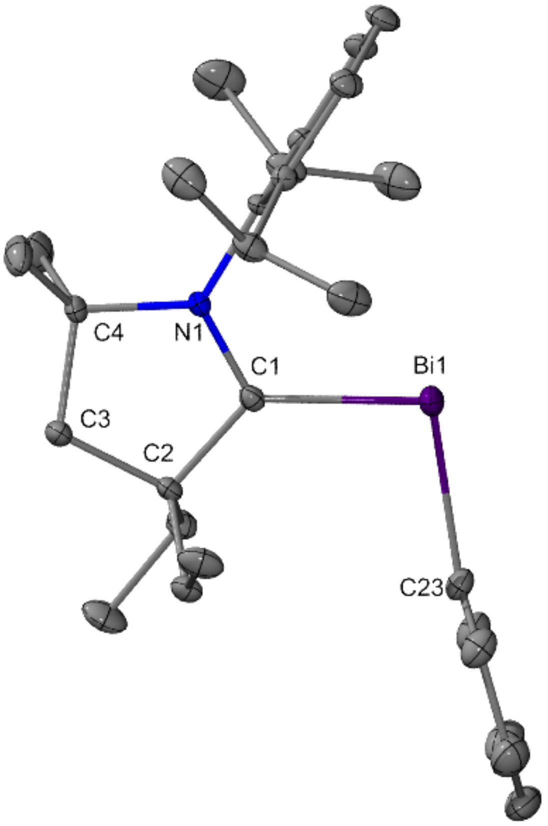


Figure S13. X-ray crystal structure of [(^{Et2}CAAC)BiPh] (**1**). Ellipsoids represent 50% probability and all hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°) in Table S2.

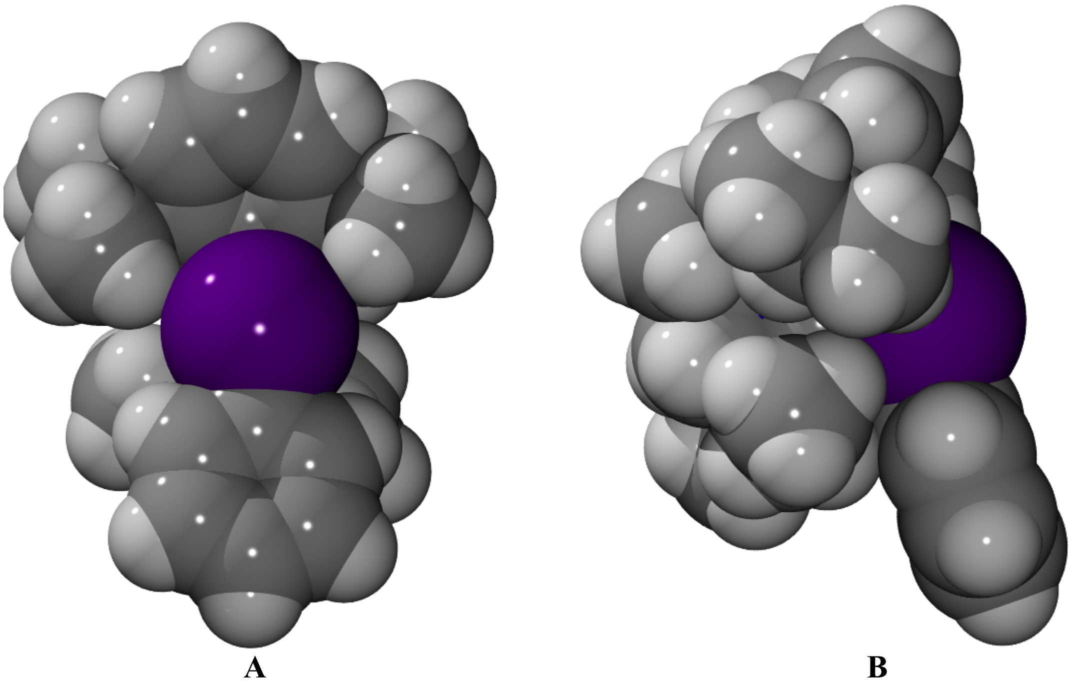


Figure S14. **A**) Front view and (**B**) side view of a space-filling model of crystal structure of compound **3**. Carbon atoms, partially masked, are in grey, all hydrogens are in white and bismuth atom is presented as purple spheres.

Table S1. Data collection and structure refinement details for compounds **1** to **3**.

	1	**2**	**3**
Formula	$C_{22}H_{35}BeCl_2N$	$C_{44}H_{70}BeN_2$	$C_{28}H_{40}BiN$
FW (g/mol)	393.42	636.03	599.59
Temp (K)	100(2)	100(2)	100(2)
λ (Å)	0.71073	0.71073	0.71073
Size (mm)	0.123x0.149x0.219	0.070x0.090x0.230	0.108x0.140x0.343
Crystal habit	colorless rod	purple rod	red rod
Crystal system	triclinic	triclinic	triclinic
Space group	P -1	P -1	P -1
a (Å)	9.639(5)	9.5312(15)	8.3680(8)
b(Å)	9.657(5)	11.986(2)	10.6800(10)
c (Å)	13.988(7)	17.614(3)	14.7724(13)
α (°)	92.742(13)	84.676(5)	81.317(2)
β (°)	108.132(13)	84.916(5)	83.500(2)
γ (°)	113.597(12)	76.034(4)	82.605(2)
Volume ($Å^3$)	1111.5(10)	1939.8(6)	1288.3(2)
Z	2	2	2
Density (g/cm^3)	1.175	1.089	1.546
μ (mm^{-1})	0.298	0.061	6.857
θ range (°)	1.56 - 26.37	1.16 - 25.38	1.40 - 29.61
Index ranges	$-12 \le h \le 12$ $-12 \le k \le 12$ $-17 \le l \le 17$	$-11 \le h \le 11$ $-14 \le k \le 14$ $-20 \le l \le 21$	$-11 \le h \le 11$ $-14 \le k \le 14$ $-20 \le l \le 20$
Reflns collected	19908	26660	26485
Independent reflns	4532[R(int)=0.1016]	7119[R(int)=0.1083]	7250[R(int)=0.0325]
Data / restraints / parameters	4532 / 0 / 243	7119 / 0 / 443	7250 / 0 / 279
GOF on F^2	1.007	1.059	1.036
R_1 ($I>2\sigma(I)$)	0.0461	0.0873	0.0205
wR_2 (all data)	0.1200	0.2978	0.0428

Table S2. Selected bond lengths (Å) and bond angles (°) for compounds **1**-**3** and ^{Et2}CAACBi(Ph)Cl_2

	1	**2**	**3**	^{Et2}CAACBi(Ph)Cl_2
Bi1-C1			2.199(2)	2.4566(15)
Bi1-C23			2.278(2)	2.2732(16)
C1-Be1	1.794(3)	1.660(5)		
Cl1-Be1	1.896(3)			
Cl2-Be1	1.923(3)			
N1-C1	1.306(3)	1.391(6)	1.334(3)	1.304(2)
N1-C11	1.463(3)	1.428(6)	1.452(2)	1.466(2)
N1-C4	1.544(3)	1.503(6)	1.516(3)	1.552(2)
C1-C2	1.523(3)	1.534(7)	1.519(3)	1.532(2)
C2-C3	1.546(3)	1.561(7)	1.540(3)	1.554(2)
C3-C4	1.519(3)	1.529(7)	1.532(3)	1.523(2)
C1-Bi1-C23			99.60(8)	92.95(5)
N1-C1-Bi1			119.65(14)	118.81(11)
C2-C1-Bi1			130.77(14)	129.66(10)
N1-C1-Be1	128.17(19)	125.3(3)		
C2-C1-Be1	122.43(17)	127.5(4)		
C1-N1-C11	124.60(17)	118.4(4)	120.45(17)	123.54(13)
C1-N1-C4	114.71(17)	116.8(4)	115.43(16)	113.40(13)
C11-N1-C4	120.52(15)	124.6(4)	124.08(16)	123.05(12)
N1-C1-C2	109.40(17)	107.0(4)	109.53(17)	110.43(13)

Computational details

The computations were carried out with the Gaussian 09 program package.[6] All structures were optimised using the ωB97XD functional. The all valence cc-pVDZ basis set was applied for H, C and N while for Bi the cc-pVDZ-PP basis sets were used, which include pseudopotentials for the simulation of relativistic effects. The basis sets with pseudo potentials were obtained from the EMSL Basis Set Library.[7] At each of the optimised structures vibrational analysis was performed to check that the stationary point located is a minimum of the potential energy hypersurface. To investigate the convergence of the basis set on the optimised geometries optimalization and each of the optimized structures vibrational analysis have been performed with the larger cc-pVTZ(-PP) basis set using the ωB97XD functional, and the difference was found to be negligible. For visualisation of the molecules the Molden program was used.[8,9] The Wiberg Bond Indices and NPA charges were calculated with the NBO program version 3.1.[10] The AIM analysis was obtained with the Multiwfn code.[11] The molecular orbitals were plotted with Avogadro program.[12]

Table S3. Bond lengths (d, Å), Wiberg bond indices (WBI, –), electron density at the bond critical point (ρ, a.u.) and ellipcticity (ε, –) of selected bonds for **3M** and reference molecules at ωB97XD/cc-pVTZ(-PP) level. Partial NPA charges (q, e) of selected atoms at ωB97XD/cc-pVTZ(-PP) level.

		3M		**H_2C=BiMe**	**$BiMe_3$**
	Bi–$C_{carbene}$	N–$C_{carbene}$	Bi–Me	Bi=C	Bi–C
d	2.183	1.334	2.286	2.050	2.262
WBI	1.28	1.28	0.87	1.84	0.87
ρ	0.107	0.334	0.094	0.136	0.099
ε	0.282	0.051	0.044	0.282	0.011
q(Bi)		0.434		0.890	1.066

Table S4. The resonance structures and the weight of the structures (%) at ωB97XD/cc-pVTZ(-PP) level

TOPO matrix for the leading resonance structure:

```
    Atom  1   2   3   4   5   6   7   8   9  10  11  12  13  14  15  16  17
    ---- --- --- --- --- --- --- --- --- --- --- --- --- --- --- --- --- ---
  1. C   0   1   0   0   1   0   0   0   0   0   0   0   1   1   0   0   0
  2. C   1   0   1   0   0   1   1   0   0   0   0   0   0   0   0   0   0
  3. N   0   1   1   1   0   0   0   1   0   0   0   0   0   0   0   0   0
  4. C   0   0   1   0   1   0   0   0   2   0   0   0   0   0   0   0   0
  5. C   1   0   0   1   0   0   0   0   0   0   1   1   0   0   0   0   0
  6. C   0   1   0   0   0   0   0   0   0   0   0   0   0   0   1   1   1
  7. C   0   1   0   0   0   0   0   0   0   0   0   0   0   0   0   0   0
  8. C   0   0   1   0   0   0   0   0   0   0   0   0   0   0   0   0   0
  9. Bi  0   0   0   2   0   0   0   0   1   1   0   0   0   0   0   0   0
 10. C   0   0   0   0   0   0   0   0   1   0   0   0   0   0   0   0   0
 11. C   0   0   0   0   1   0   0   0   0   0   0   0   0   0   0   0   0
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```
 12. C  0  0  0  0  1  0  0  0  0  0  0  0  0  0  0  0  0
 13. H  1  0  0  0  0  0  0  0  0  0  0  0  0  0  0  0  0
 14. H  1  0  0  0  0  0  0  0  0  0  0  0  0  0  0  0  0
 15. H  0  0  0  0  0  1  0  0  0  0  0  0  0  0  0  0  0
 16. H  0  0  0  0  0  1  0  0  0  0  0  0  0  0  0  0  0
 17. H  0  0  0  0  0  1  0  0  0  0  0  0  0  0  0  0  0
 18. H  0  0  0  0  0  0  1  0  0  0  0  0  0  0  0  0  0
 19. H  0  0  0  0  0  0  1  0  0  0  0  0  0  0  0  0  0
 20. H  0  0  0  0  0  0  1  0  0  0  0  0  0  0  0  0  0
 21. H  0  0  0  0  0  0  0  0  0  0  0  1  0  0  0  0  0
 22. H  0  0  0  0  0  0  0  0  0  0  0  1  0  0  0  0  0
 23. H  0  0  0  0  0  0  0  0  0  0  0  1  0  0  0  0  0
 24. H  0  0  0  0  0  0  0  0  0  0  1  0  0  0  0  0  0
 25. H  0  0  0  0  0  0  0  0  0  0  1  0  0  0  0  0  0
 26. H  0  0  0  0  0  0  0  0  0  0  1  0  0  0  0  0  0
 27. H  0  0  0  0  0  0  0  1  0  0  0  0  0  0  0  0  0
 28. H  0  0  0  0  0  0  0  1  0  0  0  0  0  0  0  0  0
 29. H  0  0  0  0  0  0  0  1  0  0  0  0  0  0  0  0  0
 30. H  0  0  0  0  0  0  0  0  0  1  0  0  0  0  0  0  0
 31. H  0  0  0  0  0  0  0  0  0  1  0  0  0  0  0  0  0
 32. H  0  0  0  0  0  0  0  0  0  1  0  0  0  0  0  0  0

   Atom 18  19  20  21  22  23  24  25  26  27  28  29  30  31  32
   ---- --- --- --- --- --- --- --- --- --- --- --- --- --- --- ---
  1. C  0  0  0  0  0  0  0  0  0  0  0  0  0  0  0
  2. C  0  0  0  0  0  0  0  0  0  0  0  0  0  0  0
  3. N  0  0  0  0  0  0  0  0  0  0  0  0  0  0  0
  4. C  0  0  0  0  0  0  0  0  0  0  0  0  0  0  0
  5. C  0  0  0  0  0  0  0  0  0  0  0  0  0  0  0
  6. C  0  0  0  0  0  0  0  0  0  0  0  0  0  0  0
  7. C  1  1  1  0  0  0  0  0  0  0  0  0  0  0  0
  8. C  0  0  0  0  0  0  0  0  0  1  1  1  0  0  0
  9. Bi  0  0  0  0  0  0  0  0  0  0  0  0  0  0  0
 10. C  0  0  0  0  0  0  0  0  0  0  0  0  1  1  1
 11. C  0  0  0  0  0  0  1  1  1  0  0  0  0  0  0
 12. C  0  0  0  1  1  1  0  0  0  0  0  0  0  0  0
 13. H  0  0  0  0  0  0  0  0  0  0  0  0  0  0  0
 14. H  0  0  0  0  0  0  0  0  0  0  0  0  0  0  0
 15. H  0  0  0  0  0  0  0  0  0  0  0  0  0  0  0
 16. H  0  0  0  0  0  0  0  0  0  0  0  0  0  0  0
 17. H  0  0  0  0  0  0  0  0  0  0  0  0  0  0  0
 18. H  0  0  0  0  0  0  0  0  0  0  0  0  0  0  0
 19. H  0  0  0  0  0  0  0  0  0  0  0  0  0  0  0
 20. H  0  0  0  0  0  0  0  0  0  0  0  0  0  0  0
 21. H  0  0  0  0  0  0  0  0  0  0  0  0  0  0  0
 22. H  0  0  0  0  0  0  0  0  0  0  0  0  0  0  0
 23. H  0  0  0  0  0  0  0  0  0  0  0  0  0  0  0
 24. H  0  0  0  0  0  0  0  0  0  0  0  0  0  0  0
 25. H  0  0  0  0  0  0  0  0  0  0  0  0  0  0  0
 26. H  0  0  0  0  0  0  0  0  0  0  0  0  0  0  0
```

```
 27. H  0  0  0  0  0  0  0  0  0  0  0  0  0  0  0
 28. H  0  0  0  0  0  0  0  0  0  0  0  0  0  0  0
 29. H  0  0  0  0  0  0  0  0  0  0  0  0  0  0  0
 30. H  0  0  0  0  0  0  0  0  0  0  0  0  0  0  0
 31. H  0  0  0  0  0  0  0  0  0  0  0  0  0  0  0
 32. H  0  0  0  0  0  0  0  0  0  0  0  0  0  0  0

     Resonance
   RS   Weight(%)                  Added(Removed)
---------------------------------------------------------------------------
    1*(2)  42.44
    2*(2)  20.58    N  3- C  4, ( C  4-Bi  9), ( N  3), Bi  9
    3 (2)   1.81   ( C  2- N  3),  N  3- C  4, ( C  4-Bi  9),  C  2
    4       1.70    N  3- C  4,  C  4- C  5, ( C  4-Bi  9), ( C  4-Bi  9),
                   ( C  5- C 11), ( N  3), Bi  9, Bi  9
    5       1.69   ( C  1- C  5),  N  3- C  4,  C  4- C  5, ( C  4-Bi  9),
                   ( C  4-Bi  9), ( N  3), Bi  9, Bi  9
    6       1.50    N  3- C  4, ( C  4- C  5), ( N  3),  C  5
    7       1.48   ( C  2- N  3),  N  3- C  4,  N  3- C  4, ( C  4-Bi  9),
                   ( C  4-Bi  9), ( N  3), Bi  9, Bi  9
    8       1.34    C  4- C  5, ( C  4-Bi  9), ( C  5- C 11), Bi  9
    9 (2)   1.20   ( C  1- C  5),  C  4- C  5, ( C  4-Bi  9),  C  1
   10       1.20   ( C  1- C  5),  C  4- C  5, ( C  4-Bi  9), Bi  9
   11 (2)   1.12    C  4- C  5, ( C  4-Bi  9), ( C  5- C 11),  C 11
   12       1.12    C  4- C  5, ( C  4-Bi  9), ( C  5- C 12), Bi  9
   13       1.00    C  4- C  5, ( C  4-Bi  9), ( C  5- C 12),  C 12
   14       0.97   ( C  2- N  3),  N  3- C  4, ( C  4-Bi  9), Bi  9
   15       0.86    N  3- C  4, ( C  4-Bi  9), Bi  9- C 10, ( C 10- H 31),
                   ( N  3),  H 31
   16       0.85    N  3- C  4, ( C  4-Bi  9), Bi  9- C 10, ( C 10- H 32),
                   ( N  3),  H 32
   17       0.66    C  1- C  2, ( C  1- H 14), ( C  2- C  6),  C  6
   18       0.60   ( C  4-Bi  9),  C  4- C 11, ( C 11- H 24),  H 24
   19       0.56   ( C  4-Bi  9), Bi  9- C 10, ( C 10- H 32),  H 32
   20       0.52    C  1- C  5, ( C  1- H 13), ( C  4- C  5),  H 13
   21       0.52    C  2- C  6, ( C  2- C  7), ( C  6- H 17),  C  7
   22       0.51    C  1- C  5, ( C  1- H 13), ( C  4- C  5),  C  4
   23       0.48    C  1- C  2, ( C  1- H 14), ( C  2- C  6),  H 14
   24       0.43    N  3- C  8, ( C  8- H 29), ( N  3),  H 29
   25       0.42   ( N  3- C  4),  C  4-Bi  9, (Bi  9- C 10),  N  3
   26       0.39   ( N  3- C  4), ( N  3- C  8),  N  3,  C  8
   27       0.38   ( C  2- C  6),  C  2- C  7, ( C  7- H 18),  C  6
   28       0.37    N  3- C  8, ( C  8- H 28), ( N  3),  H 28
   29       0.35   ( C  4- C  5),  C  4-Bi  9,  C  5, (Bi  9)
   30       0.34    N  3- C  8, ( C  4-Bi  9), ( C  8- H 29), ( N  3),
                   Bi  9,  H 29
   31       0.33   ( C  1- C  2),  C  2- C  6, ( C  6- H 15),  C  1
   32       0.33    C  2- N  3, ( C  2- C  7), ( N  3- C  4),  C  4
   33       0.32   ( C  1- C  2),  C  2- C  7, ( C  7- H 20),  H 20
   34       0.32   ( C  1- C  2),  C  2- N  3, ( N  3- C  8),  C  8
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35	0.31	C 2- C 6, (C 2- C 7), (C 6- H 17), H 17
36	0.31	(C 4- C 5), C 5- C 12, (C 12- H 21), H 21
37	0.31	(C 1- C 2), C 2- C 6, (C 6- H 15), H 15
38	0.31	N 3- C 8, (C 4-Bi 9), (C 8- H 28), (N 3), Bi 9, H 28
39	0.31	N 3- C 4, (C 4-Bi 9), (C 4-Bi 9), (Bi 9- C 10), (N 3), Bi 9, Bi 9, C 10
40	0.30	(C 4- C 5), C 5- C 11, (C 11- H 24), C 4
41	0.30	(C 4- C 5), C 5- C 12, (C 12- H 21), C 4
42	0.30	(C 1- C 2), C 2- N 3, (N 3- C 8), C 1
43	0.30	(C 1- C 2), C 2- C 7, (C 7- H 20), C 1
44	0.29	C 1- C 2, (C 1- H 13), (C 2- N 3), N 3- C 4, (C 4-Bi 9), Bi 9
45	0.28	C 2- C 6, (C 2- C 7), N 3- C 4, (C 4-Bi 9), (C 6- H 17), (N 3), C 7, Bi 9
46	0.28	C 1- C 2, (C 1- H 14), (C 2- C 6), N 3- C 4, (C 4-Bi 9), (N 3), Bi 9, H 14
47	0.28	(C 2- C 6), C 2- C 7, N 3- C 4, (C 4-Bi 9), (C 7- H 18), (N 3), C 6, Bi 9
48	0.26	N 3- C 4, (C 4-Bi 9), (C 5- C 11), C 5- C 12, (C 12- H 23), (N 3), Bi 9, C 11
49	0.26	(N 3- C 8), (C 4-Bi 9), C 8, Bi 9
50	0.26	C 1- C 2, (C 1- H 14), (C 2- C 6), N 3- C 4, (C 4-Bi 9), (N 3), C 6, Bi 9
51	0.25	(C 2- C 6), C 2- C 7, (C 7- H 18), H 18
52	0.23	(C 2- N 3), N 3- C 4, N 3- C 8, (C 4-Bi 9), (C 8- H 28), C 2, (N 3), Bi 9
53	0.23	(C 2- N 3), C 2- C 7, N 3- C 4, (C 4-Bi 9), (C 7- H 19), Bi 9
54	0.23	N 3- C 4, (C 4-Bi 9), C 5- C 11, (C 5- C 12), (C 11- H 25), (N 3), Bi 9, H 25
55	0.23	(C 1- C 5), N 3- C 4, C 4- C 5, (C 4-Bi 9), (C 4-Bi 9), C 1, (N 3), Bi 9
56	0.22	N 3- C 4, (C 4-Bi 9), C 5- C 11, (C 5- C 12), (C 11- H 25), (N 3), Bi 9, C 12
57	0.22	(C 1- C 2), C 2- N 3, N 3- C 4, (N 3- C 8), (C 4-Bi 9), (N 3), C 8, Bi 9
58	0.22	(C 2- N 3), N 3- C 4, N 3- C 4, (C 4-Bi 9), (C 4-Bi 9), C 2, (N 3), Bi 9
59	0.22	(C 2- N 3), N 3- C 4, N 3- C 8, (C 4-Bi 9), (C 8- H 29), C 2, (N 3), Bi 9
60	0.21	(C 2- N 3), C 2- C 6, N 3- C 4, (C 4-Bi 9), (C 6- H 16), Bi 9
61	0.21	(N 3- C 4), N 3- C 8, (C 8- H 27), C 4
62	0.21	(C 2- N 3), N 3- C 8, (C 8- H 28), C 2
63	0.21	(C 2- N 3), C 2- C 7, (C 7- H 19), N 3
64	0.21	C 2- C 6, (C 2- C 7), N 3- C 4, (C 4-Bi 9), (C 6- H 17), (N 3), Bi 9, H 17
65	0.20	C 1- C 5, (C 1- H 13), N 3- C 4, (C 4- C 5), (C 4-Bi 9), (N 3), Bi 9, H 13

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  66       0.20  ( C  1- C  2),  C  1- C  5,  N  3- C  4, ( C  4-Bi  9),
                 ( C  5- C 12),  C  2, ( N  3), Bi  9
  67       0.18   C  1- C  5, ( C  1- H 14),  N  3- C  4, ( C  4-Bi  9),
                 ( C  5- C 11), ( N  3), Bi  9,  C 11
  68       0.18  ( C  2- N  3),  N  3- C  8, ( C  8- H 29),  C  2
  69       0.18   N  3- C  4, ( N  3- C  8), ( C  4- C  5),  C  8
  70       0.18  ( C  2- N  3),  C  2- C  6, ( C  6- H 16),  N  3
  71       0.18   C  2- N  3, ( C  2- C  7), ( C  4-Bi  9), ( N  3),
                  C  7, Bi  9
  72       0.16   N  3- C  4, ( C  4- C  5), ( C  4-Bi  9),  C  5- C 11,
                 ( C 11- H 24), ( N  3), Bi  9,  H 24
  73       0.16  ( C  1- C  5),  N  3- C  4, ( C  4-Bi  9),  C  5- C 12,
                 ( C 12- H 22),  C  1, ( N  3), Bi  9
  74       0.15  ( C  1- C  5),  N  3- C  4, ( C  4-Bi  9),  C  5- C 11,
                 ( C 11- H 26),  C  1, ( N  3), Bi  9
  75       0.15  ( C  1- C  2),  C  2- C  6,  N  3- C  4, ( C  4-Bi  9),
                 ( C  6- H 15), ( N  3), Bi  9,  H 15
  76       0.15   N  3- C  4, ( C  4- C  5), ( C  4-Bi  9),  C  5- C 12,
                 ( C 12- H 21), ( N  3), Bi  9,  H 21
  77       0.15  ( C  2- C  6),  C  2- C  7,  N  3- C  4, ( C  4-Bi  9),
                 ( C  7- H 18), ( N  3), Bi  9,  H 18
  78       0.14   C  1- C  2, ( C  1- C  5), ( C  2- C  7),  N  3- C  4,
                 ( C  4-Bi  9), ( N  3),  C  5, Bi  9
  79       0.14  ( C  1- C  2),  C  2- C  6,  N  3- C  4, ( C  4-Bi  9),
                 ( C  6- H 15),  C  1, ( N  3), Bi  9
  80       0.14  ( C  1- C  2),  C  2- C  7,  N  3- C  4, ( C  4-Bi  9),
                 ( C  7- H 20), ( N  3), Bi  9,  H 20
  81       0.14  ( C  1- C  2),  C  2- C  7,  N  3- C  4, ( C  4-Bi  9),
                 ( C  7- H 20),  C  1, ( N  3), Bi  9
  82       0.12  ( C  1- C  2),  C  2- N  3,  N  3- C  4, ( N  3- C  8),
                 ( C  4-Bi  9),  C  1, ( N  3), Bi  9
  83       0.12   N  3- C  4, ( C  4- C  5), ( C  4-Bi  9), ( C  5- C 12),
                 ( N  3),  C  5, Bi  9,  C 12
  84       0.11   C  1- C  2, ( C  1- C  5), ( C  2- C  7),  C  7
  85-147   0.39
--------------------------------------------------------------------------
         100.00   * Total *                [* = reference structure]
```

Total energies and Cartesian coordinates at the ωB97XD /cc-pVTZ(-PP) level

3M

HF= -662.5777581

C	-2.8943072183	-0.3037345707	-0.0438082373
N	-1.4998634242	-0.7904461462	-0.0774598538
C	-0.5472134938	0.1429160888	-0.0714137988
C	-1.2113884647	1.5122042283	-0.0514879716
C	-2.6935436721	1.1874941928	-0.3366799467
C	-1.1889794239	-2.1917807589	0.0162063352
Bi	1.5565142415	-0.4335810022	0.0047322937
C	2.5136639933	1.6419082979	-0.0111274920
C	-1.0323727629	2.1487121266	1.3346196439
C	-0.6646919135	2.4572133690	-1.1212862128
C	-3.5105682146	-0.5624336145	1.3322514225
C	-3.7348088717	-0.9709185776	-1.1304689403
H	-3.3675410292	1.8078219847	0.2528418957
H	-2.9074699245	1.3777393260	-1.3886655812
H	-3.5660457031	-1.6313010413	1.5430597522
H	-4.5242390294	-0.1625960500	1.3686177926
H	-2.9266003897	-0.0901400711	2.1202847905
H	-3.2481703035	-0.8782624425	-2.1011507216
H	-4.7084101449	-0.4834352781	-1.1868555976
H	-3.9100160798	-2.0277425661	-0.9279380586
H	-1.2678102805	3.3672351013	-1.1500755803
H	0.3638225977	2.7396153586	-0.9152545752
H	-0.6984499216	1.9895311720	-2.1053693118
H	-1.5633999588	3.1018369989	1.3759907604
H	-1.4174284156	1.5053005083	2.1247365202
H	0.0205126463	2.3302065262	1.5411158833
H	-2.0980579031	-2.7855573596	0.0056709082
H	-0.5594646870	-2.4955561419	-0.8264514164
H	-0.6388469728	-2.3986640067	0.9410398619
H	3.5597794671	1.4732059159	0.2441870781
H	2.4668732925	2.0987455160	-0.9966138459
H	2.0845847762	2.3128780576	0.7294392321

H_2C=BiMe

HF= -293.8772688

C	1.1493124644	1.5240647300	0.0000024812
Bi	0.1057518010	-0.2404574551	-0.0000330502
C	-1.9535817142	0.7038839523	0.0000675195
H	0.6670187639	2.4943910101	-0.0017697057
H	2.2327142247	1.5353631978	0.0026866106
H	-1.8516966968	1.7819329794	-0.0985918031
H	-2.4638087850	0.4664509635	0.9318284371
H	-2.5360114749	0.3121385546	-0.8318303810

$BiMe_3$

HF= -334.4473998

C	1.8510303039	-0.4015075700	0.9182605769
Bi	0.0006540419	-0.0008649014	-0.3194109682
C	-0.5781691063	1.8064456266	0.9115203357
C	-1.2783333292	-1.3978348146	0.9159131680
H	-1.0235589196	-2.4316710276	0.6893918736
H	-1.1027389856	-1.2042305386	1.9723438191
H	-2.3299116581	-1.2330556043	0.6873027560
H	-1.6168602186	2.0668505398	0.7157150159
H	-0.4545643062	1.5758164511	1.9678622808
H	0.0566399131	2.6506521977	0.6481521412
H	2.2334688896	-1.3974268189	0.7016428340
H	2.6178006809	0.3336468638	0.6800431433
H	1.5982719219	-0.3314147081	1.9744920087

Total energies and Cartesian coordinates at the ωB97XD /cc-pVDZ(-PP) level

3M

HF= -662.4366108

Bi	1.5638851720	-0.4350159673	0.0046186238
C	-0.5508158147	0.1456631223	-0.0788042576
C	-1.2217489818	1.5181978216	-0.0566819303
C	-2.7080210768	1.1874242144	-0.3359208256
C	-2.9047791219	-0.3078536130	-0.0376816840
N	-1.5072356300	-0.7952928538	-0.0905163150
C	-1.1896930352	-2.1979109594	0.0002901071
C	2.5155251042	1.6568480129	0.0005677887
C	-1.0380905861	2.1593547534	1.3303211851
C	-0.6770811638	2.4600833986	-1.1360907496
C	-3.4994416393	-0.5659243849	1.3522280155
C	-3.7623664733	-0.9777071010	-1.1146454358
H	-3.3903293842	1.8129429543	0.2573050741
H	-2.9287968138	1.3750246892	-1.3972665100
H	-3.5447804101	-1.6440480206	1.5712808574
H	-4.5248453607	-0.1697653513	1.4060509787
H	-2.8999880203	-0.0835090488	2.1367136526
H	-3.2828468891	-0.8907267883	-2.1008919381
H	-4.7444260198	-0.4832346283	-1.1624032449
H	-3.9419480454	-2.0431293671	-0.9050678240
H	-1.2822756517	3.3810347888	-1.1665604346
H	0.3632279645	2.7432155258	-0.9353361147
H	-0.7166804997	1.9852887213	-2.1279163725
H	-1.5705101902	3.1234617779	1.3722460961
H	-1.4275408280	1.5141473405	2.1309804991
H	0.0253148568	2.3397852052	1.5386423714
H	-2.1036911903	-2.8024426794	-0.0169437257
H	-0.5490917553	-2.4980187897	-0.8488733268
H	-0.6357693416	-2.4092359513	0.9343926023
H	3.5680792835	1.4981951825	0.2847268810

H	2.4914112926	2.1170411142	-0.9977294943
H	2.0627439606	2.3382970319	0.7354250995

H$_2$C=BiMe

HF= -293.8374006

Bi	-0.1083749260	-0.2414133820	0.0000000613
H	-0.6489865425	2.5182875680	-0.0000233199
H	-2.2380218562	1.5597835830	0.0000077455
C	-1.1416892963	1.5385724195	0.0000065082
C	1.9688391843	0.6975171885	0.0000065802
H	2.5223796213	0.3737694999	-0.8942443509
H	1.8753460178	1.7929086915	-0.0014326867
H	2.5215022772	0.3760236868	0.8956089931

BiMe$_3$

HF= -334.3892899

C	-1.8544504926	0.4341247164	0.9224692609
Bi	-0.0002261958	0.0004982406	-0.3216934227
C	1.3057035862	1.3853128149	0.9221868496
C	0.5504589746	-1.8233577544	0.9194051343
H	1.0692794864	2.4343198665	0.6884440854
H	1.1234861877	1.1990949055	1.9909263953
H	2.3661112633	1.1986312987	0.6953764445
H	1.5893810463	-2.1177638062	0.7078052772
H	0.4496776500	-1.5834546267	1.9882715768
H	-0.1167949525	-2.6618602398	0.6687570899
H	-2.2322669324	1.4419875299	0.6936686150
H	-2.6390964492	-0.3020061557	0.6916508676
H	-1.6012754577	0.3732185793	1.9912862464

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