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Supporting Information

A Dicationic Bismuth(III) Lewis Acid: Catalytic Hydrosilylation of Olefins

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1. Experimental Methods:

All manipulations were performed under argon atmosphere using standard Schlenk and glove-box techniques.[1] Solvents used for the synthesis and NMR experiments were dried, distilled and degassed before use by standard methods.[2] Anhydrous $BiCl_3$ was purchased from Sigma-Aldrich. The starting materials potassium hydridotris(3,5-dimethylpyrazolyl)borate (KTp^*) [3] and triethylsilyliumtetrakis(pentafluorophenyl)borate $[Et_3Si][B(C_6F_5)_4]$ [4] were prepared according to the literature procedure. NMR measurements were performed on Bruker 500 MHz spectrometer. The chemical shifts (δ ppm) in ^1H NMR spectra were referenced to the residual proton signals in the deuterated solvents. The chemical shifts (δ ppm) in ^{11}B NMR spectra were referenced to $NaBH_4$ in D_2O. The chemical shifts (δ ppm) in ^{19}F NMR spectra were referenced to $CFCl_3$. Samples for elemental analysis, dried at 1×10^{-3} mbar at ambient temperature, packed under inert conditions were analysed using Elementar Vario Micro Cube instrument.

2. Synthesis and Characterization

Compound **1:** Toluene (50 mL) was condensed to a mixture of KTp^{Me2} (1 mmol, 0.336 g) and $BiCl_3$ (1 mmol, 0.315 g) at -196 °C. The reaction mixture was allowed to warm to ambient temperature and stirred for 12 hours. Toluene was evaporated under vacuum resulting colorless powder, which was mixed with $B(C_6F_5)_3$ (2 mmol, 1.024 g). The mixture was extracted with 30 mL of CH_2Cl_2 and filtered to separate KCl. The filtrate was concentrated and layered with n-pentane at room temperature. After 7 days, colorless crystals of 1 were obtained (yield 80%, 0.460 g); ^{1}H NMR (CD_2Cl_2, 500 MHz): δ 6.01 (s, 3H, CH), δ 4.73 (s(br), 1H, BH), δ 2.58 (s, 9H, CH3), δ 2.41 (s, 9H, CH3); ^{11}B NMR (CD_2Cl_2, 160 MHz): δ -4.69 (s(br), BH); ^{13}C NMR (CD_2Cl_2, 125 MHz): δ 152.1 (CH_3*C*NN), δ 146.6 (CH_3*C*NB), δ 107.6 (*C*H), δ 14.2 (*C*H_3CNB), δ 12.6 (*C*H_3CNN); Elemental analysis: calculated for $C_{15}H_{22}N_6BBiCl_2$: C 31.2 H 3.8 N 14.5 Found C 31.4 H 3.5 N 14.5.

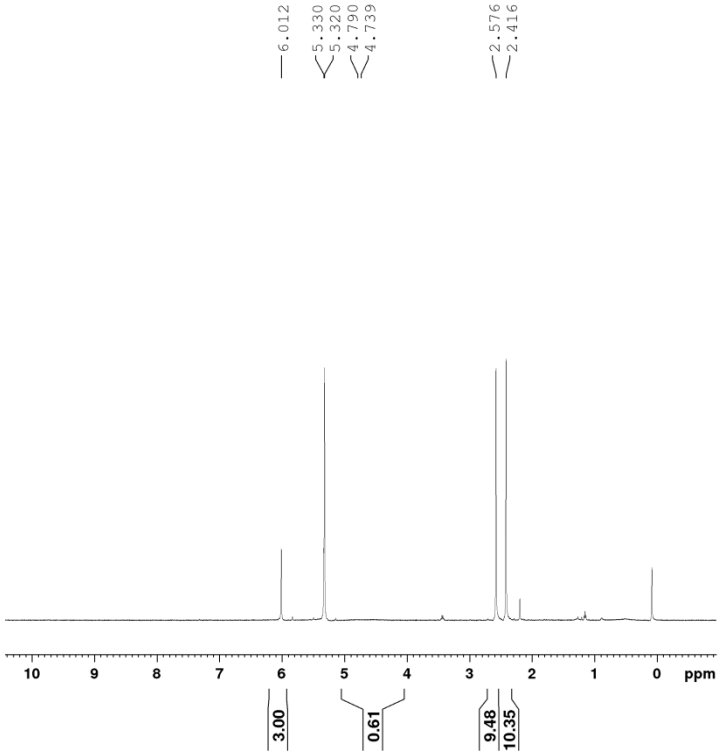


Figure S1: ^{1}H NMR spectrum of **1** in CD_2Cl_2.

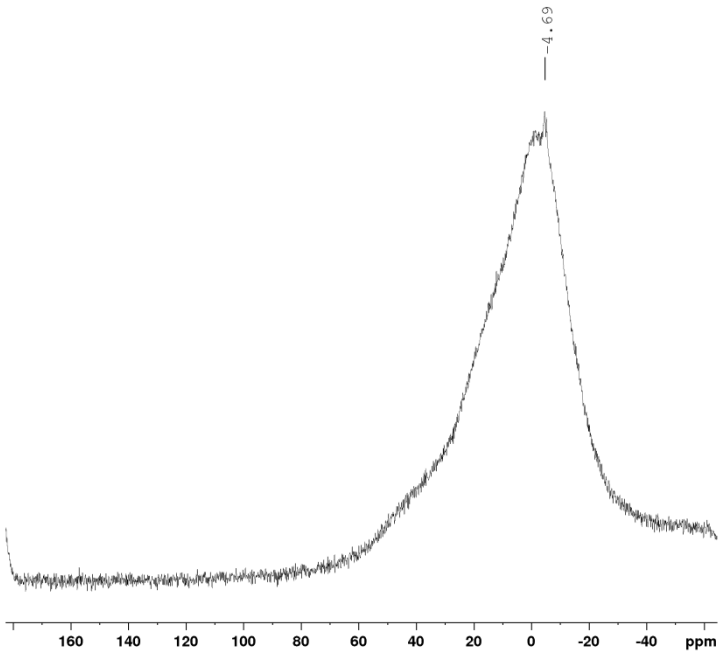


Figure S2: ^{11}B NMR spectrum of **1** in CD_2Cl_2.

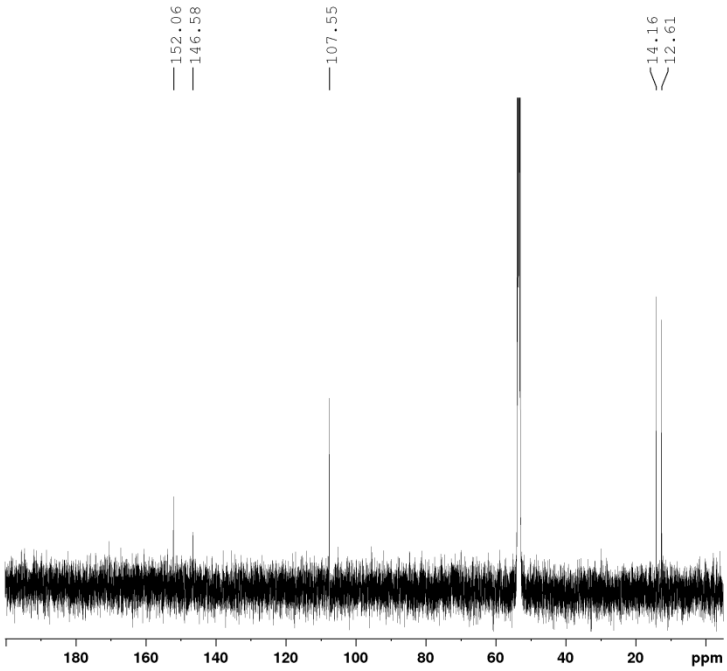


Figure S3: ^{13}C NMR spectrum of **1** in CD_2Cl_2.

Compound **2**: Ortho-dichlorobenzene (10 mL) was added to a mixture of $Tp^{Me2}BiCl_2$ (0.17 mmol, 0.100 g) and $[Et_3Si.(C_9H_{12})][B(C_6F_5)_4]$ (0.35 mmol, 0.320 g) at room temperature. The reaction mixture was allowed to stir for two hours. A pale yellow solution was obtained. n-Pentane (30 mL) was added to the reaction mixture with vigorous stirring. An oily precipitate separated from mother liquor and it was dried under vacuum to obtain a colorless precipitate of 2 (Yield 70%, 0.240 g). 2 was crystallized from a mixture of *ortho*-dichlorobenzene and chlorobenzene at room temperature after several days. ^{1}H NMR (*ortho*-dichlorobenzene-D4, 500 MHz): δ 6.35 (s, 3H, CH), δ 4.89 (s(br), 1H, BH), δ 2.63 (s, 9H, CH3), δ 2.51 (s, 9H, CH3); ^{11}B NMR (*ortho*-dichlorobenzene-D4, 160 MHz): δ (s, -13.53, $B(C_6F_5)_4$); ^{13}C NMR (*ortho*-dichlorobenzene-D4, 125 MHz): δ 155.1 (CH_3*C*NN), δ 153.5 (CH_3*C*NB), δ 153.5 (*o*-CF - $[B(C_6F_5)]_4$), δ 137.4 ppm (*p*-CF - $[B(C_6F_5)]_4$), δ 135.5 ppm (*m*-CF - $[B(C_6F_5)]_4$), δ 123.9, (ipso-C - $[B(C_6F_5)]_4$), δ 111.1 (*C*H), δ 12.9 (*C*H_3CNB), δ 12.3 (*C*H_3CNN), ^{19}F NMR (*ortho*-dichlorobenzene-D4, 470.58 MHz): δ (s, -131.52, *o*-CF - $[B(C_6F_5)]_4$), δ (s, -165.45, m-CF - $[B(C_6F_5)]_4$),δ (s, -161.26, *p*-CF - $[B(C_6F_5)]_4$). Elemental analysis: calculated for $C_{69}H_{27}N_6B_3F_{40}Cl_1Bi_1$: C 41.9 H 1.4 N 4.2 Found C 42.0 H 1.2 N 4.0.

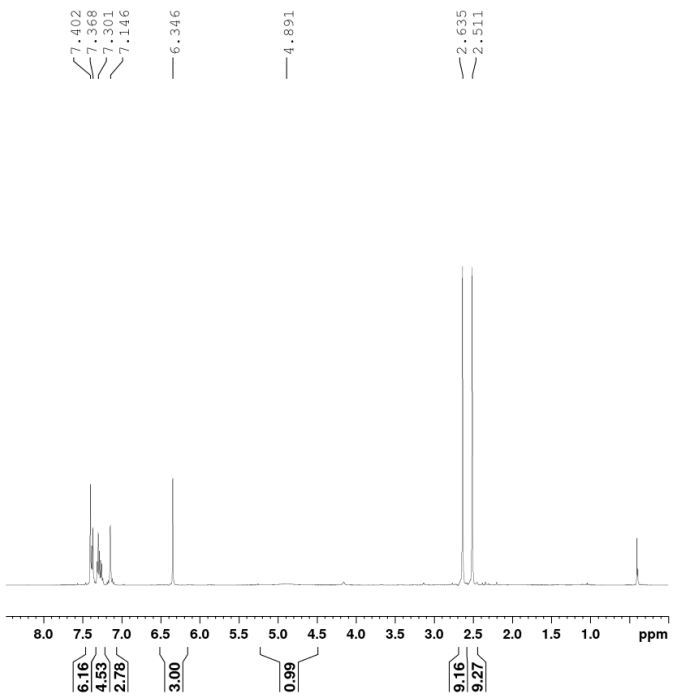


Figure S4: ^{1}H NMR spectrum of **2** in *ortho*-dichlorobenzene-D4.

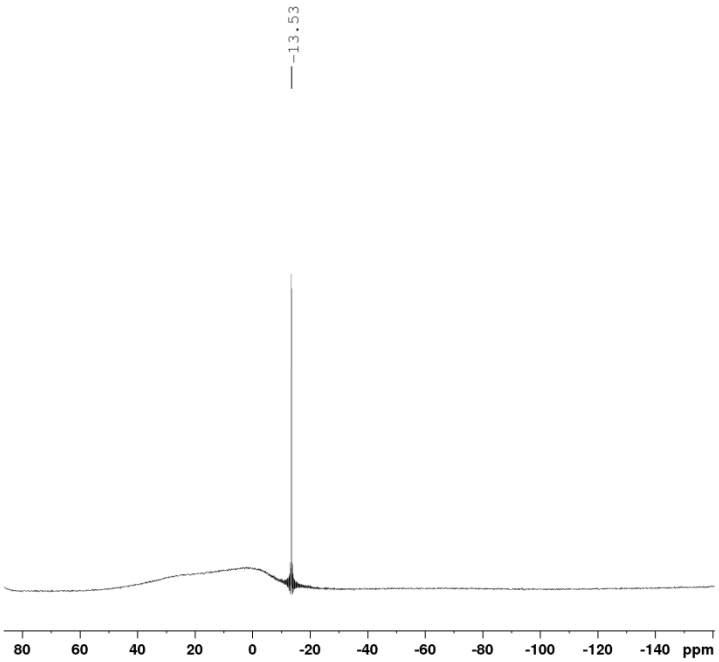


Figure S5: ^{11}B NMR spectrum of **2** in *ortho*-dichlorobenzene-D4.

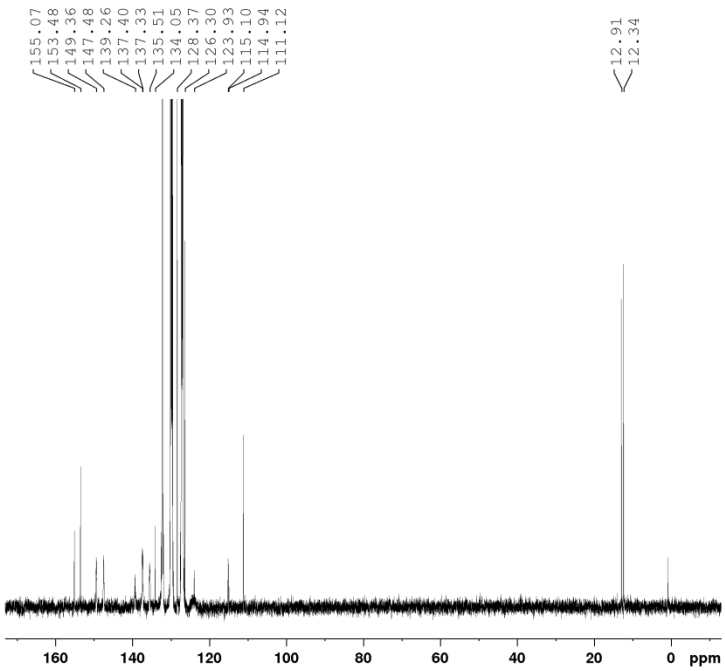


Figure S6: ^{13}C NMR spectrum of **2** in *ortho*-dichlorobenzene-D4.

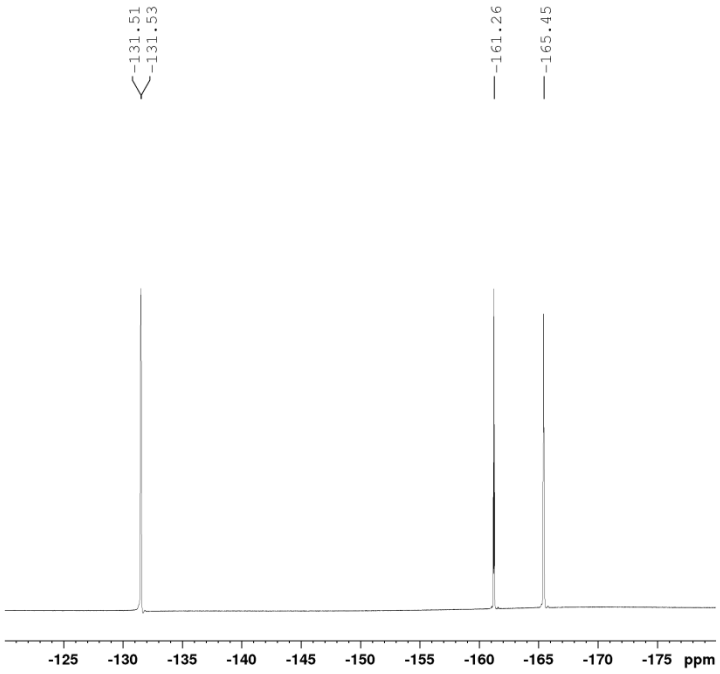


Figure S7: ^{19}F NMR spectrum of **2** in *ortho*-dichlorobenzene-D4.

3. Modified Gutmann Test:

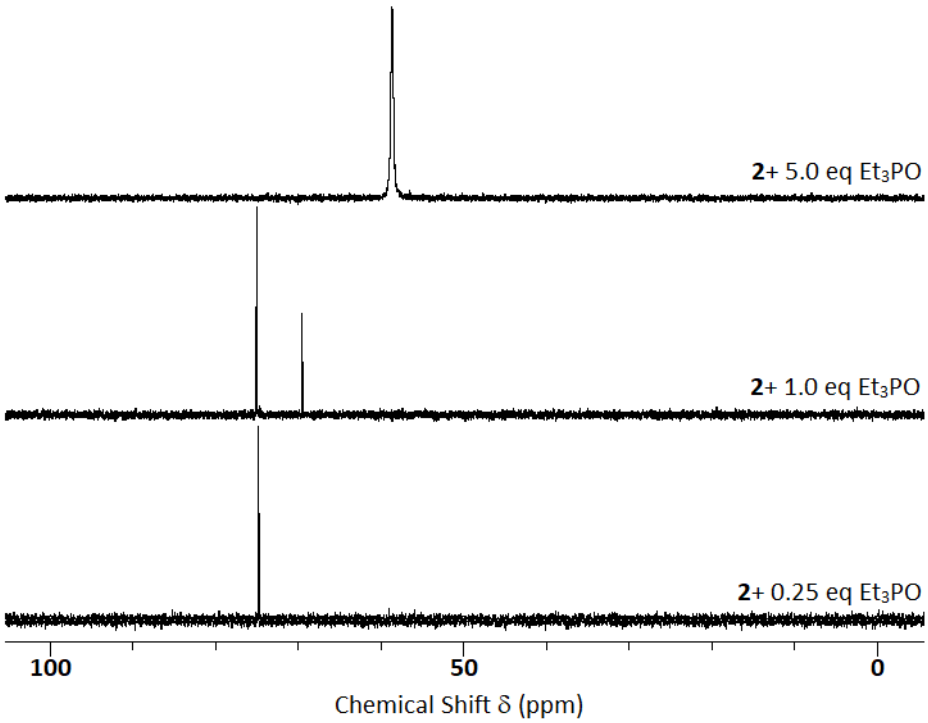


Figure S8: *In situ* reaction between **2** and Et_3PO in *ortho*-dichlorobenzene-D4 as monitored using ^{31}P NMR spectroscopy.

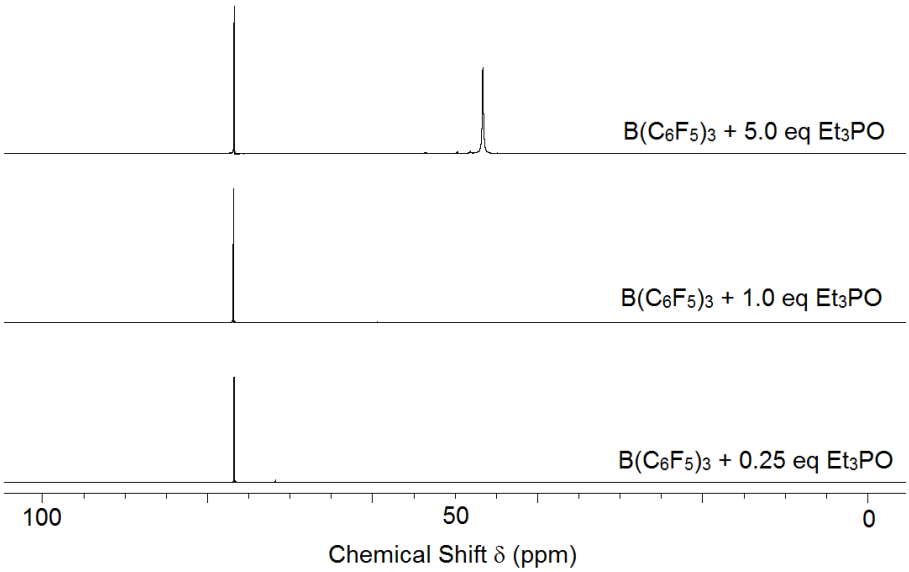


Figure S9: *In situ* reaction between $B(C_6F_5)_3$ and Et_3PO in *ortho*-dichlorobenzene-D4 as monitored using ^{31}P NMR spectroscopy.

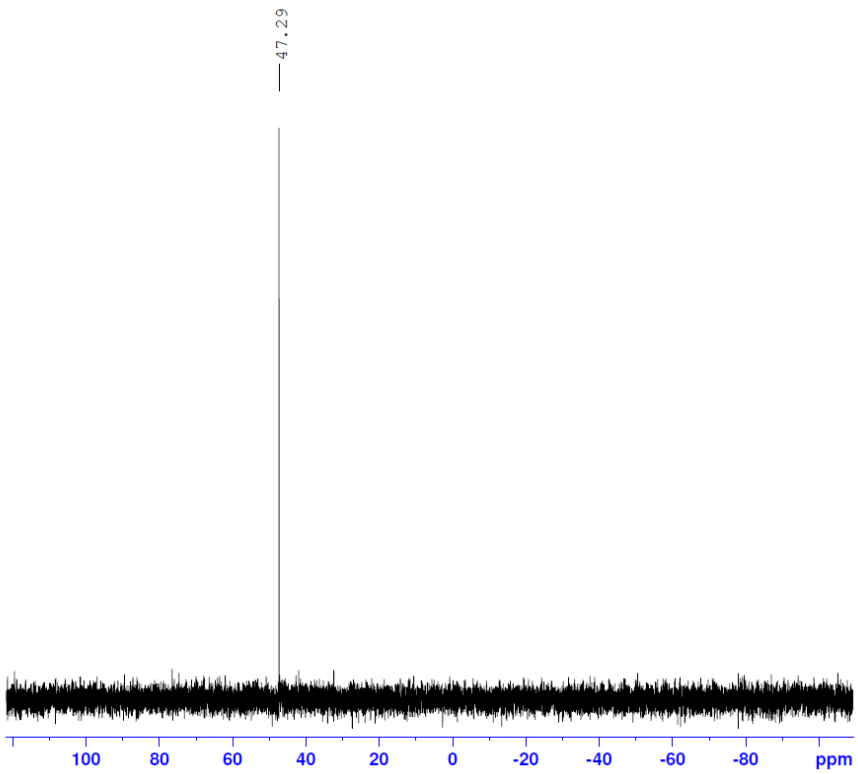
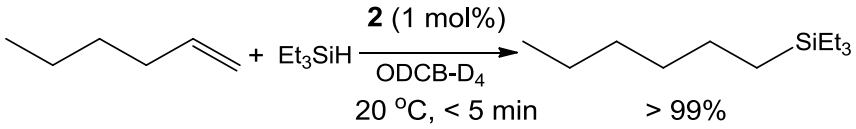


Fig S10: ^{31}P NMR spectrum of triethylphosphine oxide in *ortho*-dichlorobenzene-D4

4. Catalytic Hydrosilylation

Typical procedure: 1 mmol of triethylsilane (0.158 ml) and 1 mmol of olefin were mixed in a J-young nmr tube followed by the addition of 0.6 ml of *ortho*-dichlorobenzene-D_4. ^{1}H NMR spectrum of the solution was recorded 0.001 mmol of compound **2** was added to this solution at 20 °C and the completion of hydrosilylation was confirmed by NMR spectroscopy. 0.1 mmol of mesitylene was used as an internal reference.

4.1. Hydrosilylation of 1-hexene



Scheme S1: Catalytic hydrosilylation of 1-hexene.

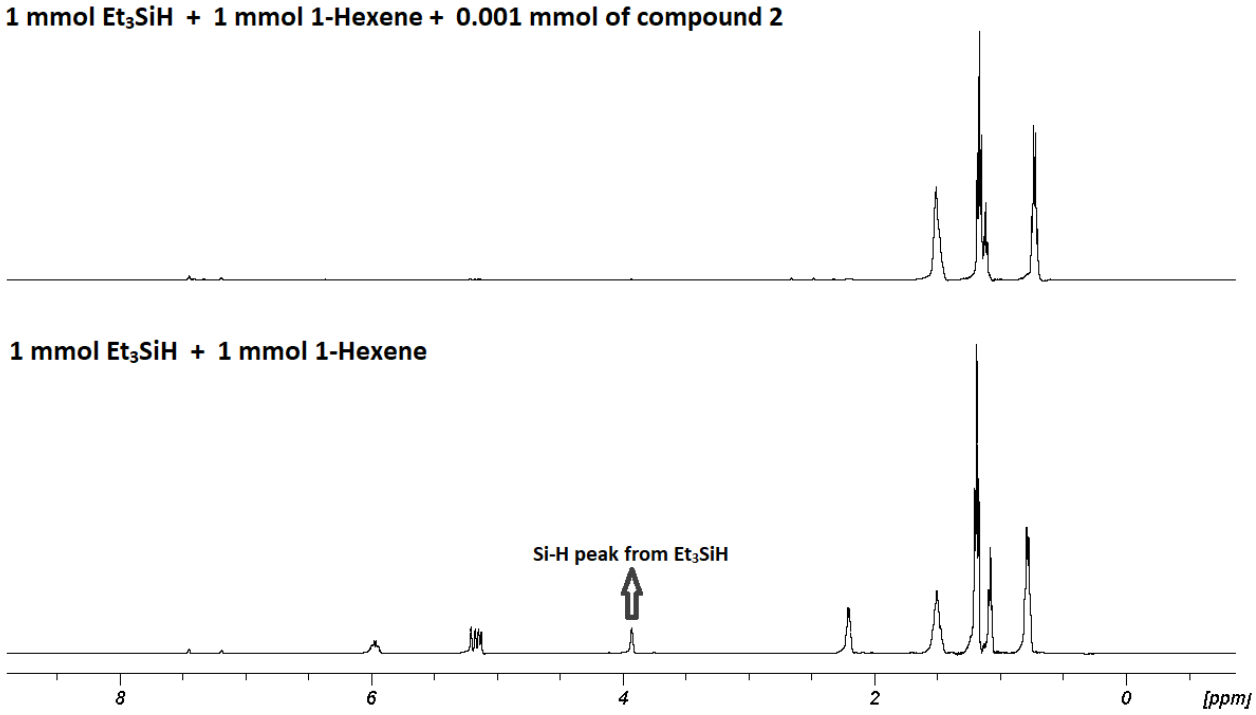


Figure S11: Stacking of ^{1}H NMR spectra of hydrosilylation mixture (Et_3SiH and 1-hexene) before (bottom) and after (top) the addition of compound **2** recorded in in *ortho*-dichlorobenzene-D4.

4.1.1 Characterization of triethyl(hexyl)silane

^{1}H NMR (*ortho*-dichlorobenzene-D_4, 500 MHz) : δ: 1.23 (m, $CH_2CH_2CH_2CH_2$, 8H), δ 0.89 (t, $SiCH_2CH_3$,9H), δ 0.84 (t, $-CH_2CH_3$, 3H), δ 0.45 (m, $SiCH_2$, 8H).

^{13}C NMR (*ortho*-dichlorobenzene-D_4, 125 MHz) : δ 34.0 (CH_2), δ 31.9 (CH_2), δ 24.2 (CH_2), δ 23.0 (CH_2), δ 14.4 (CH_2CH_3), δ 11.16 ($SiCH_2$), δ 7.7 ($SiCH_2CH_3$), δ 3.7 ($SiCH_2$).

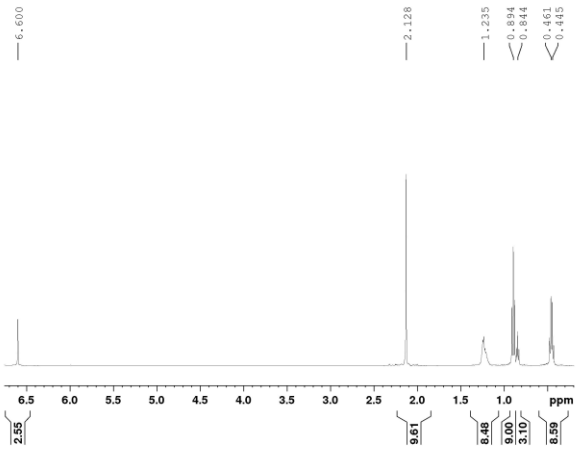


Figure S12: ^{1}H NMR spectrum of triethyl(hexyl)silane in *ortho*-dichlorobenzene-D4.

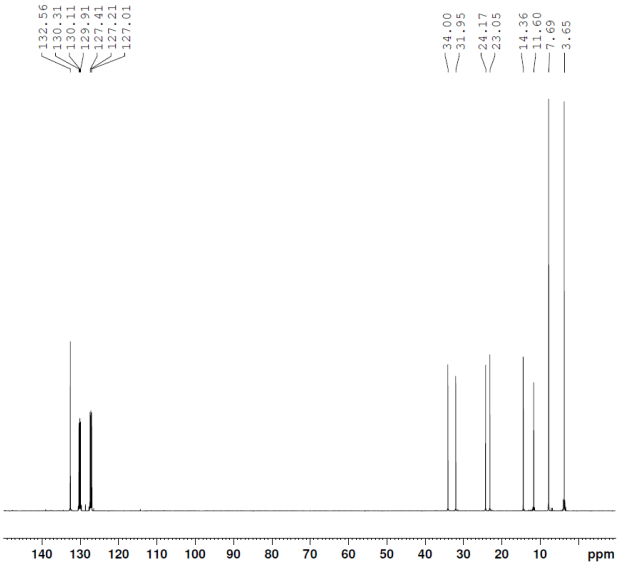
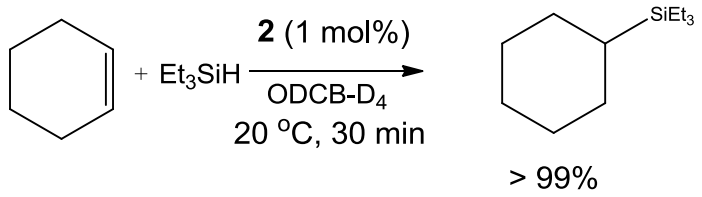


Figure S13: ^{13}C NMR spectrum of triethyl(hexyl)silane in *ortho*-dichlorobenzene-D4.

4.2 Hydrosilylation of Cyclohexene



Scheme S2: Catalytic hydrosilylation of cyclohexene.

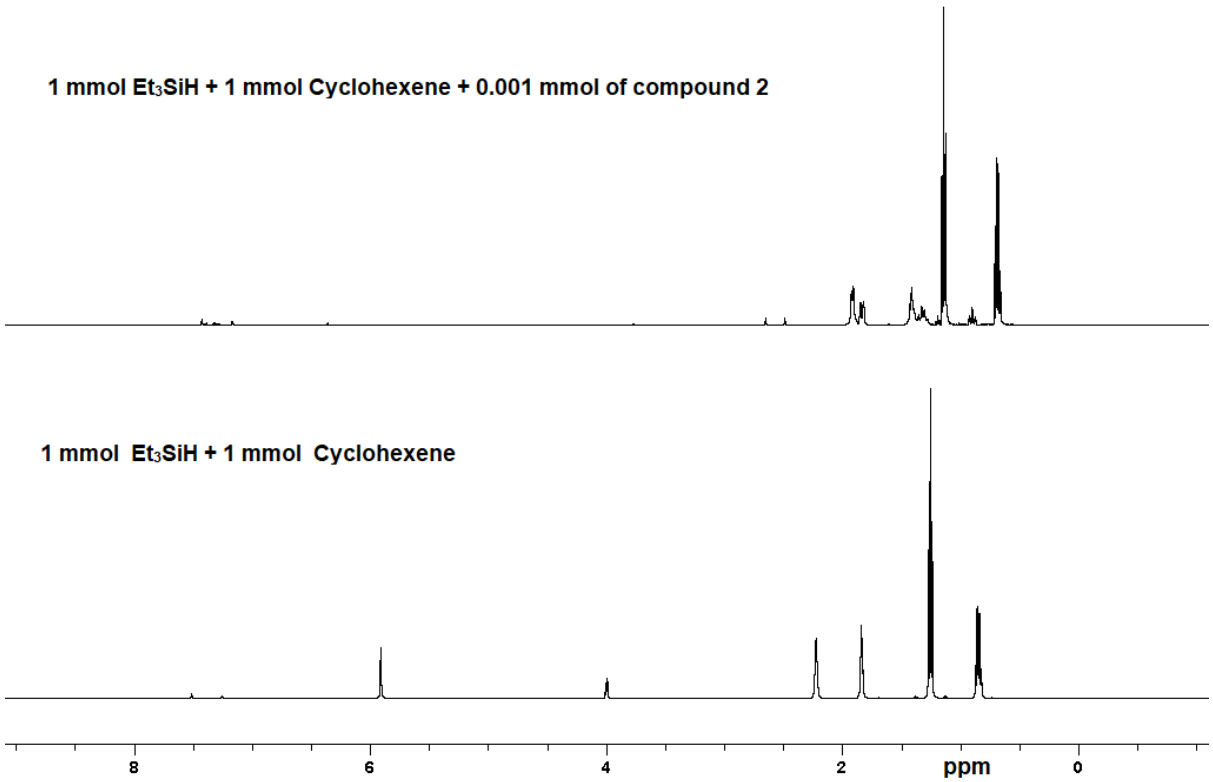


Figure S14: Stacking of ^{1}H NMR spectra of hydrosilylation mixture (Et_3SiH and Cyclohexene) before (bottom) and after (top) the addition of compound **2** in *ortho*-dichlorobenzene-D4.

4.2.1 Characterization of triethyl(cyclohexyl)silane

^{1}H NMR (*ortho*-dichlorobenzene-D_4, 500 MHz) : δ: 1.92 (m, C*H*$_2$C*H*$_2$C*H*(H), 5H), δ: 1.42 (m, C*H*$_2$C*H*$_2$C*H*(H), 5H), δ 1.14 (t, SiCH$_2$C*H*$_3$, 9H), δ 0.90 (m, -SiCHC*H*$_3$, 1H), δ 0.69 (m, SiC*H*$_2$, 6H).

^{13}C NMR (*ortho*-dichlorobenzene-D_4, 125 MHz) : δ 28.6 (*C*H$_2$), δ 28.1 (*C*H$_2$),. δ 27.1 (*C*H$_2$), δ 23.8 (Si*C*H), δ 7.9 (SiCH$_2$*C*H$_3$), δ 2.2 (Si*C*H$_2$).

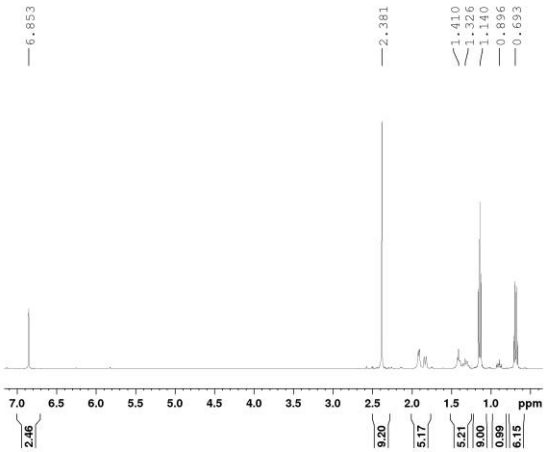


Figure S15: ^{1}H NMR spectrum of triethyl(cyclohexyl)silane in *ortho*-dichlorobenzene-D4.

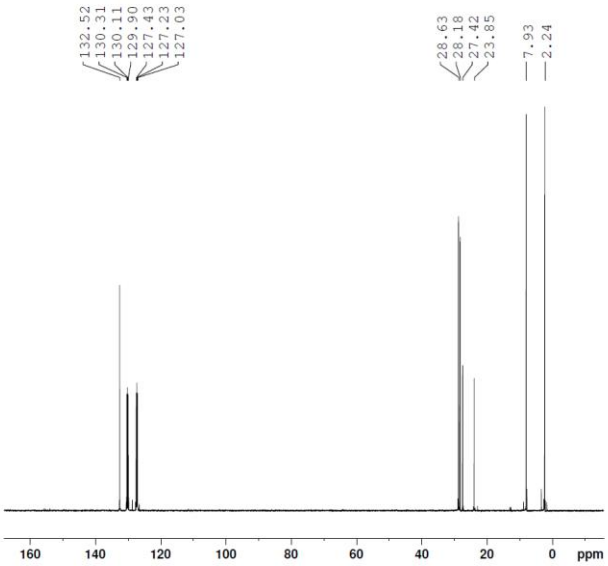
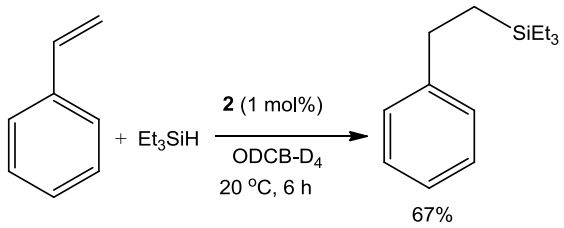


Figure S16: ^{13}C NMR spectrum of triethyl(cyclohexyl)silane in *ortho*-dichlorobenzene-D4.

4.3 Hydrosilylation of Styrene



Scheme S3: Catalytic hydrosilylation of styrene.

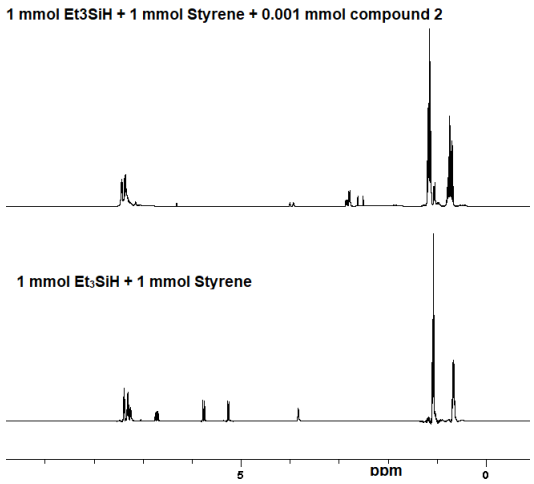


Figure S17: Stacking of ^{1}H NMR spectra of hydrosilylation mixture (Et_3SiH and styrene) before (bottom) and after (top) the addition of compound **2** in *ortho*-dichlorobenzene-D4.

4.3.1 Characterization of triethyl(phenylethyl)silane

^{1}H NMR (*ortho*-dichlorobenzene-D_4, 500 MHz) : δ 7.37 (m, C_6H_5, 5H), δ 2.81 (m, $SiCH_2CH_2$, 2H),. δ 1.16 (m, $SiCH_2CH_3$, 9H), δ 1.04 (m, $SiCH_2CH_2$, 2H), δ 0.75 (m, $SiCH_2CH_3$, 6H).

^{13}C NMR (*ortho*-dichlorobenzene-D_4, 125 MHz) : δ 128.5, C_6H_5), δ 30.35 ($C_6H_5CH_2$), δ 7.68 ($SiCH_2CH_3$), δ 3.05 ($SiCH_2CH_2$), δ 2.76 ($SiCH_2CH_3$).

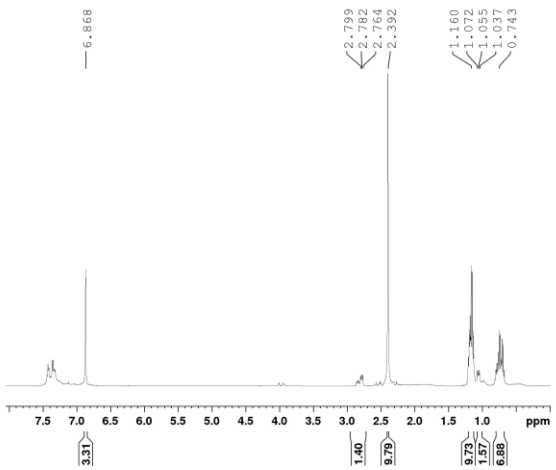


Figure S18: ^{1}H NMR spectrum of triethyl(phenylethyl)silane in *ortho*-dichlorobenzene-D4.

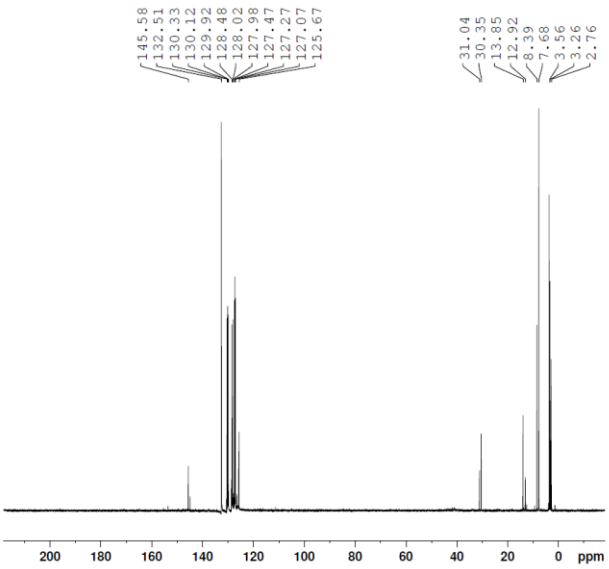
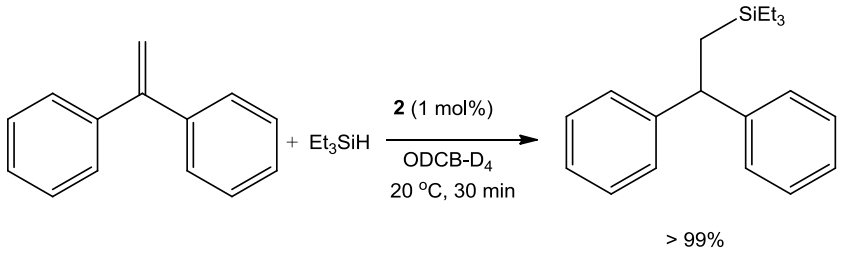


Figure S19: ^{13}C NMR spectrum of triethyl(phenylethyl)silane in *ortho*-dichlorobenzene-D4.

4.4 Hydrosilylation of diphenylethylene



Scheme S4: Catalytic hydrosilylation of diphenylethylene.

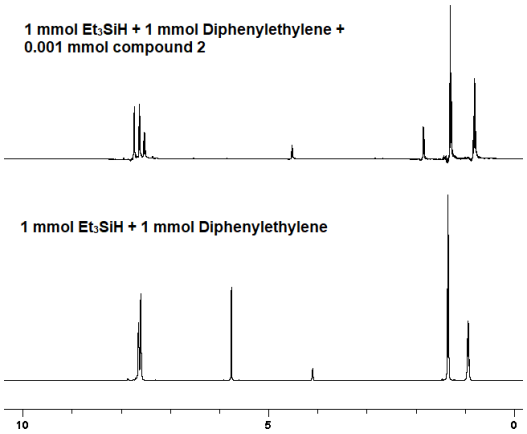


Figure S20: Stacking of ^{1}H NMR spectra of hydrosilylation mixture (Et_3SiH and diphenylethylene) before (bottom) and after (top) the addition of compound **2** in *ortho*-dichlorobenzene-D4.

4.4.1 Characterization of (2,2-diphenylethyl)triethylsilane

^{1}H NMR (*ortho*-dichlorobenzene-D_4, 500 MHz) : δ 7.56 (d, o-C*H*-Phenyl, 4H), δ 7.45 (t, m-C*H*-Phenyl, 4H), δ 7.35 (t, p-C*H*-Phenyl, 2H), δ 4.34 (t, Ph_2CH, 1H), δ 2.05 (d, CH_2CH, 2H), δ 1.12 (t, $SiCH_2CH_3$, 9H), δ 0.63 (q, $SiCH_2CH_3$, 6H).

^{13}C NMR (*ortho*-dichlorobenzene-D_4, 125 MHz) : δ 127.7 (C_6H_5), δ 47.58 (C_6H_5CH), δ 19.30 ($SiCH_2CH$), δ 7.68 ($SiCH_2CH_3$), δ 3.89 ($SiCH_2CH_3$).

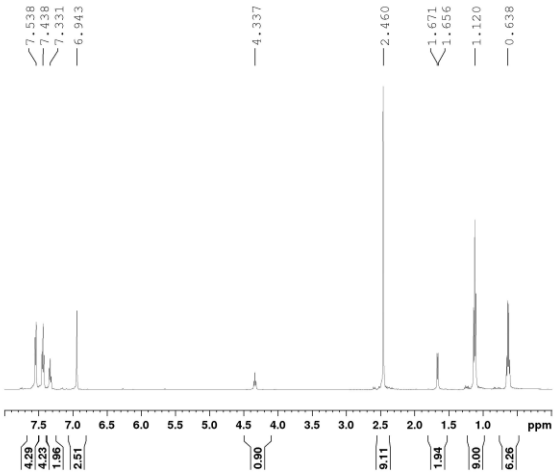


Figure S21: ^{1}H NMR spectrum of (2,2-diphenylethyl)triethylsilane in *ortho*-dichlorobenzene-D4.

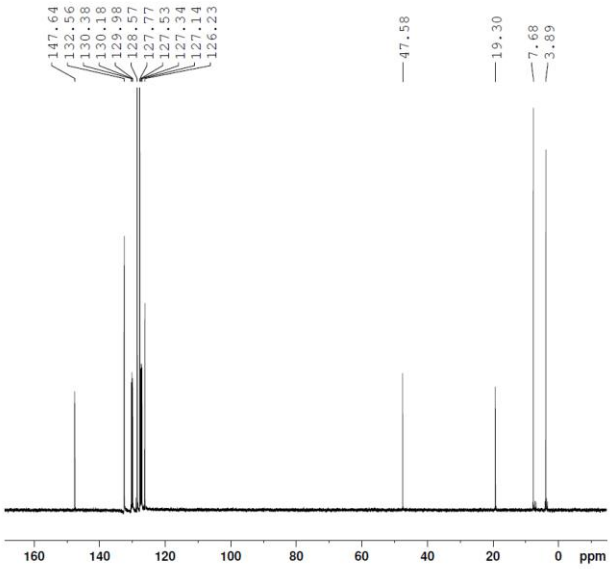
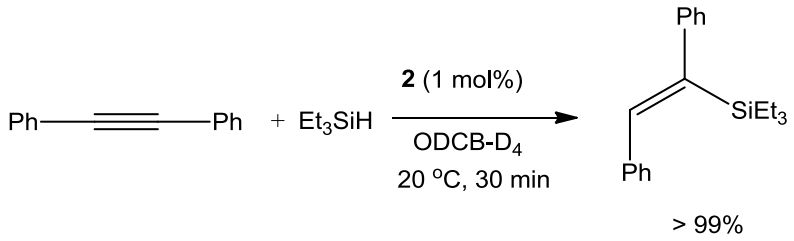


Figure S22: ^{13}C NMR spectrum of (2,2-diphenylethyl)triethylsilane in *ortho*-dichlorobenzene-D4.

4.5 Hydrosilylation of diphenylacetylene



Scheme S5: Catalytic hydrosilylation of diphenylacetylene.

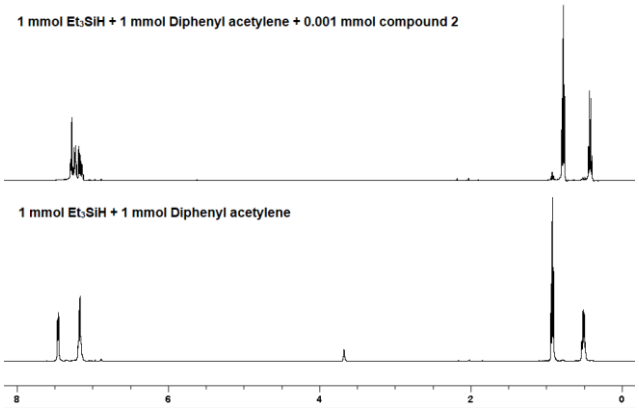


Figure S23: Stacking of ^{1}H spectra of hydrosilylation mixture (Et_3SiH and diphenylacetylene) before (bottom) and after (top) the addition of compound **2** in *ortho*-dichlorobenzene-D4.

4.5.1 Characterization of (2,2-diphenylvinyl)triethylsilane

^{1}H NMR (*ortho*-dichlorobenzene-D_4, 500 MHz) : δ 7.2 (m, C_6H_5, 10H), δ 7.2 (m, C*H*, 1H), δ 0.78 (m, $SiCH_2CH_3$, 9H), δ 0.43 (m, $SiCH_2CH_3$, 6H).

^{13}C NMR (*ortho*-dichlorobenzene-D_4, 125 MHz) : δ 146.9 (*C*H), δ 139.9 (C_6H_5C), δ 127.3 (C_6H_5), δ 7.58 ($SiCH_2CH_3$), δ 4.58 ($SiCH_2CH_3$).

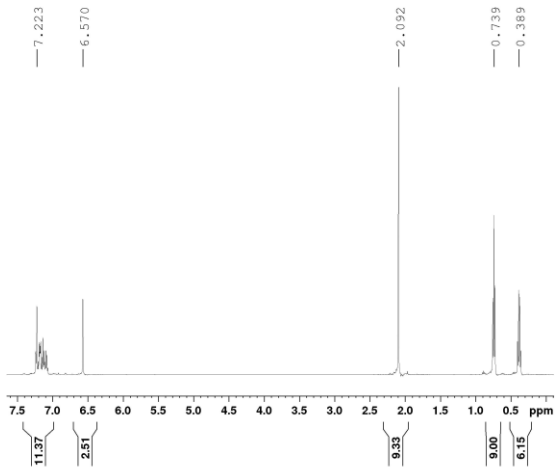


Figure S24: ^{1}H NMR spectrum of (2,2-diphenylvinyl)triethylsilane in *ortho*-dichlorobenzene-D4.

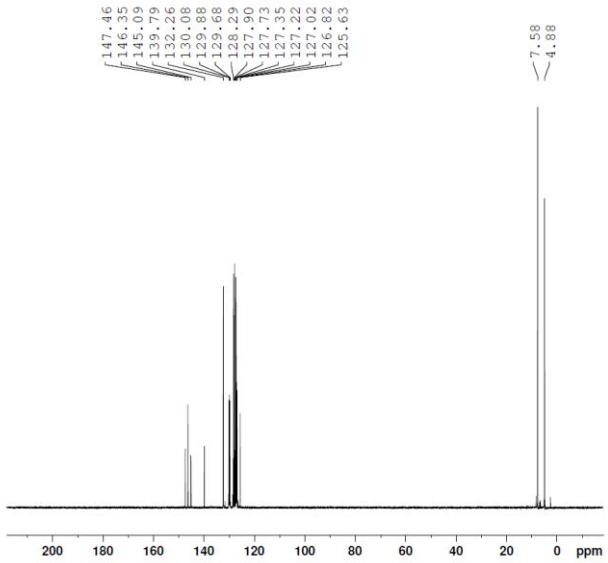


Figure S25: ^{13}C NMR spectrum of (2,2-diphenylvinyl)triethylsilane in *ortho*-dichlorobenzene-D4.

5. Crystallographic Details:

Single-crystal X-ray crystallography for structural analysis was performed with a Bruker Kappa Apex-II CCD diffractometer at 298 K and with Mo-Kα irradiation (λ = 0.71073 Å). The structures were solved by direct methods using either SHELX2014 or SHELX-2017. Crystallographic data, details of data collection and structure refinement parameters for compounds **1**, and **2** are presented below:

Table S1. Crystal data and structure refinement for **1**.

Identification code	compound1	
CCDC Number	CCDC 1410594	
Empirical formula	C15 H22 B Bi Cl2 N6	
Formula weight	577.07	
Temperature	150 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/n	
Unit cell dimensions	a = 14.6366(17) Å	α= 90°.
	b = 7.7961(10) Å	β= 106.437(5)°.
	c = 17.985(2) Å	γ = 90°.
Volume	1968.4(4) $Å^3$	
Z	4	
Density (calculated)	1.947 Mg/m^3	
Absorption coefficient	9.239 mm^{-1}	
F(000)	1104	
Crystal size	0.150 x 0.100 x 0.100 mm^3	
Theta range for data collection	2.867 to 25.996°.	
Index ranges	-17<=h<=17, -9<=k<=9, 0<=l<=22	
Reflections collected	6964	
Independent reflections	6964 [R(int) = ?]	
Completeness to theta = 26.000°	97.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.591 and 0.442	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6964 / 172 / 236	
Goodness-of-fit on F^2	1.073	
Final R indices [I>2sigma(I)]	R1 = 0.0387, wR2 = 0.0993	
R indices (all data)	R1 = 0.0496, wR2 = 0.1054	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.239 and -2.217 e.$Å^{-3}$	

Table S2.Crystal data and structure refinement for 2.

Identification code	compound2	
CCDC Number	CCDC 1847457	
Empirical formula	C93 H45.83 B3 Bi Cl6.18 F40 N6	
Formula weight	2467.49	
Temperature	150 K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 13.48(5) Å	α= 70.79(7)°.
	b = 16.02(6) Å	β= 80.64(7)°.
	c = 24.09(9) Å	γ = 67.07(6)°.
Volume	4523(29) $Å^3$	
Z	2	
Density (calculated)	1.812 Mg/m^3	
Absorption coefficient	2.268 mm^{-1}	
F(000)	2418	
Crystal size	0.150 x 0.120 x 0.012 mm^3	
Theta range for data collection	2.547 to 25.000°.	
Index ranges	-16<=h<=16, -19<=k<=19, -28<=l<=28	
Reflections collected	41181	
Independent reflections	15828 [R(int) = 0.1052]	
Completeness to theta = 25.000°	99.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.74 and 0.55	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	15828 / 430 / 1426	
Goodness-of-fit on F^2	1.025	
Final R indices [I>2sigma(I)]	R1 = 0.0698, wR2 = 0.1513	
R indices (all data)	R1 = 0.1206, wR2 = 0.1786	
Extinction coefficient	0.0039(3)	
Largest diff. peak and hole	3.180 and -1.196 $e.Å^{-3}$	

6. Computational Details:

Quantum chemical calculations were performed using Gaussian 09[5] quantum chemistry program package. All geometries were optimized using density functional theory (DFT) with the hybrid functional PBE0[6] and def2-TZVP[7] basis set for all atoms. The nature of stationary points were characterized by the Hessian matrix of force constants. All structures were obtained as minima on their potential energy surfaces (PES). Natural bond orbital (NBO)[8] analysis was carried out to analyse the nature of lone-pair and charge on the Bi atom.

The nature of Bi-N bonds was analyzed using energy partitioning scheme [9] of Amsterdam Density Functional (ADF)[10] program package with the hybrid functional PBE0. A triple zeta plus double polarization (TZ2P) basis set was employed for all the atoms. Slater-type orbitals (STOs) were used as basis functions[11]. Scaler relativistic effects were considered using zero-order regular approximation (ZORA)[12].

The interaction energy, ΔE_{int} was calculated between Bi^{3+} and $[Tp^{Me2}]^-$ fragments for the complex **2** and $BiCl_2^+$ and $[Tp^{Me2}]^-$ for the complex **1**. Further, the total interaction energy, ΔE_{int} was decomposed into three components:

$$\Delta E_{int} = \Delta E_{elstat} + \Delta E_{Pauli} + \Delta E_{orb}$$

The electrostatic (ΔE_{elstat}) interaction energy between two fragments is calculated using the frozen electron density distribution of the fragments in the complex. The repulsive (ΔE_{Pauli}) interactions are calculated by enforcing the Kohn-Sham determinant on the superimposed fragments to obey the Pauli principle by anti-symmetrization and renormalization. The orbital interaction term (ΔE_{orb}) constitutes the covalent contribution to the total interaction energy. This term accounts for all contributions resulting from electron pair bonding, charge transfer and intrafragment polarization.

The topology of the electron density at bond critical point (BCP) was calculated using Quantum Theory of Atoms in Molecules (QTAIM)[13]. AIMALL[14] program package was used with the wave function files generated at PBE0/Def2-TZVP method.

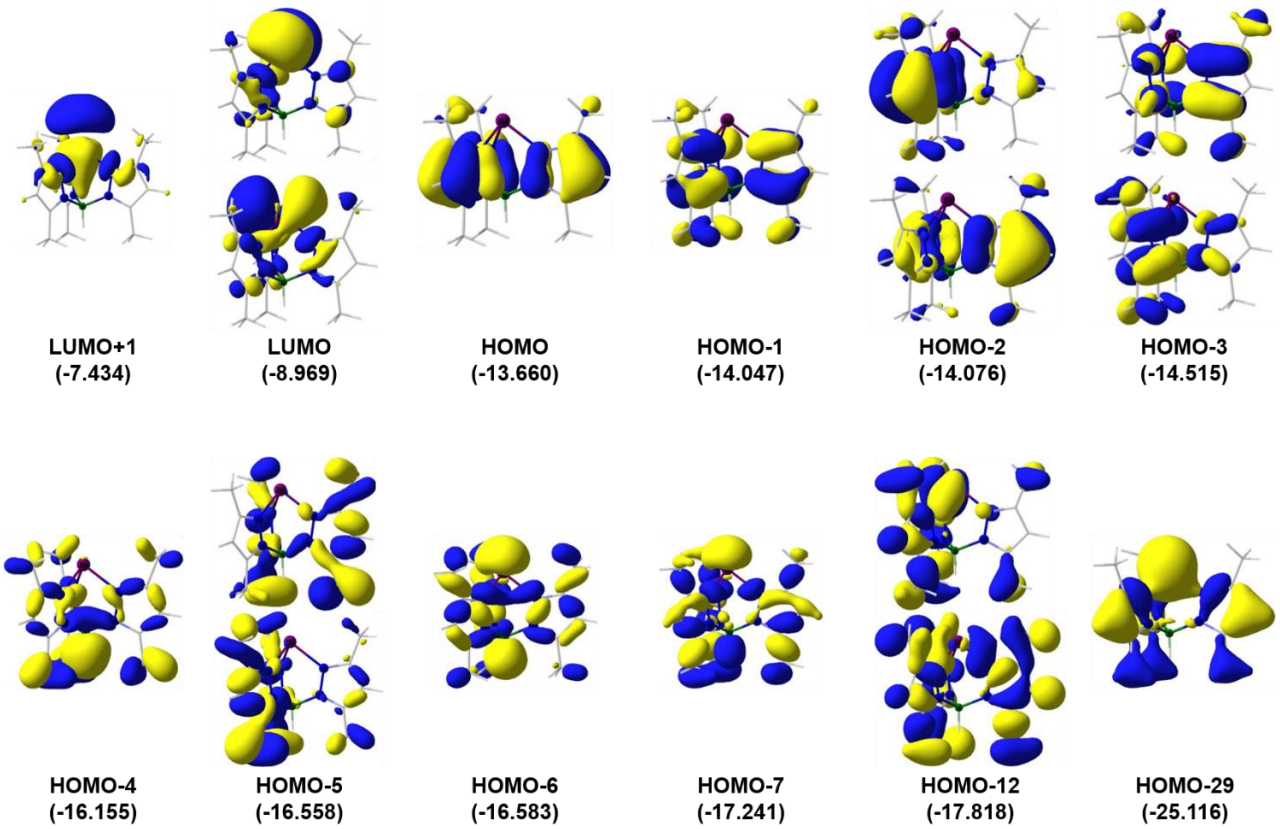
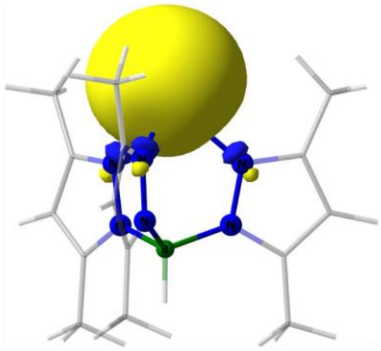


Figure S26. Plots of the frontier valence orbitals (isovalue = 0.03) of $[Tp^{Me2}Bi]^{2+}$ molecule at PBE0 functional using def2-TZVP basis set for all atoms. The eigenvalues [eV] are given below.

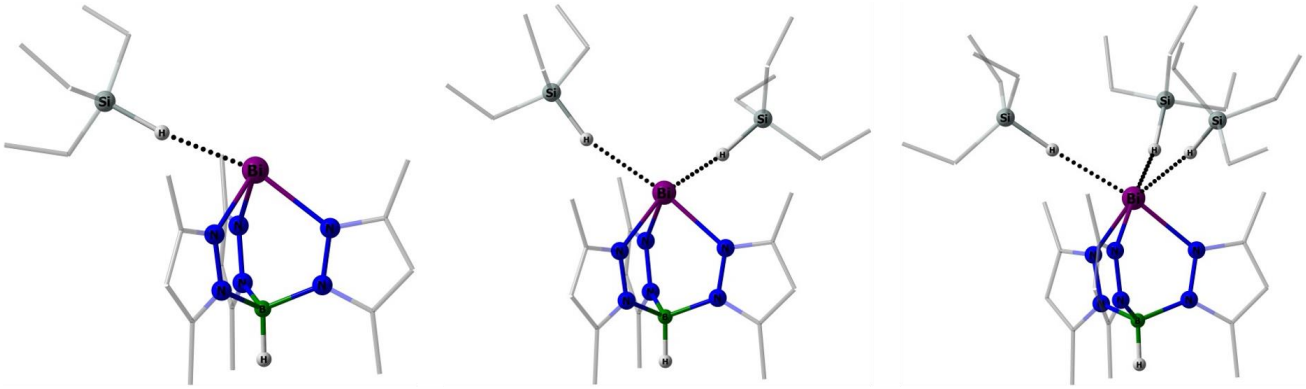
The MO delocalized over three pyrazole rings of the ligand viz. HOMO, HOMO-1, HOMO-2, HOMO-3, HOMO-4, HOMO-5, do not contribute to Bi-N bonding. So, these molecular orbitals are not considered in MO interaction diagram for simplicity (Fig 3). This makes HOMO-6 as the highest occupied orbital in the interaction diagram.



LP_{occ} = 1.98

(88.34% s, 11.64% p, 0.00% d)

Figure S27. Plot of Bi centred NBO non-bonding lone-pair orbital of s-character (isovalue = 0.02) for complex **2**.



(a) (b) (c)

Figure S28. Optimized geometries $[Tp^{Me2}Bi\cdots(H—SiEt_3)_n]^{2+}$ (n=1 - 3) complexes at DFT method using PBE0 functional with def2-TZVP basis set for all atoms.

Table S3. Selected interatomic distances (Å) and WBI index of $[Tp^{Me2}Bi\cdots(H—SiEt_3)_n]^{2+}$ (n = 1 and 3) calculated at PBE0 level with Def2-TZVP basis set for all atoms.

		Bond Length (Å)	WBI Index
$[Tp\text{-}Bi\text{---}H\text{-}SiEt_3]^{2+}$	Bi---H	2.394	0.13
	Si-H	1.579	0.70
$[Tp\text{-}Bi\text{---}(H\text{-}SiEt_3)_3]^{2+}$	Bi---H1	2.555	0.106
	Bi---H2	2.601	0.097
	Bi---H3	2.622	0.094
	Si1-H1	1.556	0.75
	Si2-H2	1.552	0.76
	Si3-H3	1.550	0.77

Table S4. Selected bond angles (°) and NBO charges of $[Tp^{Me2}Bi\cdots(H—SiEt_3)_n]^{2+}$ (n = 1 - 3) calculated at PBE0 level with Def2-TZVP basis set for all atoms.

		Bond Angle (°)	NBO Charge
$[Tp\text{-}Bi\text{---}H\text{-}SiEt_3]^{2+}$	Bi-H-Si	171.1	Si +1.57
			H -0.34
$[Tp\text{-}Bi\text{---}(H\text{-}SiEt_3)_2]^{2+}$	Bi---H1-Si1	161.6	Si1 +1.55
			H1 -0.32
	Bi---H2-Si2	160.8	Si2 +1.53
			H2 -0.31
$[Tp\text{-}Bi\text{---}(H\text{-}SiEt_3)_3]^{2+}$	Bi---H1-Si1	171.0	Si1 +1.53
			H1 -0.31
	Bi---H2-Si2	174.7	Si2 +1.52
			H2 -0.31
	Bi---H3-Si3	149.2	Si3 +1.51
			H3 -0.29

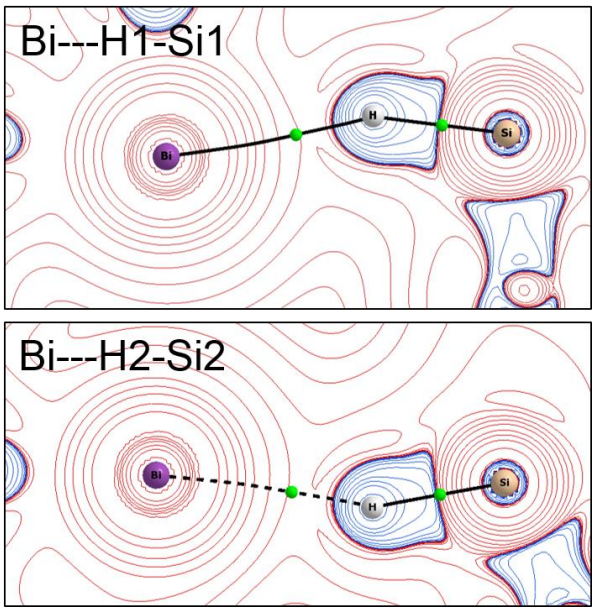


Figure S29. Contour line diagram of the Laplacian $-\nabla^2\rho(r)$ maps of σ-Si1-H1-Bi (Top) and σ-Si2-H2-Bi (Down) complex in the plane defined by Bi, H1/H2 and Si1/Si2 atoms. Bond paths are shown as black lines and BCP as solid green dots.

Optimized coordinates of molecules by DFT

Cartesian coordinates and the total energy (a.u.) of the optimized structures using PBE0 hybrid functional and def2-TZVP basis set for all atoms.

Complex **1**

E_{Total} = -2072.42260381 a.u.

H	-3.13432600	-0.02573100	1.05073000
C	0.31837700	-3.22901600	-2.37493900
H	0.12192300	-4.27899800	-2.59315300
H	1.25838500	-3.16242700	-1.82398500
H	0.44329900	-2.71335200	-3.33200700
C	-0.80555900	-2.64715500	-1.59378000
C	-2.12101900	-3.10516300	-1.48431400
H	-2.54687500	-3.98495900	-1.93982100
C	-2.76648100	-2.20198000	-0.66053300
C	-4.18061200	-2.20450900	-0.20347100
H	-4.25445800	-2.23872200	0.88561900
H	-4.69044500	-3.07955900	-0.60604100
H	-4.71785900	-1.31524900	-0.54075600
C	0.29775300	3.31201700	-2.26546300
H	0.09241500	4.36622700	-2.45289700
H	0.42839900	2.82586400	-3.23712000
H	1.23750800	3.23709500	-1.71527000
C	-0.82225100	2.69754900	-1.50393100
C	-2.14145000	3.14161500	-1.38273700
H	-2.57331200	4.03199800	-1.81122500
C	-2.78139400	2.20784800	-0.58933900
C	-4.19643100	2.18504100	-0.13562500
H	-4.71415800	3.06439300	-0.51826400
H	-4.27312400	2.19266300	0.95383500
H	-4.72395500	1.29878000	-0.49526800
C	2.39906500	-0.08504700	2.98053100
H	2.90103000	0.73202300	2.46150100

H	2.83774800	-1.01729600	2.62156200
H	2.58548900	0.00589500	4.05041700
C	0.93540400	-0.06115400	2.74255600
C	-0.06241000	-0.07439400	3.71008100
H	0.08059000	-0.09498300	4.77817600
C	-1.26571000	-0.05594800	3.03209500
C	-2.63588000	-0.06074900	3.60706100
H	-3.20096400	0.82607700	3.31411800
H	-2.56586600	-0.07728400	4.69447100
H	-3.20564400	-0.93548500	3.28786100
N	-0.67324800	-1.53497000	-0.87474200
N	-1.86681000	-1.26349400	-0.30963100
N	-0.68249800	1.56439600	-0.81975800
N	-1.87498500	1.26594400	-0.26622100
N	0.34753400	-0.03356800	1.53705900
N	-1.00143800	-0.03132100	1.71599100
B	-2.04142100	-0.01378300	0.56735900
Bi	1.29558400	0.01517400	-0.54672400
Cl	2.79313200	-1.95712400	0.12241200
Cl	2.76683900	1.98476600	0.19292900

Complex **2**

E_{Total} = -1151.66142594 a.u.

H	2.93302400	0.00250400	-0.00313000
C	-1.71811600	3.60138500	-0.32193500
H	-1.71681400	4.61166600	0.08658100
H	-2.45309200	3.02594300	0.24864000
H	-2.06049300	3.67003900	-1.35834500
C	-0.35686800	3.01719100	-0.25023200
C	0.87821600	3.63190100	-0.31073100
H	1.06599100	4.69019900	-0.39859900

C	1.83949500	2.62613100	-0.23385100
C	3.31481500	2.76038800	-0.25321400
H	3.76236600	2.37051300	0.66307000
H	3.58527500	3.81090900	-0.34334100
H	3.75240700	2.22237400	-1.09639000
C	-1.71626600	-2.08269300	-2.95628200
H	-2.04666100	-3.02762300	-2.51595700
H	-1.72068000	-2.21010700	-4.03864600
H	-2.45753400	-1.31325300	-2.72103700
C	-0.35547700	-1.72625300	-2.48680800
C	0.87990200	-2.08459300	-2.98933600
H	1.06818300	-2.69011900	-3.86161400
C	1.84077000	-1.51241500	-2.15827100
C	3.31614800	-1.59404500	-2.26614200
H	3.58665800	-2.19356100	-3.13347600
H	3.75479500	-2.05868400	-1.38086900
H	3.76272300	-0.60473700	-2.38281900
C	-1.70922600	-1.52385300	3.28369200
H	-2.45685100	-1.67888800	2.50021400
H	-2.02921100	-0.68237000	3.90443200
H	-1.71699800	-2.41333000	3.91355700
C	-0.34986700	-1.29233100	2.73817200
C	0.88677000	-1.54675100	3.29799400
H	1.07707300	-1.99994900	4.25787500
C	1.84557100	-1.10974200	2.38657900
C	3.32121700	-1.15881100	2.50946800
H	3.76831000	-1.75343500	1.71050200
H	3.59398400	-1.60948800	3.46201500
H	3.75733900	-0.15876000	2.46853000
N	-0.13844200	1.68820900	-0.13804700
N	1.20353500	1.44868700	-0.12933000
N	-0.13750300	-0.96322400	-1.39287200
N	1.20434600	-0.83313500	-1.19114900
N	-0.13448700	-0.72518900	1.53069300

N	1.20688400	-0.61183400	1.31596300
B	1.74526600	0.00166700	-0.00202700
Bi	-1.48757800	-0.00091400	0.00153600

Complex **[Tp^{Me2}Bi---H-$SiEt_3$]$^{2+}$**

E_{TOTAL} = -1679.14163606 a.u.

H	3.16442500	-0.21285900	2.14650100
C	2.76394800	0.16229200	-3.70547600
H	3.46583800	0.74063400	-4.30613600
H	1.78646000	0.64362800	-3.79791000
H	2.69850100	-0.83416500	-4.15058100
C	3.22965900	0.08543800	-2.29818800
C	4.52050300	0.01930300	-1.79992500
H	5.43491400	0.03697200	-2.37104400
C	4.41123100	-0.07183900	-0.41748100
C	5.49333600	-0.16461500	0.59159900
H	5.45939300	0.67153100	1.29263300
H	6.46084900	-0.14945800	0.09296300
H	5.42348400	-1.08889900	1.16846800
C	-1.16379800	-3.18939800	-0.47963800
H	-1.82345800	-3.89021500	0.03133200
H	-0.71870100	-3.72130800	-1.32542900
H	-1.78360300	-2.37737300	-0.86749100
C	-0.11299300	-2.70066400	0.44407200
C	0.49512300	-3.33974600	1.50763700
H	0.26514700	-4.32331900	1.88481700
C	1.47046700	-2.47444200	1.99416200
C	2.41103000	-2.68727200	3.11984800
H	2.19280900	-3.63786900	3.60339600
H	2.32826400	-1.89560800	3.86628800
H	3.44591600	-2.71385900	2.77250000

C	-0.89272800	3.41099200	-0.06409800
H	-1.49992700	2.71132500	-0.64348700
H	-0.38905100	4.09065800	-0.75697300
H	-1.57439000	4.00894600	0.54040800
C	0.09629900	2.71934500	0.79566800
C	0.72496100	3.15408300	1.94757700
H	0.56015800	4.08958200	2.45770600
C	1.62377100	2.15836500	2.31681600
C	2.55115100	2.13855200	3.47301500
H	2.38879500	1.26080300	4.10073100
H	2.39479100	3.02770800	4.08121800
H	3.59324600	2.12980900	3.14696100
N	2.38252000	0.03657800	-1.25388900
N	3.10375100	-0.05939800	-0.10545400
N	0.46727100	-1.49045000	0.31181200
N	1.44155400	-1.35584900	1.25330600
N	0.59162100	1.50125200	0.49848600
N	1.53154000	1.16122600	1.42288500
B	2.38032200	-0.12358800	1.25769600
Bi	0.14657700	0.11623000	-1.12729800
H	-2.11345700	0.18529600	-0.34155700
Si	-3.64894900	0.05996400	0.00584200
C	-4.37618600	-0.88104900	-1.44704800
C	-5.71520300	-1.56521000	-1.15261700
H	-3.65933100	-1.63450400	-1.79283200
H	-4.48811100	-0.17782200	-2.28071100
H	-6.09271200	-2.07094800	-2.04308900
H	-5.61990600	-2.31710300	-0.36623100
H	-6.47877400	-0.85239800	-0.83678200
C	-3.63051300	-0.86680800	1.63686600
C	-4.92380200	-0.76742700	2.45132300
H	-2.79432600	-0.48052200	2.23137500
H	-3.39546600	-1.91817100	1.43426000
H	-4.84486800	-1.34853600	3.37202300

H	-5.13874100	0.26392700	2.73706400
H	-5.78724000	-1.14567900	1.90116300
C	-4.24989900	1.83180500	0.11870600
C	-5.77504900	1.98395500	0.09373200
H	-3.82491500	2.39467500	-0.72022100
H	-3.84042500	2.28121500	1.03073300
H	-6.05600800	3.03483600	0.18383700
H	-6.20014400	1.61569200	-0.84207300
H	-6.25728600	1.44729800	0.91233500

Complex **[Tp^{Me2}Bi---(H-$SiEt_3$)$_2$]$^{2+}$**

E_{TOTAL} = -2206.61692175 a.u.

H	-4.30202700	-0.83538700	1.12827800
C	-1.40541700	2.45202200	-2.76487300
H	-1.46842600	1.95029700	-3.73442500
H	-0.38145900	2.35657900	-2.39548500
H	-1.59541900	3.51156100	-2.93623000
C	-2.40075900	1.88887400	-1.81977600
C	-3.74717400	2.18310900	-1.68229400
H	-4.30478500	2.92928200	-2.22520000
C	-4.24569300	1.32013400	-0.71398200
C	-5.63214800	1.21142300	-0.19939800
H	-6.07099300	0.24034800	-0.43732300
H	-6.25207000	1.98186500	-0.65467800
H	-5.66931000	1.33903700	0.88384500
C	1.26539000	0.01729300	2.78213100
H	1.74764700	-0.96194200	2.72216300

H	1.54894500	0.46790100	3.73253200
H	1.66164100	0.64673300	1.98296700
C	-0.20657500	-0.12280300	2.70357400
C	-1.13323600	-0.20519900	3.72569600
H	-0.93214600	-0.14397500	4.78308900
C	-2.37489200	-0.39229400	3.12850300
C	-3.69588800	-0.54935000	3.78326800
H	-3.58077100	-0.45676500	4.86184700
H	-4.13197300	-1.52741500	3.57098600
H	-4.40221600	0.21204700	3.44813100
C	-0.26566000	-3.43178900	-2.25187600
H	0.64192000	-2.94402500	-1.88948000
H	-0.42432300	-3.13852900	-3.29336100
H	-0.08663100	-4.50691600	-2.24276800
C	-1.45008700	-3.09920700	-1.42422700
C	-2.61301800	-3.82511500	-1.22358400
H	-2.84335000	-4.79985700	-1.62263100
C	-3.42909400	-3.05137500	-0.40900900
C	-4.78655200	-3.36161900	0.10083000
H	-4.82085600	-3.33620300	1.19138000
H	-5.08049800	-4.35774800	-0.22553100
H	-5.52591600	-2.65108800	-0.27419000
N	-2.10392000	0.90159900	-0.95631000
N	-3.23190000	0.54849800	-0.28798500
N	-0.87154400	-0.24658700	1.53713400
N	-2.19701500	-0.41548500	1.79937000
N	-1.56205500	-1.94241500	-0.74815300
N	-2.77388600	-1.91111200	-0.13206100
B	-3.21987000	-0.66593900	0.66591500
Bi	-0.18841000	-0.17634100	-0.54568400
H	1.78886100	-1.66700100	-0.00745000
H	0.68895700	2.00597800	0.13606800
Si	3.23723700	-2.24289800	0.00912500
Si	1.42166500	3.38993800	0.10053100

C	4.32903800	-0.74830200	0.34047300
C	5.74039000	-1.07359600	0.83801800
H	3.82720100	-0.11131300	1.07789000
H	4.38405300	-0.15622900	-0.58152900
H	6.32153400	-0.16110400	0.98524200
H	5.71690100	-1.60030600	1.79431100
H	6.29066600	-1.69740000	0.13177800
C	3.20512500	-3.51403200	1.38875300
C	4.33549500	-4.54570600	1.34606800
H	2.23845900	-4.02903500	1.34440900
H	3.21801200	-2.98634100	2.34997800
H	4.24799100	-5.24908600	2.17631300
H	4.31148600	-5.12990500	0.42383800
H	5.32029000	-4.08045300	1.41730900
C	3.48691100	-2.97041900	-1.70610000
C	4.94821000	-3.18451100	-2.11105200
H	3.00929200	-2.30443700	-2.43585500
H	2.94220300	-3.91999900	-1.76224600
H	5.01286900	-3.61853500	-3.11055500
H	5.50122500	-2.24348000	-2.12924500
H	5.46742900	-3.86033700	-1.42939000
C	2.45927900	3.42760000	1.66307200
C	2.97922600	4.81730500	2.04455800
H	3.29740700	2.72985500	1.54904100
H	1.84537000	3.03861700	2.48321600
H	3.57923800	4.76725300	2.95509600
H	3.60698400	5.25153300	1.26483000
H	2.15925400	5.51232900	2.23532700
C	0.02971800	4.64846100	0.09886700
C	0.40748200	6.03287900	-0.43451300
H	-0.34557600	4.72827600	1.12574600
H	-0.80422700	4.24522400	-0.48573600
H	-0.44461500	6.71346700	-0.38323900
H	1.21764700	6.48669600	0.13899600

H	0.72780000	5.99031700	-1.47789400
C	2.42087600	3.30376100	-1.48916500
C	3.56057800	4.31983100	-1.60933000
H	1.73669900	3.41799300	-2.33866800
H	2.83432300	2.29029300	-1.56987600
H	4.07207500	4.21600500	-2.56805300
H	3.20104900	5.34819700	-1.54230100
H	4.30800200	4.17884300	-0.82603300

Complex **[Tp^{Me2}Bi---(H-$SiEt_3$)$_3$]$^{2+}$**

E_{TOTAL} = -2734.08805606 a.u.

H	-4.88780800	-0.72915800	0.48463500
C	0.19836100	-3.39143600	1.68697300
H	0.51704200	-3.14050500	2.70156300
H	0.86323400	-2.88236700	0.98671800
H	0.33317300	-4.46521400	1.55605800
C	-1.22141500	-3.02468000	1.47854000
C	-2.36157800	-3.74872800	1.78579400
H	-2.40307200	-4.73739900	2.21367800
C	-3.44329600	-2.95202900	1.43686900
C	-4.88993600	-3.25406300	1.56141800
H	-5.39420800	-2.53533400	2.21002000
H	-5.01928000	-4.24649800	1.98985700
H	-5.38816500	-3.23526000	0.59036100
C	-0.67144000	0.16019300	-3.49178600
H	-0.81987700	0.78945500	-4.36930800
H	-0.29964500	-0.80682000	-3.83954300
H	0.10202100	0.62132900	-2.87500300
C	-1.94740100	-0.00954700	-2.75894600
C	-3.23304000	-0.10197800	-3.26460500
H	-3.52699800	-0.02985400	-4.29932900

C	-4.07198900	-0.31185400	-2.17857200
C	-5.54543000	-0.48123700	-2.17062200
H	-5.92317300	-0.43135200	-3.19041200
H	-6.03485400	0.30158100	-1.58811300
H	-5.83561600	-1.44422800	-1.74671100
C	-0.62263900	2.77676300	2.45461300
H	0.11083400	2.68843800	1.65092800
H	-0.19928200	2.33368700	3.35915400
H	-0.77531500	3.83828900	2.64821800
C	-1.90865800	2.12781800	2.11085900
C	-3.18558100	2.43753700	2.54804800
H	-3.46475500	3.24601800	3.20427600
C	-4.03806600	1.50044500	1.97987900
C	-5.50864900	1.38026400	2.13055500
H	-6.01801400	1.44534100	1.16746800
H	-5.87666900	2.18490400	2.76485300
H	-5.78653800	0.43065200	2.59199200
N	-1.60491600	-1.84384900	0.96217000
N	-2.96370900	-1.80069400	0.93878100
N	-2.01361200	-0.15182100	-1.42316400
N	-3.31347600	-0.33892800	-1.07131700
N	-1.99429100	1.05301600	1.30666700
N	-3.29616600	0.66915800	1.23092400
B	-3.71314700	-0.56267500	0.40169500
Bi	-0.43653000	-0.09350700	0.17333800
H	0.31568500	2.16102500	-0.76343400
H	1.07452400	-1.66259300	-1.24900900
Si	0.90431000	3.40283500	-1.49350700
Si	2.07792200	-2.57814400	-2.00002300
C	2.37973900	2.73204900	-2.44581900
C	2.87487600	3.61523900	-3.59388600
H	2.12282100	1.74181000	-2.83929000
H	3.18937200	2.55953900	-1.72625300
H	3.74101000	3.16681800	-4.08472400

H	2.10511800	3.75314500	-4.35638300
H	3.17545600	4.60595700	-3.24887200
C	-0.51266100	4.01661400	-2.56275800
C	-0.38869100	5.45970600	-3.05795100
H	-1.43447600	3.90984800	-1.97877700
H	-0.62119400	3.33697500	-3.41607600
H	-1.24739300	5.73305700	-3.67434900
H	-0.34965000	6.16708700	-2.22706700
H	0.50688200	5.61173800	-3.66339300
C	1.39594900	4.59749900	-0.12859500
C	2.36852000	5.69821600	-0.56129600
H	1.84919600	4.02220400	0.68738000
H	0.48399700	5.04289100	0.28558200
H	2.58540800	6.37233000	0.26968100
H	3.32032900	5.28201200	-0.89727800
H	1.96771400	6.30477600	-1.37507800
C	2.88653800	-1.47506800	-3.28977900
C	3.57217900	-2.21239100	-4.44305700
H	3.60592900	-0.82510000	-2.77723100
H	2.12255100	-0.80441100	-3.69724300
H	4.02965800	-1.50544000	-5.13814200
H	4.36207700	-2.88006300	-4.09448100
H	2.86131100	-2.81350900	-5.01378900
C	1.00750300	-3.94908700	-2.70871400
C	1.76026400	-5.21494300	-3.12422800
H	0.44849600	-3.54687100	-3.56215700
H	0.25180800	-4.20350400	-1.95592600
H	1.07458300	-5.96061300	-3.53136500
H	2.51139000	-5.01214700	-3.88962600
H	2.27147800	-5.67412400	-2.27526200
C	3.28740600	-3.16048700	-0.68175400
C	4.63052400	-3.67157400	-1.20886700
H	2.80456300	-3.94102300	-0.08242900
H	3.46440700	-2.32143200	0.00210900

H	5.27337300	-3.99423900	-0.38733900
H	4.50995800	-4.52461400	-1.87924300
H	5.16906100	-2.89550500	-1.75640400
H	1.10432000	-0.20053200	2.29173300
Si	2.49041200	0.03957600	2.94247700
C	3.47017800	0.93163400	1.60338200
H	3.75171700	0.19835300	0.83744800
H	2.79255300	1.63748800	1.10512400
C	3.15535800	-1.67104700	3.34362500
H	2.89765800	-2.33906000	2.51465300
H	2.60720700	-2.04951300	4.21472400
C	2.16309000	1.09758800	4.46096800
H	2.00610100	2.13222100	4.13436900
H	1.21419900	0.76988600	4.90168700
C	4.66304600	-1.74876800	3.59669100
H	4.97671200	-1.11027500	4.42402000
H	4.96209300	-2.76929500	3.84409700
H	5.23305200	-1.44910100	2.71446600
C	3.25862600	1.05383400	5.52895100
H	3.00296900	1.69839600	6.37220000
H	3.39453400	0.04492500	5.92320300
H	4.22237200	1.39137300	5.14278400
C	4.71070200	1.68572200	2.08737100
H	5.43037000	1.02098900	2.56811000
H	5.22546100	2.17386100	1.25706400
H	4.44979100	2.46185600	2.80982000

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