Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Accessing heavy allyl-analogous $[(TerN)_2E]^-$ (E = Sb, Bi) ions and their reactivity towards ECl_3

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Content

Experimental Details

General Information. All manipulations were carried out under oxygen- and moisture-free conditions under argon using standard Schlenk or drybox techniques. Benzene was dried over Na and freshly distilled prior to use. $SbCl_3$ and $BiCl_3$ were purified by sublimation prior to use. $[ClSb(\mu\text{-NTer})]_2$ and $[ClBi(\mu\text{-NTer})]_2$ were prepared according to literature procedures.[1,2]

NMR: $^{31}P\{^1H\}$, $^{13}C\{^1H\}$, ^{13}C DEPT, and ^1H NMR spectra were obtained on a Bruker Avance 250, 300 or 500 spectrometer and were referenced internally to the deuterated solvents (^{13}C, C_6D_6: $\delta_{reference}$ = 128.39 ppm) or to protic impurities (^1H, C_6D_5H: $\delta_{reference}$ = 7.16 ppm)[3] or externally (^{31}P: 85 % $H_3PO_{4(aq)}$). C_6D_6 and d^8-toluene were dried over Na/benzophenone and freshly distilled prior to use.

IR: Nicolet 380 FT-IR with a Smart Orbit ATR device was used.

Raman: Horiba Scientific LabRam HR 800 was used.

CHN analyses: Analysator Flash EA 1112 from Thermo Quest, or C/H/N/S-Mikronalysator TruSpec-932 from Leco were used.

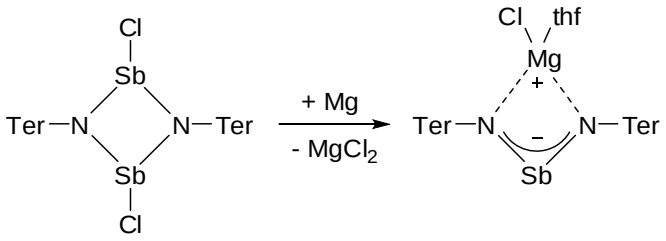
DSC: DSC 823e from Mettler-Toledo (Heating rate 5 °C/min).

MS: Finnigan MAT 95-XP von Thermo Electron.

X-ray Structure Determination: X-ray quality crystals of all compounds were selected in Fomblin YR-1800 perfluoroether (Alfa Aesar) at ambient temperatures. The samples were cooled to 173(2) K during measurement. The data were collected on a Bruker Apex Kappa-II CCD diffractometer or on a Bruker-Nonius Apex X8 CCD diffractometer using graphite monochromated Mo K_α radiation (λ = 0.71073). The structures were solved by direct methods (*SHELXS-2013*)[4] and refined by full-matrix least squares procedures (*SHELXL-2013*).[5] Semi-empirical absorption corrections were applied (SADABS).[6] All non-hydrogen atoms were refined anisotropically, hydrogen atoms were included in the refinement at calculated positions using a riding model.

Synthetic Protocols

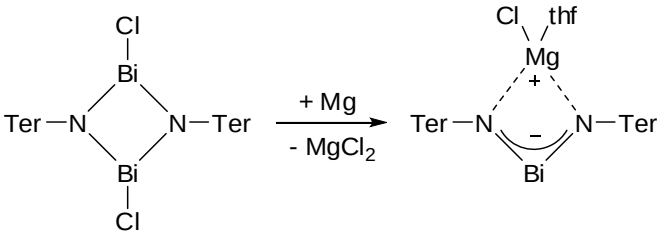
Synthesis of **2Sb**



$[ClSb(\mu\text{-}NTer)]_2$ (242 mg, 0.250 mmol) and magnesium turnings (80 mg) were combined in a flask. 15 ml THF were added and the mixture was vigorously stirred with a glass-covered stirring bar for two days. The solution slowly turned deep blue from initially yellow. Volatiles were removed in vacuo at ambient temperature. The black residue was dissolved in 5 ml benzene, the solution was filtered through a sinter padded with kieselguhr (Celite) and washed with another 3 ml benzene. The combined filtrates were concentrated to incipient crystallization and left undisturbed overnight at ambient temperature, resulting in the deposition of dark blue crystals. The mother liquor was removed via syringe and the crystals were dried in vacuo (82 mg, 0.90 mmol, 36%).

Mp. 228 °C (dec.). **EA** for $C_{52}H_{58}N_2SbMgClO$ found (calc.): C 68.20 (68.74), H 6.72 (6.43), N 3.40 (3.08). **^{1}H NMR** (298 K, C_6D_6, 250.1 MHz): 1.30 (br s, 4 H, OCH_2CH_2), 2.11 (br s, 24 H, *o*-CH_3), 2.20 (s, 12 H, *p*-CH_3), 3.30 (br s, 4 H, OCH_2CH_2), 6.76 (dd, 2 H, J_{HH} = 7.7, 7.0 Hz, *p*-C*H*), 6.83 (s, 8 H, CH_{Mes}), 6.97 (d, 4 H, $^3J_{HH}$ = 7.4 Hz, *p*-C*H*). **^{13}C{^{1}H} NMR** (298 K, C_6D_6, 62.9 MHz): 21.61 (s, *o*-CH_3), 21.64 (s, *o*-CH_3), 25.23 (s, OCH_2CH_2), 69.84 (s, OCH_2CH_2), 120.12 (s, *C*H), 128.25 (s, *C*H), 128.50 (s, *C*H), 129.26 (s, *C*H), 130.26 (s, *C*H), 130.42 (s, *C*H), 132.97 (s), 137.42 (s), 137.92 (s), 137.96 (s), 138.60 (s), 151.75 (s). **IR** (ATR, cm^{-1}): 547 (m), 563 (m), 628 (m), 655 (s), 684 (s), 717 (m), 748 (s), 783 (m), 796 (m), 848 (s), 869 (m), 916 (w), 981 (s), 998 (m), 1027 (m), 1079 (m), 1126 (s), 1182 (s), 1228 (vs), 1305 (m), 1375 (m), 1388 (m), 1444 (m), 1484 (w), 1577 (w), 1600 (w), 2728 (vw), 2854 (w), 2914 (w), 2944 (w). **Raman** (632 nm, cm^{-1}): dec. **UV/vis**: λ_{max} (nm): 585.

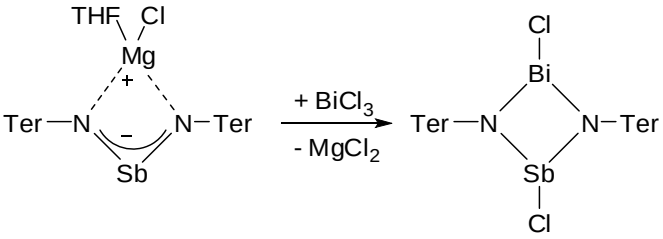
Synthesis of **2Bi**



In the glove box, 260 mg (0.227 mmol) [ClBi(μ-NTer)]$_2$, magnesium turnings (105 mg) and a glass-covered stirring bar were combined in a flask. 10 ml THF were added to the mixture and vigorous stirring was initiated. Already after one hour, the initally red solution turned black. After stirring overnight, volatiles were removed in vacuo and the residue was redissolved in 10 ml benzene. The solution was filtered over a sinter padded with kieselguhr (Celite). The filtrate was concentrated to approx. 2 ml and left undisturbed overnight, resulting in the deposition of dark blueish-green crystals. The supernatant was transferred into another flask, concentrated to approx. 0.5 ml and left undisturbed for eight hours, affording a second crop of crystals. The mother liqor was discarded and the crystals were dried in vacuo, giving a combined yield of **2Bi** (102 mg, 0.098 mmol, 43%).

Mp. 246 °C (dec.). **EA** for $C_{52}H_{58}N_2BiMgClO$ found (calc.): C 64.70 (64.87), H 6.23 (6.01), N 2.75 (2.61). **^{1}H NMR** (298 K, C_6D_6, 250.1 MHz): 1.30 (br s, 4 H, OCH_2CH_2), 2.16 (s, 24 H, *o*-CH_3), 2.20 (s, 12 H, *p*-CH_3), 3.40 (br s, 4 H, OCH_2CH_2), 6.39 (t, $^3J_{HH}$ = 7.4 Hz, 2 H, *p*-C*H*), 6.83 (s, 8 H, *m*-CH_{Mes}), 7.24 (d, $^3J_{HH}$ = 7.4 Hz, 4 H, *m*-C*H*). **^{13}C{^{1}H} NMR** (298 K, C_6D_6, 62.9 MHz): 21.50 (s, *m*-CH_3), 21.56 (s, *p*-CH_3), 25.65 (s, OCH_2CH_2), 69.31 (s, OCH_2CH_2), 112.48 (s, *C*H), 128.24 (s, *C*H), 128.56 (s, *C*H), 128.92 (s, C_6H_6), 129.26 (s, *C*H), 129.99 (s, *C*H), 130.13 (s, *C*H), 137.54 (s), 137.90 (s), 138.16 (s), 139.61 (s), 139.90 (s), 153.70 (s). **IR** (ATR, cm^{-1}): 549 (s), 563 (s), 597 (s), 626 (s), 649 (s), 661 (s), 675 (vs), 740 (s), 750 (s), 779 (m), 796 (m), 848 (vs), 875 (m), 914 (w), 945 (w), 1004 (m), 1025 (m), 1072 (m), 1228 (s), 1259 (m), 1280 (m), 1375 (s), 1444 (s), 1479 (m), 1575 (m), 1600 (m), 2728 (w), 2852 (m), 2914 (m), 2942 (m), 2964 (m), 3023 (w). **Raman**: –. **UV/vis**: λ_{max} (nm): 455, 697.

Synthesis of **3**



45 mg $[(TerN)_2Sb]MgCl{\cdot}THF$ (0.050 mmol) and 19 mg $BiCl_3$ (0.060 mmol) were combined as solids. To the mixture, 2 ml benzene were added via syringe at ambient temperature and the suspension was stirred for two hours. A dark precipitate formed. The solution was filtered over a sinter padded with kieselguhr (Celite) and the red solution was concentrated to approx 0.5 ml. After standing undisturbed overnight, red crystals were obtained. The supernatant was removed via syringe and the crystals were dried in vacuo (33 mg, 0.032 mmol, 62%).

Mp. 266 °C (dec.). **EA** for $C_{48}H_{50}N_2SbBiCl_2$ found (calc.): C 54.31 (54.56), H 4.92 (4.77), N 2.15 (2.65). **^{1}H NMR** (298 K, C_6D_6, 250.1 MHz): 2.14 (s, 24 H, *o*-CH_3), 2.20 (s, 12 H, *o*-CH_3), (t, $^3J_{HH}$ = 7.4 Hz, 2 H, *p*-C*H*), 6.89 (s, 24 H, CH_{Mes}), 6.85-6.95 (m, 4 H, *m*-C*H*). **^{13}C{^{1}H} NMR** (298 K, C_6D_6, 62.9 MHz): 20.65 (s, *C*H_3), 21.51 (s, *C*H_3), 22.07 (s, *C*H_3), 119.04 (s, *C*H), 119.81 (s, *C*H), 126.71 (s, *C*H), 128.92 (s, *C*H), 129.27 (s, *C*H), 129.41 (s, *C*H), 136.25 (s), 137.28 (s), 137.42 (s), 141.59 (s), 144.10 (s). **IR** (ATR, cm^{-1}): 3032 (vw), 2972 (w), 2947 (w), 2916 (m), 285 (w), 2733 (vw), 1608 (m), 1576 (w), 1479 (w), 1450 (m), 1394 (vs), 1250 (w), 1240 (w), 1217 (vs), 1080 (m), 1032 (m), 1005 (m), 960 (vw), 947 (vw), 908 (w), 883 (w), 856 (vs), 850 (vs), 791 (s), 758 (s), 692 (s), 654 (s), 629 (w), 563 (m), 546 (m), 536 (m). **Raman** (632 nm, cm^{-1}): 111 (14), 151 (5), 185 (45), 229 (21), 251 (54), 261 (61), 276 (25), 307 (2), 335 (2), 381 (1), 420 (5), 449 (2), 464 (2), 483 (2), 497 (2), 534 (7), 545 (5), 555 (15), 560 (14), 664 (6), 678 (5), 691 (2), 736 (5), 757 (1), 857 (1), 884 (14), 943 (3), 958 (3), 1002 (9), 1081 (26), 1096 (6), 1184 (1), 1243 (100), 1282 (6), 1302 (10), 1358 (1), 1383 (7), 1399 (74), 1429 (7), 1476 (3), 1550 (2), 1576 (36), 1609 (1), 2733 (1), 2854 (1), 2922 (6), 3032 (3). **MS** (CI, pos., *iso*-butane) m/z (%): 330 (88) $[TerNH_3]^+$, 386 (18) $[TerNH_2+C_4H_9]^+$, 1021 (81) $[M–Cl]^+$, 1056 (100) $[M]^+$, 1113 (6) $[M+C_4H_9]^+$.

$[TerN(MgCl)_2]_2 \cdot 4THF$

Red $[ClBi(\mu\text{-}NTer)]_2$ (135 mg, 0.118 mmol) and magnesium turnings (70 mg) were combined in a flask. 10 ml THF were added and the mixture was vigorously stirred with a glass-covered stirring bar for three days. The solution quickly darkened from initially being red. Volatiles were removed in vacuo at ambient temperature. The black residue was dissolved in 4 ml benzene, the solution was filtered through a sinter padded with kieselguhr (Celite) and washed with another 2 ml benzene. The combined filtrates were concentrated to incipient crystallization and left undisturbed overnight at ambient temperature, resulting in the deposition of colourless crystals of $[TerN(MgCl)_2]_2 \cdot 4THF$. The mother liquor was removed via syringe and the crystals were dried in vacuo.

Reduction of $[ClSb(\mu\text{-}NTer)]_2$ with KC_8 – $[K(\mu\text{-}N(H)Ter)]_2$

$[ClSb(\mu\text{-}NTer)]_2$ (150 mg, 0.155 mmol) was dissolved in toluene (10 ml). To the solution, KC_8 was added (48 mg, 0.355 mmol) at −80 °C. The suspension was stirred for further 30 min at the and then warmed to ambient temperature. The suspension was filtered through a sinter padded with kieselguhr (Celite). The dark greenish solution was concentrated to incipient crystallisation (approx. 1 ml) and left undisturbed overnight. Only the starting $[ClSb(\mu\text{-}NTer)]_2$ material could be obtained in various experiments, even though its colour varied between pale yellowish, orange, green and black.

$[ClSb(\mu\text{-}NTer)]_2$ (101 mg, 0.104 mmol) was dissolved in toluene (8 ml). To the solution, KC_8 was added (125 mg, 0.925 mmol) at −80 °C. The suspension was stirred for further 30 min at the and then warmed to ambient temperature. The suspension was filtered through a sinter padded with kieselguhr (Celite). The yellowish solution was concentrated to incipient crystallisation (approx. 4 ml) and left undisturbed overnight, affording colourless crystals of $[K(\mu\text{-}N(H)Ter)]_2$.

Reduction of $[ClSb(\mu\text{-}NTer)]_2$ with $Na[Ph_2CO]$ – $[Ter_4N_4Sb_6O_5]$

To a solution of benzophenon (200 mg, 1.099 mmol) in THF (20 ml), Na (25 mg, 1.09 mmol) was added. Of th red-violet solution, 4 ml were transferred to a solution of 208 mg (0.215 mmol) $[ClSb(\mu\text{-}NTer)]_2$ in 10 ml THF, affording a dark yellowish solution. Stirring was continued for 15 minutes, then volatiles were removed in vacuo. The residue was redissolved in toluene (8 ml), filtered, and concentrated to approx. 1 ml. After standing undisturbed for three days, pale yellowish crystals of $[Ter_4N_4Sb_6O_5]$ were obtained in small yield (ca. 15 mg).

Crystallographic Data

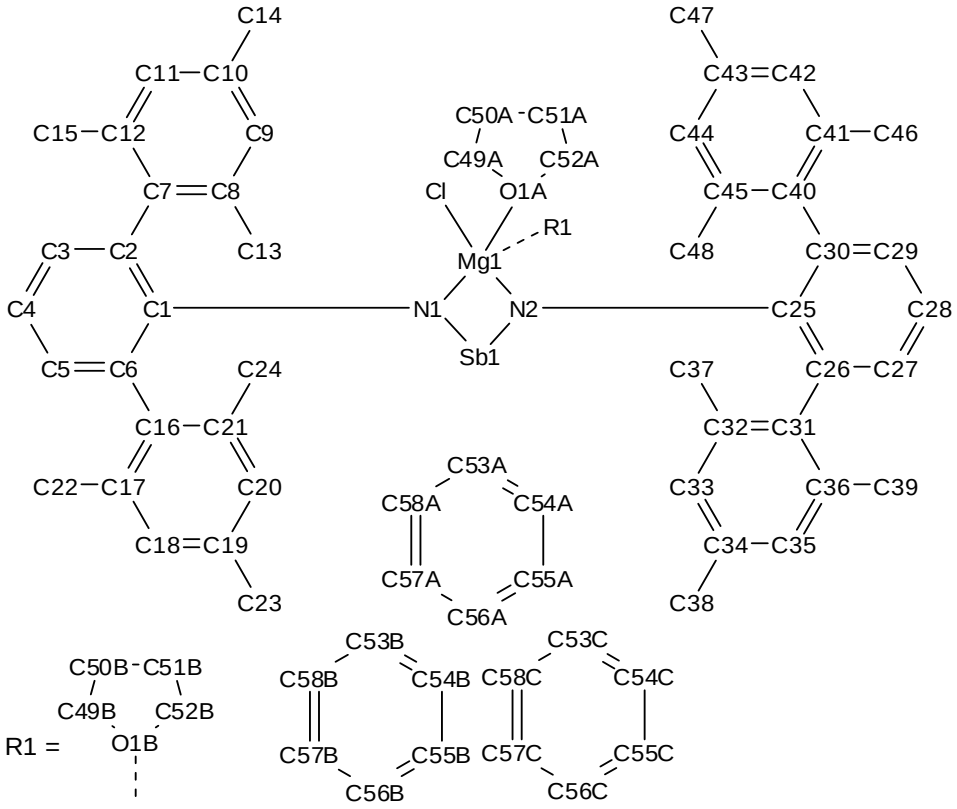
Table S1. Crystallographic data of **2Sb**, **2Bi**, and **3**.

compound	**2Sb**	**2Bi**	**3**
sum formula	$C_{58}H_{64}ClMgN_2OSb$	$C_{58}H_{64}BiClMgN_2O$	$C_{48}H_{50}BiCl_2N_2Sb$
formula weight [g·mol^{-1}]	986.62	1073.85	1056.53
colour	blue	blue	orange
crystal system	monoclinic	monoclinic	orthorhombic
space group	$P2_1/n$	$P2_1/n$	*Pbca*
a [Å]	13.7235(5)	13.7359(12)	14.6206(12)
b [Å]	16.6434(6)	16.6363(10)	15.5222(12)
c [Å]	23.2770(8)	23.257(2)	18.7038(14)
α [°]	90	90	90
β [°]	106.733(2)	106.645(3)	90
γ [°]	90	90	90
V [Å^3]	5091.5(3)	5091.9(7)	4244.7(6)
Z	4	4	4
$\rho_{calc.}$ [g cm^{-3}]	1.287	1.401	1.653
μ [mm^{-1}]	0.647	3.568	4.938
$\lambda_{MoK\alpha}$ [Å]	0.71073	0.71073	0.71073
T [K]	173	173	173
measured reflexes	132273	106709	38840
independent reflexes	18410	18429	7633
reflexes $I > 2\sigma(I)$	13723	13294	4974
$R_{int.}$	0.0479	0.0427	0.0551
$2\Theta_{max.}$ [°]	65	65	65
F(000)	2056	2184	2080
R_1 (R [$F^2 > 2\sigma(F^2)$])	0.0368	0.0377	0.0342
wR_2 (all data)	0.0975	0.0818	0.0692
GooF	1.014	1.014	1.011
parameter	802	638	262
CCDC #	1059323	1059324	1059325

Table S2. Crystallographic data of the decomposition products $[TerN(MgCl)_2]_2 \cdot 4THF$ and $[K(\mu\text{-}N(H)Ter)]_2$.

compound	**$[K(\mu\text{-}N(H)Ter)]_2$**	**$[Ter_4N_4Sb_6O_5]$**	**$[TerN(MgCl)_2]_2 \cdot 4THF$**
sum formula	$C_{48}H_{52}K_2N_2$	$C_{103}H_{108}N_4O_5Sb_6$	$C_{41}H_{50}Cl_2Mg_2NO_2$
formula weight [$g \cdot mol^{-1}$]	735.11	2212.43	708.34
colour	colourless	colourless	colourless
crystal system	monoclinic	triclinic	monoclinic
space group	$P2_1/n$	$P\text{-}1$	$C2/c$
a [Å]	12.1703(8)	13.0038(4)	28.174(3)
b [Å]	13.0783(9)	13.7006(4)	18.5585(17)
c [Å]	13.8685(9)	14.9997(4)	17.118(2)
α [°]	90	109.078(2)	90
β [°]	112.817(4)	100.764(1)	120.909(3)
γ [°]	90	106.268(1)	90
V [$Å^3$]	2034.7(2)	2307.53(12)	7679.4(15)
Z	2	1	8
$\rho_{calc.}$ [$g\ cm^{-3}$]	1.200	1.592	1.225
μ [mm^{-1}]	0.268	1.786	0.237
$\lambda_{MoK\alpha}$ [Å]	0.71073	0.71073	0.71073
T [K]	173	173	173
measured reflexes	26991	61812	38411
independent reflexes	4658	13364	7536
$I > 2\sigma(I)$	2430	8998	4414
$R_{int.}$	0.0959	0.0638	0.0792
$2\Theta_{max.}$ [°]	55	60	52
$F(000)$	784	1100	3016
R_1 (R [$F^2 > 2\sigma(F^2)$])	0.0531	0.0376	0.0543
wR_2 (all data)	0.1269	0.0729	0.1511
GooF	1.000	1.005	1.018
parameter	246	578	439
CCDC #	1403025	1403026	1403027

Numbering scheme of **2Sb**

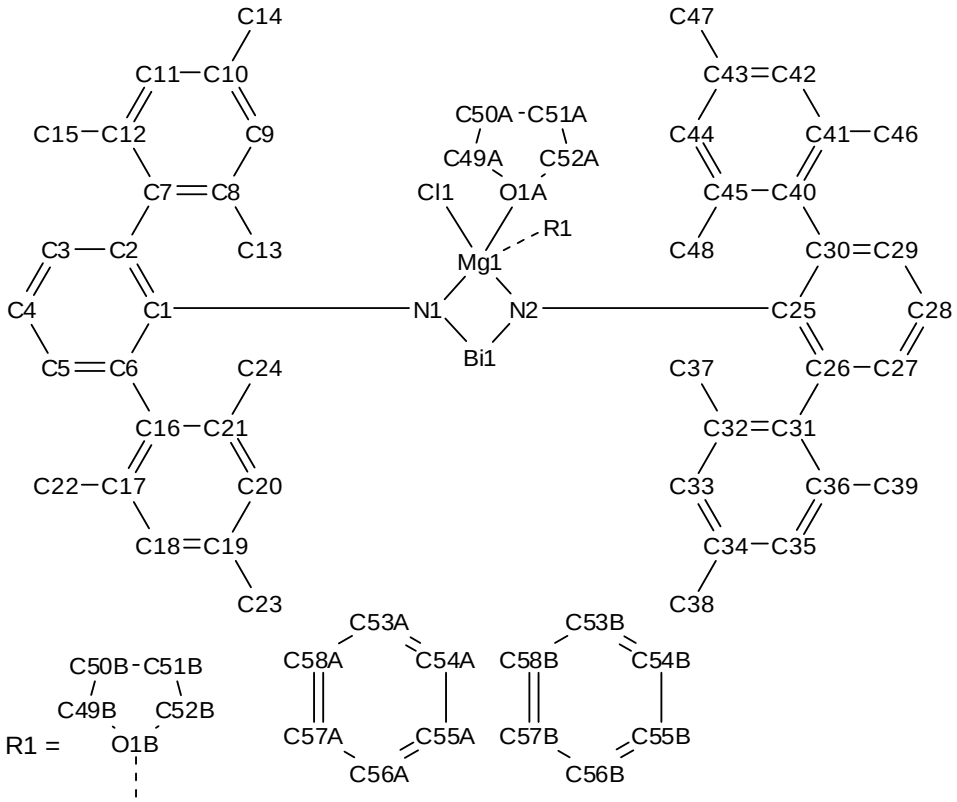


Selected bond lengths [Å] and angles [°] of **2Sb**.

Sb1–N1	1.9633(13)	**Mg1–N2**	2.0921(15)
Sb1–N2	1.9713(13)	**N1–Sb1–N2**	85.97(6)
Sb1–Mg1	3.0330(5)	**N1–Mg1–N2**	80.04(5)
Cl1–Mg1	2.2834(7)	**Sb1–N1–Mg1**	97.17(6)
Mg1–N1	2.0797(14)	**Sb1–N2–Mg1**	96.52(6)

Structural details: Several parts of the structure of **2Sb** were found to be disordered. The coordinated thf molecule (occupancy: 0.589(8), 0.421(8)), one 2,4,6-trimethylphenyl group (occupancy: 0.578(9), 0.422(9)) and one (2,4,6-trimethylphenyl)phenyl group (occupancy: 0.568(10), 0.432(10)) were split into two positions each, while the disorder of the benzene molecule was modeled with three positions (occupancy: 0.396(3), 0.393(3), 0.211(3)).

Numbering scheme of **2Bi**

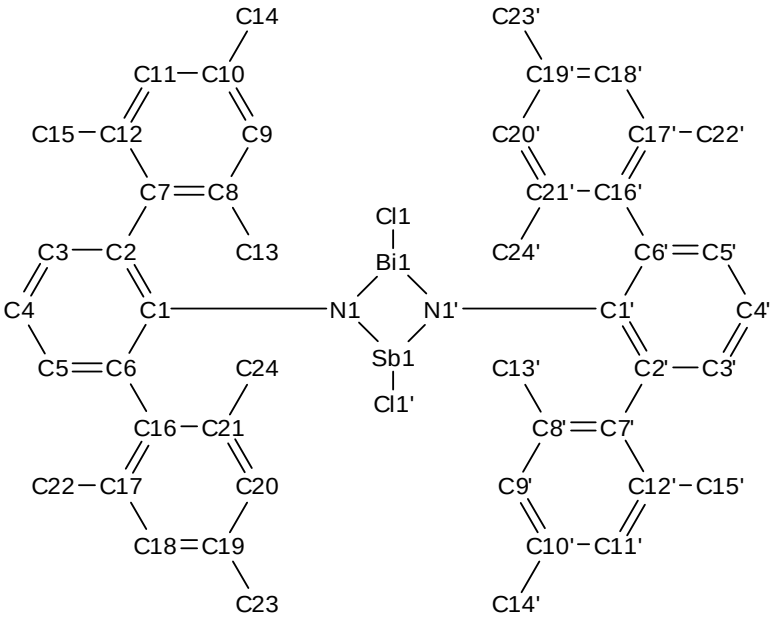


Selected bond lengths [Å] and angles [°] of **2Bi**.

Bi1–N1	2.075(2)	**Mg1–N1**	2.070(2)
Bi1–N2	2.086(2)	**Mg1–N2**	2.078(2)
Bi1–Mg1	3.1087(8)	**N1–Bi1–N2**	82.78(8)
Cl1–Mg1	2.2936(11)	**Mg1–N1–Bi1**	97.18(9)
Mg1–N2–Bi1	96.59(9)	**Cl1–Mg1–Bi1**	133.57(4)

Structural details: Several parts of the structure of **2Bi** were found to be disordered. The coordinated thf molecule (occupancy: 0.533(5), 0.467(5)), one 2,4,6-trimethylphenyl group (occupancy: 0.574(10), 0.426(10)), one (2,4,6-trimethylphenyl)phenyl group (occupancy: 0.507(6), 0.493(6)) and the benzene molecule (occupancy: 0.532(18), 0.468(18)) were split into two positions each.

Numbering scheme of **3**



Selected bond lengths [Å] and angles [°] of **3**.

Bi1–N1	2.196(3)	**Sb1'–N1**	2.034(4)
Bi1'–N1	2.183(3)	**Sb1–Cl2**	2.44(2)
Bi1–Cl1	2.55(2)	**N1–Bi1–N1**	73.89(10)
Bi1–Sb1	3.3079(15)	**N1–Sb1–N1**	80.36(14)
Sb1–N1	2.045(4)	**Cl2–Sb1–Bi1'**	97.2(5)

symmetry code: (') 2-x, 1-y, 2-z.

Structural details: The asymmetric unit of the structure consists of a half molecule of **3**. The centroid of the molecule is located on a centre of inversion, hence the asymmetric unit contains only a half SbCl and a half BiCl moiety.

Computational Details

Utilizing the experimental structural data, all calculations were carried out with the Gaussian 09 package of molecular orbital programs.[6] The wave functions and structures for the model compounds (R = Ph instead of terphenyl) were optimized at the pbe1pbe/6-31G(d,p) level of density functional theory (for Sb and Bi a relativistic pseudopotential was used, Sb: ECP46MDF 4 46; Bi: ECP60MDF 5 60). and the optimized structures were checked to be a minimum on the energy hypersurface. All stationary points were characterized by frequency analyses.

ELF[8] and NBO/NRT[9–11] analyses were carried out to study the bonding, hybridization and polarization effects. Again To generate a consistent set of data,these computations have been carried out for a model system with R = Ph.

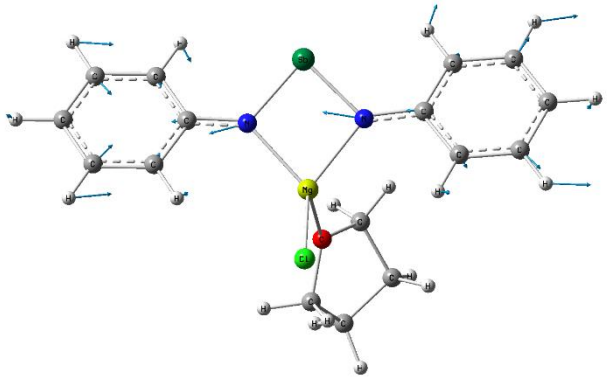
It should be emphasized that the computation was carried out for a single, isolated (gas-phase) molecule.

Vibrational Modes

Table S3. Observed (computed) vibrational spectroscopic data for **2E** in cm^{-1}.

	assignment	**2Sb**	**2Bi**
A	δ(N–E–N) (a)	876 (859)	870 (855)
B	δ(N–E–N) (b)	686 (678)	676 (654)

A



B

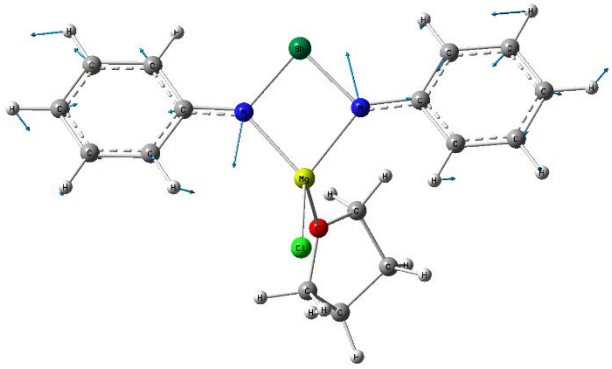


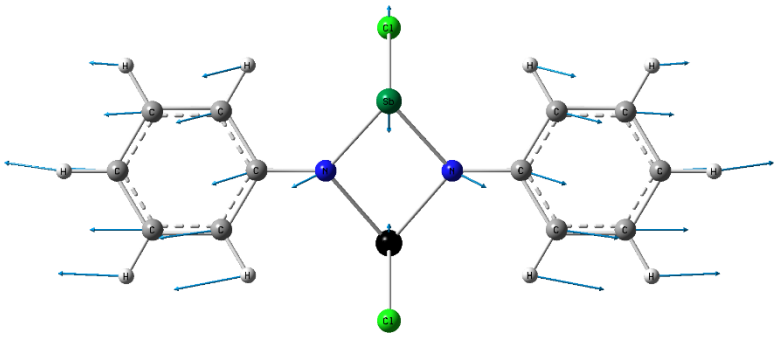
Figure S1. Displacement vectors of selected vibrations in descending order (Table S3).

Vibrational Modes

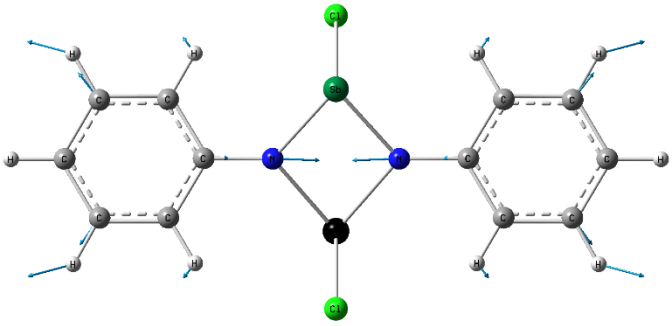
Table S4. Observed (computed) vibrational spectroscopic data for **3**.

	assignment	**3**
A	δ(N–E–N)	888 (898)
B	ν(E–Cl)	280 (300)
C	ν(E–Cl)	265 (279)
D	δ(E–N–E)	188 (223)

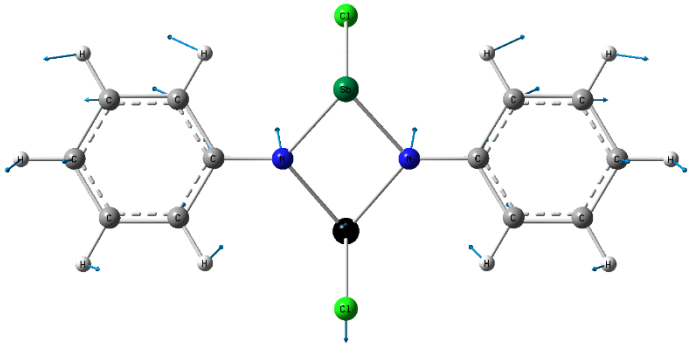
A



B



C



D

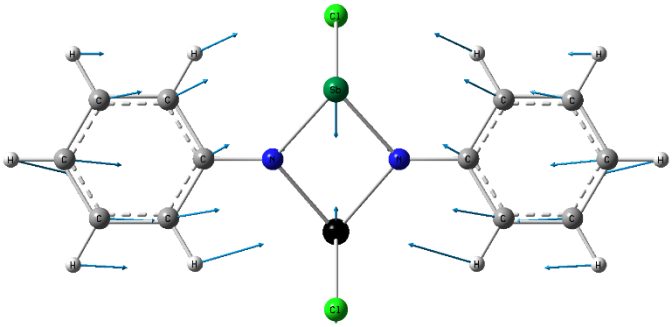


Figure S2. Displacement vectors of selected vibrations in descending order (Table S4).

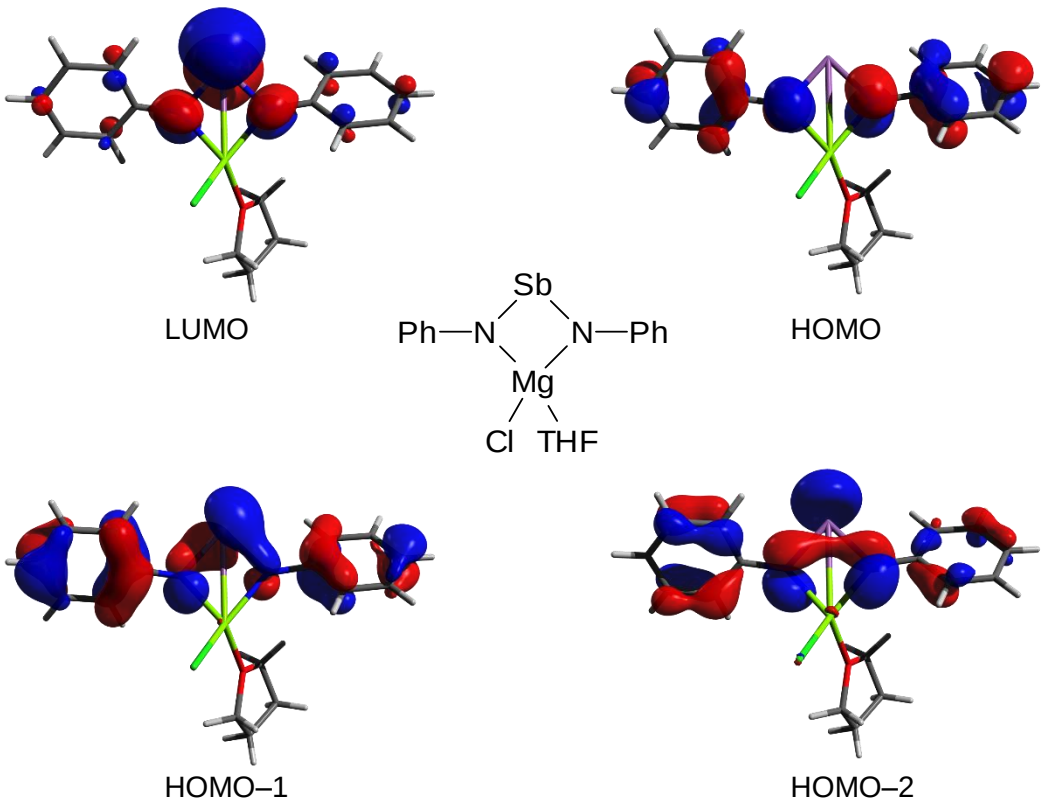


Figure S3. MOs of **2Sb** (phenyl substituents).

NBO Data (Model compounds with R = Ph instead of terphenyls)

2P

1. (1.97543) BD (1) P 1 - N 4
(25.86%) 0.5085* P 1 s(15.58%)p 5.31(82.80%)d 0.10(1.62%)
0.0000 0.0000 -0.3831 0.0950 -0.0002
-0.0003 -0.6294 0.0462 0.0000 -0.6291
0.0241 0.0000 -0.1823 -0.0030 -0.1088
-0.0269 -0.0247 0.0057 0.0549
(74.14%) 0.8610* N 4 s(29.15%)p 2.43(70.76%)d 0.00(0.10%)
0.0002 -0.5399 0.0007 0.0035 0.5082
0.0081 0.6679 0.0082 0.0543 -0.0056
-0.0217 -0.0032 -0.0079 0.0100 0.0181
2. (1.97623) BD (1) P 1 - N 5
(25.78%) 0.5077* P 1 s(15.41%)p 5.38(82.97%)d 0.11(1.62%)
0.0000 -0.0001 0.3810 -0.0945 0.0000
-0.0003 -0.7511 0.0515 0.0000 0.4520
-0.0099 0.0001 0.2418 -0.0052 -0.0949
-0.0460 0.0262 0.0456 -0.0481
(74.22%) 0.8615* N 5 s(29.27%)p 2.41(70.63%)d 0.00(0.10%)
-0.0002 0.5410 -0.0006 -0.0040 0.6555
0.0111 -0.4992 -0.0048 -0.1652 0.0043
-0.0222 -0.0098 0.0107 0.0018 -0.0159
80. (1.96595) LP (1) P 1 s(70.24%)p 0.42(29.70%)d 0.00(0.06%)
0.0000 -0.0009 0.8378 0.0227 0.0000
0.0000 0.0582 0.0021 -0.0004 -0.5174
-0.0236 -0.0002 -0.1586 -0.0119 -0.0019
0.0041 -0.0087 -0.0043 0.0216

2As

1. (1.97384) BD (1)As 1 - N 4
(25.47%) 0.5047*As 1 s(12.14%)p 7.19(87.36%)d 0.04(0.50%)
0.0000 0.0000 -0.0001 -0.3379 0.0852
0.0001 -0.0004 0.0001 0.0000 -0.0003
-0.6734 -0.0371 0.0000 0.0000 -0.5960
-0.0219 0.0000 -0.0001 -0.2511 -0.0018
-0.0003 -0.0571 -0.0003 -0.0228 -0.0001
-0.0199 -0.0003 -0.0032 0.0000 0.0283
(74.53%) 0.8633* N 4 s(24.99%)p 3.00(74.95%)d 0.00(0.06%)
0.0002 -0.4999 -0.0036 0.0020 0.5127
0.0031 0.6878 -0.0019 0.1158 -0.0085
-0.0148 -0.0042 -0.0103 0.0083 0.0139
2. (1.97300) BD (1)As 1 - N 5
(25.42%) 0.5042*As 1 s(12.00%)p 7.29(87.50%)d 0.04(0.49%)
0.0000 0.0000 0.0001 0.3361 -0.0841
-0.0003 0.0005 -0.0001 0.0000 -0.0003
-0.7300 -0.0397 0.0000 0.0000 0.5061
0.0150 0.0000 0.0001 0.2900 0.0067
-0.0002 -0.0528 -0.0004 -0.0288 0.0000
0.0194 0.0003 0.0164 0.0000 -0.0257
(74.58%) 0.8636* N 5 s(24.57%)p 3.07(75.37%)d 0.00(0.06%)
-0.0002 0.4957 0.0043 -0.0022 0.6024
0.0046 -0.5919 0.0016 -0.2009 0.0077
-0.0152 -0.0079 0.0120 -0.0039 -0.0120
89. (1.96686) LP (1)As 1 s(76.84%)p 0.30(23.14%)d 0.00(0.02%)
0.0000 -0.0004 0.0005 0.8764 0.0171
0.0003 -0.0001 0.0000 0.0000 0.0000
0.0229 -0.0011 0.0000 -0.0005 -0.4485
0.0233 0.0000 -0.0002 -0.1702 0.0109
0.0000 -0.0006 0.0000 0.0017 0.0000
-0.0067 -0.0001 -0.0012 0.0000 0.0135

2Sb

14. (1.97616) BD (1) N   8 -Sb 10
(77.69%) 0.8814* N   8 s(20.84%)p 3.80(79.11%)d 0.00(0.05%)
0.0003 -0.4565 0.0060 0.4228 0.0046
0.6851 -0.0067 0.3779 -0.0063 -0.0100
-0.0016 -0.0131 0.0103 0.0093
(22.31%) 0.4724*Sb 10 s(9.30%)p 9.75(90.70%)
-0.2946 0.0786 -0.0050 0.0004 -0.6247
0.0320 -0.0075 -0.0016 -0.7177 0.0097
-0.0179 0.0006 -0.0108 -0.0010 -0.0065
-0.0012
15. (1.85371) BD (2) N   8 -Sb 10
(76.49%) 0.8746* N   8 s(0.25%)p99.99(99.72%)d 0.13(0.03%)
-0.0001 0.0498 0.0007 0.0529 0.0006
-0.4811 -0.0047 0.8734 0.0100 -0.0025
0.0041 -0.0110 -0.0067 -0.0112
(23.51%) 0.4849*Sb 10 s(0.61%)p99.99(99.39%)
0.0740 -0.0251 -0.0044 -0.0008 0.1260
0.0017 -0.0005 0.0025 -0.1576 -0.0007
0.0090 0.0012 0.9761 0.0129 -0.0096
0.0016
17. (1.97567) BD (1) N   9 -Sb 10
(77.75%) 0.8818* N   9 s(20.89%)p 3.78(79.06%)d 0.00(0.04%)
0.0003 -0.4570 0.0061 -0.5389 -0.0039
0.5944 -0.0076 0.3831 -0.0051 0.0121
0.0055 -0.0125 0.0055 0.0090
(22.25%) 0.4717*Sb 10 s(9.55%)p 9.47(90.45%)
-0.2985 0.0796 -0.0063 0.0012 0.7680
-0.0326 0.0108 0.0007 -0.5360 0.0005
-0.0156 0.0001 -0.1609 0.0012 -0.0064
-0.0012
88. (1.97032) LP (1)Sb 10   s(81.70%)p 0.22(18.30%)
0.9038 0.0123 -0.0010 0.0000 0.0401
0.0010 0.0001 -0.0005 -0.4027 -0.0105
0.0019 0.0027 -0.1383 -0.0054 0.0018
0.0000

2Bi

1. (1.97227) BD (1)Bi 1 - N 4
(21.35%) 0.4620*Bi 1 s(6.72%)p13.80(92.66%)d 0.02(0.15%)
f 0.07(0.48%)
-0.2521 -0.0592 -0.0093 0.0000 -0.5824
0.0223 0.0079 -0.0004 -0.7609 0.0084
0.0146 -0.0011 0.0869 0.0002 0.0023
-0.0018 -0.0080 0.0065 0.0055 0.0281
-0.0037 0.0005 0.0197 -0.0010 0.0030
0.0009 -0.0025 -0.0062 0.0050 0.0071
-0.0062 0.0064 0.0056 0.0266 0.0100
0.0320 0.0079 0.0026 0.0080 -0.0074
-0.0012 0.0455 -0.0201 -0.0143 0.0001
(78.65%) 0.8869* N 4 s(18.79%)p 4.32(81.15%)d 0.00(0.06%)
0.0003 -0.4335 0.0053 0.3825 0.0120
0.7113 -0.0028 0.3989 -0.0076 -0.0087
0.0007 -0.0137 0.0129 0.0117
2. (1.84624) BD (2)Bi 1 - N 4
(21.96%) 0.4686*Bi 1 s(0.86%)p99.99(97.94%)d 0.94(0.80%)
f 0.46(0.39%)
0.0879 0.0292 -0.0024 -0.0019 0.1371
-0.0031 0.0036 0.0016 -0.0211 0.0026
-0.0056 0.0024 0.9798 0.0120 0.0069
-0.0016 -0.0077 -0.0022 0.0011 0.0630
-0.0021 0.0039 0.0555 0.0155 -0.0023
0.0209 0.0044 0.0030 0.0130 0.0052
0.0002 -0.0323 -0.0074 0.0081 -0.0050
0.0124 0.0049 -0.0136 -0.0026 0.0420
0.0008 0.0035 0.0084 0.0225 0.0028
(78.04%) 0.8834* N 4 s(0.41%)p99.99(99.55%)d 0.10(0.04%)
-0.0001 0.0642 0.0013 0.0476 -0.0013
-0.4771 -0.0057 0.8750 0.0028 -0.0024
0.0049 -0.0138 -0.0075 -0.0114
3. (1.97117) BD (1)Bi 1 - N 5
(21.22%) 0.4606*Bi 1 s(7.09%)p13.01(92.26%)d 0.02(0.17%)
f 0.07(0.48%)
0.2594 0.0591 0.0113 -0.0013 -0.7945
0.0236 0.0106 -0.0010 0.5306 0.0017
-0.0093 0.0025 0.0945 -0.0020 -0.0035
0.0011 -0.0083 0.0046 0.0096 0.0351
-0.0031 0.0015 -0.0043 0.0014 -0.0033
0.0088 -0.0014 0.0023 -0.0102 -0.0066
0.0063 -0.0174 -0.0081 0.0324 0.0100
-0.0185 -0.0029 0.0047 -0.0023 -0.0123
-0.0031 0.0144 -0.0103 0.0461 -0.0175
(78.78%) 0.8876* N 5 s(18.89%)p 4.29(81.05%)d 0.00(0.05%)
-0.0003 0.4346 -0.0064 0.5535 0.0116
-0.5820 0.0057 -0.4066 0.0059 -0.0129
-0.0051 0.0136 -0.0059 -0.0112

76. (1.97057) LP (1)Bi 1 s(86.00%)p 0.16(13.98%)d 0.00(0.01%)
f 0.00(0.00%)
0.9274 -0.0076 -0.0012 -0.0001 0.0517
0.0013 0.0004 -0.0002 -0.3571 -0.0093
-0.0032 0.0011 -0.0978 -0.0029 -0.0023
-0.0001 -0.0009 0.0007 -0.0010 0.0007
-0.0005 -0.0002 0.0003 0.0002 0.0014
-0.0030 0.0008 -0.0026 0.0069 -0.0001
-0.0023 0.0009 0.0010 0.0000 0.0004
0.0011 -0.0008 -0.0015 -0.0003 -0.0003
-0.0006 0.0021 -0.0019 -0.0043 0.0033

NBO Partial Charges

2P (R=Ph)

	charge/e
P	1.21701
Cl	-0.69614
Mg	1.33915
N	-1.08417
N	-1.0981
C	0.14818
C	-0.27776
C	-0.23817
H	0.25034
C	-0.26575
H	0.24969
C	-0.23861
H	0.25248
C	-0.25733
C	0.14306
C	-0.26305
C	-0.23826
H	0.25261
C	-0.2679
H	0.2504
C	-0.23696
H	0.25114
C	-0.28265
O	-0.6604
C	-0.13516
H	0.24328
H	0.25965
C	-0.52989
H	0.27405
H	0.25556
C	-0.5217
H	0.27051
H	0.26175
C	-0.12648
H	0.25943
H	0.22909
H	0.25872
H	0.24721
H	0.25678

N	-1.08417
N	-1.0981
P	1.21701
sum	-0.96526

2As
(R=Ph)

	charge/e
As	1.22889
Cl	-0.69534
Mg	1.33061
N	-1.07781
N	-1.0935
C	0.15032
C	-0.27872
C	-0.23792
H	0.25015
C	-0.26655
H	0.24953
C	-0.23931
H	0.25248
C	-0.25671
C	0.14512
C	-0.26696
C	-0.23793
H	0.25279
C	-0.26956
H	0.25026
C	-0.23634
H	0.25087
C	-0.28374
O	-0.6582
C	-0.1358
H	0.24488
H	0.25686
C	-0.52731
H	0.27389
H	0.25479
C	-0.52278
H	0.27043
H	0.26151
C	-0.1258
H	0.25646
H	0.23017
H	0.25867
H	0.2416
H	0.25699
H	0.24298

N	-1.07781
N	-1.0935
As	1.22889
sum	-0.94242

2Sb (R =Ph)

	charge/e
C	-0.52026
C	-0.52655
C	-0.12283
C	-0.12976
O	-0.66548
Mg	1.36115
Cl	-0.71558
N	-1.12166
N	-1.13886
Sb	1.32578
C	0.16097
C	0.15588
C	-0.25522
C	-0.2821
C	-0.26387
C	-0.28683
C	-0.2397
C	-0.23829
C	-0.23897
C	-0.23646
C	-0.26664
C	-0.27078
H	0.26023
H	0.26832
H	0.2534
H	0.27201
H	0.25742
H	0.22628
H	0.24412
H	0.25524
H	0.25186
H	0.24902
H	0.25162
H	0.24942
H	0.24845
H	0.2488
H	0.2329
H	0.25858
H	0.23318
H	0.25523

N	-1.12166
N	-1.13886
Sb	1.32578
sum	-0.93474

2Bi (R=Ph)

	charge/e
Bi	1.40092
Cl	-0.71619
Mg	1.3512
N	-1.13732
N	-1.15631
C	0.15899
C	-0.28908
C	-0.23809
H	0.24872
C	-0.27001
H	0.24821
C	-0.23751
H	0.25153
C	-0.26003
C	0.15353
C	-0.26813
C	-0.2368
H	0.25138
C	-0.27373
H	0.24859
C	-0.23643
H	0.24912
C	-0.2931
O	-0.66307
C	-0.13192
H	0.24058
H	0.25883
C	-0.52749
H	0.27183
H	0.25295
C	-0.51954
H	0.26742
H	0.26122
C	-0.12255
H	0.25825
H	0.22522
H	0.26041
H	0.23038
H	0.25785
H	0.2302

N	-1.13732
N	-1.15631
Bi	1.40092
sum	-0.89271

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