Supporting Information

Reduction of Dichloro(diaza-phospha)stibanes – Isolation of a Donor-stabilized Distibenium Dication

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This file includes:

1. General Information

All manipulations were carried out under oxygen- and moisture free conditions using standard Schlenk and Drybox techniques. $[(TerN)_2P]K{\cdot}DME$[1] and KC_8[2] were prepared according to literature procedures. Fluorobenzene was dried over CaH_2, distilled and degassed prior to use. Diethyl ether, THF, toluene and benzene were dried over Na/benzophenone and freshly distilled prior to use. Dichloromethane was purified according to a literature procedure,[3] consecutively dried over P_4O_{10} and CaH_2 and freshly distilled prior to use. $SbCl_3$ was purified by sublimation.

NMR: $^{31}P\{^1H\}$, $^{13}C\{^1H\}$ and ^1H NMR spectra were recorded on BRUKER spectrometers AVANCE 250, AVANCE 300 and AVANCE 500, respectively. The ^1H and ^{13}C NMR chemical shifts were referenced to the solvent signals ($CDHCl_2$: $\delta(^1H) = 5.32$; $\delta(^{13}C) = 53.84$).[4] The ^{31}P NMR chemical shifts are referred to H_3PO_4 (85%) respectively. CD_2Cl_2 was dried over P_4O_{10} and was degassed prior to use. C_6D_6 was dried over Na and freshly distilled prior to use.

CHN analysis: Analysator Flash EA 1112 from Thermo Quest.

IR: Nicolet 380 FT-IR with a Smart Orbit ATR module.

RAMAN: LabRAM HR 800 Horiba Jobin YVON equipped with a High Stability BX40 Microscope (Focus 1 μm) or an Olympus Mplan 50xNA 0.70 lens, the laser is variable and was chosen prior to the measurement.

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

MS: Finnigan MAT 95-XP from Thermo Electron was used.

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 ($\lambda = 0.71073$). The structures were solved by direct methods (*SHELXS-2013*)[5] and refined by full-matrix least squares procedures (*SHELXL-2013*).[6] Semi-empirical absorption corrections were applied (SADABS).[7] All non-hydrogen atoms were refined anisotropically, hydrogen atoms were included in the refinement at calculated positions using a riding model.

2. Syntheses

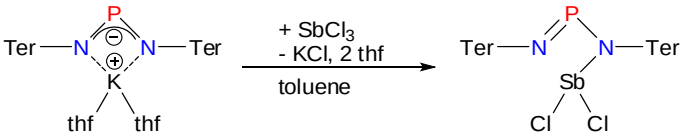
2.1. Synthesis of solvent-free K[(TerN)$_2$P]

A suspension of TerNPN(H)Ter (6.173 g, 8.99 mmol) and potassium (0.703 g, 17.97 mmol) was refluxed in toluene (30 ml) for three days. The resulting brownish suspension was cooled to ambient temperature and filtered through a sintered glass frit. The filtrate was concentrated to incipient crystallization. Pale yellowish crystals of K[(TerN)$_2$P] were obtained in 65% yield (4.234 g, 5.84 mmol).

^{1}H NMR (298 K, C_6D_6, 250.1 MHz): 2.03 (s, 24 H, *o*-CH_3), 2.27 (s, 12 H, *p*-CH_3), 6.75 (s, 8 H, *m*-CH_{Mes}), 6.78-6.91 (m, 6 H, C*H*). **^{31}P NMR** (298 K, C_6D_6, 121.5 MHz): 323.6 (s).

2.2. Synthesis of $Ter_2N_2PSbCl_2$

sum formula: $C_{48}H_{50}N_2PSbCl_2$
mw: 878.56



188 mg K[(TerN)$_2$P] (0.259 mmol) were dissolved in 5 ml toluene. To the yellow solution, a solution of 60 mg $SbCl_3$ (0.263 mml) in 3 ml toluene was added. The solution became turbid after a frew minutes and was stirred for 3 hours to ensure completion of the reaction. The solution was filtered over a sinter padded with kieselguhr (Celite, G4) and the residue was washed with further 3 ml of toluene. The filtrate was concentrated to incipient crystallization (~ 1 ml) and left undisturbed overnight at 4 °C, resulting in the deposition of yellow crystals. The mother liquor was removed via syringe and the crystals were dried in vacuo, yielding 163 mg (0.186 mmol, 72%) of the product.

Mp: 215 °C (dec.). **EA** for $C_{48}H_{50}N_2PSbCl_2$ found (calc.): C 65.03 (65.62), H 5.78 (5.74), N 3.26 (3.19). **^{1}H NMR** (298 K, C_6D_6, 250.1 MHz): 2.08 (s, 24 H, *o*-CH_3), 2.24 (s, 12 H, *p*-CH_3), 6.81 (s, 8 H, *m*-CH_{Mes}), 6.83-6.91 (m, 6 H, C*H*). **^{31}P NMR** (298 K, C_6D_6, 121.5 MHz): 331.5 (br s). **IR** (ATR, cm^{-1}): 2943 (w), 12914 (m), 2852 (w), 2731 (vw), 1610 (m), 1574 (w), 1481 (w), 1435 (m), 1404 (s), 1377 (m), 1288 (w), 1265 (vw), 1223 (vs), 1186 (w), 1159 (vw), 1099 (vw), 1080 (m), 1032 (w), 1009 (m), 964 (m), 941 (w), 895 (w), 847 (s), 827 (m), 796 (s), 777 (vw), 766 (w), 754 (s), 737 (m), 675 (m), 652 (vw), 625 (w), 598 (w), 565 (w), 548 (w), 538 (w). **Raman** (632 nm, cm^{-1}): 3048 (8), 3015 (7), 2917 (19), 2857 (5), 2734 (2), 1610 (12), 1579 (16), 1480 (5), 1413 (49), 1379 (9), 1342 (3), 1300 (37), 1288 (100), 1251 (6), 1185 (4), 1165 (4), 1159 (4), 1088 (13), 1009 (9), 969 (3), 943 (4), 825 (5), 795 (3), 787 (2), 757 (4), 739 (5), 674 (6), 595 (3), 576 (22), 556 (18), 538 (3), 522 (4), 515 (4), 485 (1), 475 (1), 419 (8), 396 (8), 380 (4), 336 (24), 308 (5), 279 (11), 269 (12), 244 (6), 232 (5), 220 (4). **MS** (CI, pos., *iso*-butane) m/z (%): 330 (70) $[TerNH_3]^+$, 386 (17) $[TerNH_2+C_4H_9]^+$, 687 (44) $[Ter_2N_2PH]^+$, 705 (49) $[M]^+$, 743 (11) $[M]^+$, 823 (13) $[M]^+$, 843 (100) $[M–Cl]^+$, 861 (41), 878 (16) $[M]^+$.

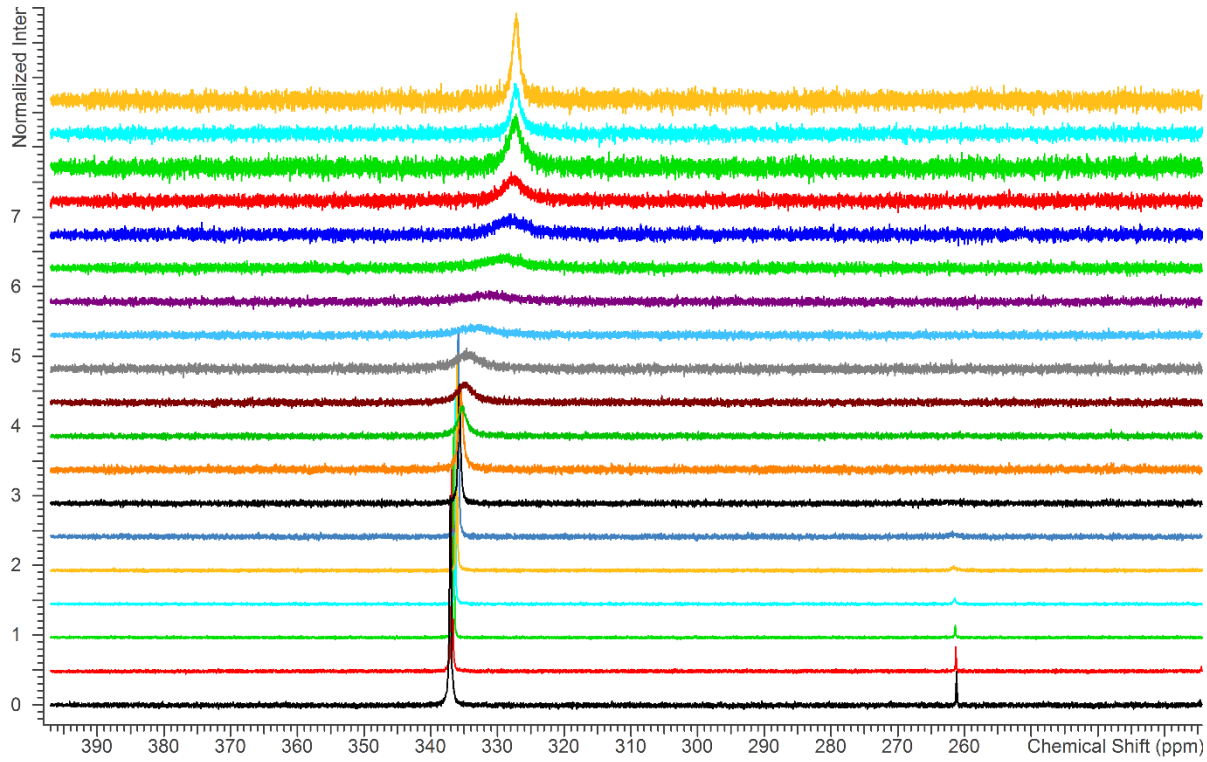
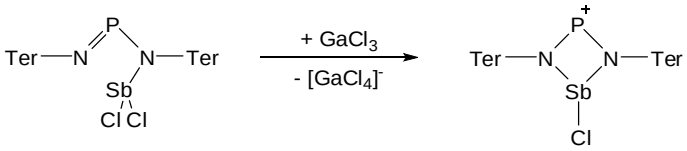


Figure S1. ^{31}P NMR spectra of **2** at various temperatures (top: 100 °C, bottom: –80 °C, 10 K steps, cf. computed NMR shifts: **2** +332, cis +242, trans +262 ppm).

2.3. Synthesis of $[Ter_2N_2PSbCl][GaCl_4]$

sum formula: $C_{48}H_{50}N_2PSbGaCl_5$
mw: 1054.65



To a solution of $[Ter_2N_2PSbCl_2]$ (191 mg, 0.217 mmol) in dichloromethane (4 ml), a solution of $GaCl_3$ (39 mg, 0.221 mmol) is added dropwise at –80 °C. The initially yellow solution immediately turns red and is stirred for further 15 minutes at the same temperature before being warmed to 20 °C. The solution is then concentrated until crystallization commences (~ 0.5 ml) and left undisturbed overnight, which leads to the formation of red needle-shaped crystals (168 mg, 0.159 mmol, 73%). Crystals suitable for X-ray structure elucidation were obtained by repeated recrystallization from dichloromethane between 25 °C and 4 °C.

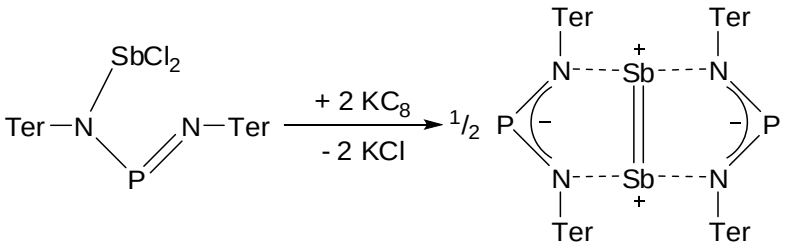
Mp: 258 °C (dec.). **EA** for $C_{48}H_{50}N_2PSbGaCl_5$ found (calc.): C 54.53 (54.66), H 5.48 (4.78), N 2.93 (2.66). **^{1}H NMR** (298 K, CD_2Cl_2, 250.1 MHz): 1.90 (s, 24 H, *o*-CH_3), 2.44 (s, 12 H, *p*-CH_3), 7.03 (d, $^3J_{HH}$ = 7.7 Hz, 4 H, *m*-C*H*), 7.06 (s, 8 H, *m*-CH_{Mes}), 7.28 (t, $^3J_{HH}$ = 7.7 Hz, 2 H, *p*-C*H*). **^{13}C{^{1}H} NMR** (298 K, CD_2Cl_2, 62.9 MHz): 20.62 (s, *C*H$_3$), 20.91 (s, *C*H$_3$), 21.65 (s, *C*H$_3$), 127.18 (s, *C*H), 131.05 (s, *C*H), 131.20 (s, *C*H), 131.48 (d, J_{CP} = 4.4 Hz), 131.54 (s, *C*H), 131.68 (s, *C*H), 133.89 3.3 (d, J_{CP} = 3.3 Hz), 133.93 (s), 134.74 (s), 138.59 (d, J_{CP} = 2.7 Hz), 139.26 (d, J_{CP} = 2.8 Hz), 142.08 (s). **^{31}P NMR** (298 K, CD_2Cl_2, 121.5 MHz): 374.0 (s). **IR** (ATR, cm^{-1}): 2949 (vw), 2920 (w), 2856 (w), 2731 (vw), 1608 (m), 1564 (vw), 1477 (w), 1441 (m), 1410 (s), 1377 (m), 1296 (w), 1269 (vw), 1227 (s), 1140 (m), 1076 (m), 1028 (w), 1014 (m), 991 (w), 960 (s), 941 (w), 852 (sh), 841 (s), 804 (s), 768 (w), 754 (s), 739 (vw), 681 (m), 658 (w), 648 (m), 590 (m), 575 (w), 565 (m), 557 (w), 549 (m), 534 (m), 526 (w). **Raman** (632, 473 nm, cm^{-1}): – decomposition/fluorescence. **MS** (CI, pos., *iso*-butane) m/z (%): 330 (100) $[TerNH_3]^+$, 372 (10), 386 (24) $[TerNH_2{+}C_4H_9]^+$, 687 (40) $[Ter_2N_2PH_2]^+$, 705 (58), 761 (5), 823 (12), 843 (3) $[Ter_2N_2PSbCl]^+$, 859 (34), 1029 (14).

2.4. Attempted Synthesis of Ter_2N_2PSb – Formation of $[(TerN)_2P]MgCl{\cdot}THF$

$[Ter_2N_2PSbCl_2]$ (200 mg, 0.228 mmol) and magnesium turnings (80 mg) were combined in a flask. To this mixture, 10 ml THF were added and the suspension was stirred overnight at ambient temperature with a glas stirring bar. Out of the initially yellow solution a black precipitate was formed. Volatiles were removed in vacuo and the residue was extracted with 10 ml benzene and washed with additional 3 ml benzene. The combined filtrate was concentrated to incipient crystallization (approx. 2 ml) and left undisturbed overnight, resulting in the deposition of light yellow crystals. The supernatant was removed via syringe and the crystals were dried in vacuo (130 mg, 0.159 mmol, 70%).

Mp: 110 °C (dec.). **EA** for $C_{52}H_{58}N_2PMgClO$ found (calc.): C 75.92 (76.37), H 7.36 (7.15), N 3.14 (3.43). **^{1}H NMR** (298 K, C_6D_6, 250.1 MHz): 1.21 (m, 4 H, OCH_2CH_2), 1.98 (s, 12 H, *o*-CH_3), 2.03 (s, 12 H, *o*-CH_3), 2.23 (s, 12 H, *p*-CH_3), 3.21 (m, 4 H, OCH_2CH_2), 6.80-6.89 (m, 6 H, *m*-/*p*-C*H*), 6.87 (s, 8 H, *m*-CH_{Mes}). **^{13}C{^{1}H} NMR** (298 K, C_6D_6, 62.9 MHz): 21.61 (s, CH_3), 21.66 (s, CH_3), 21.83 (s, CH_3), 25.22 (s, OCH_2CH_2), 70.47 (s, OCH_2CH_2), 122.69 (s, CH), 128.92 (s, CH), 129.18 (s, CH), 129.80 (s, CH), 130.22 (s), 134.15 (d, J_{CP} = 6.6 Hz), 137.30 (d, J_{CP} = 13.7 Hz), 137.47 (s), 138.17 (d, J_{CP} = 1.6 Hz), 143.84 (d, J_{CP} = 9.9 Hz). **^{31}P NMR** (298 K, C_6D_6, 121.5 MHz): 351.8 (s). **IR** (ATR, cm^{-1}): 540 (m), 549 (m), 555 (m), 567 (m), 601 (m), 630 (m), 649 (m), 676 (s), 738 (s), 756 (s), 773 (m), 800 (s), 837 (s), 846 (vs), 883 (m), 916 (m), 985 (vs), 1006 (s), 1029 (s), 1081 (s), 1182 (m), 1236 (vs), 1286 (w), 1373 (m), 1405 (s), 1434 (s), 1479 (m), 1579 (w), 1610 (m), 2728 (w), 2854 (m), 2914 (m), 2946 (m), 3025 (w). **Raman** (632, 473 nm, cm^{-1}): 153 (5), 205 (1), 233 (23), 265 (14), 335 (10), 374 (4), 383 (7), 392 (10), 415 (3), 449 (2), 476 (9), 492 (3), 503 (10), 509 (7), 521 (18), 538 (12), 557 (21), 573 (21), 593 (6), 602 (3), 630 (1), 651 (16), 675 (16), 691 (2), 737 (4), 755 (24), 782 (2), 788 (6), 800 (19), 836 (29), 883 (3), 911 (1), 916 (1), 943 (2), 961 (1), 985 (49), 1004 (19), 1086 (28), 1099 (5), 1165 (2), 1185 (2), 1248 (5), 1285 (100), 1299 (26), 1377 (7), 1381 (8), 1417 (53), 1479 (4), 1582 (17), 1610 (3), 2725 (1), 2852 (1), 2916 (1), 2946 (1), 3001 (1), 3041 (1).

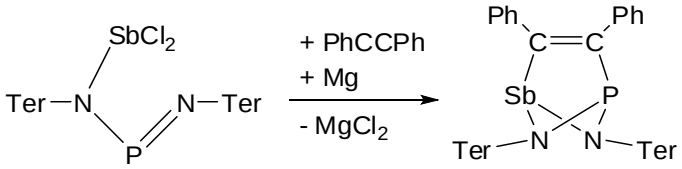
2.5. Synthesis of $[(Ter_2N_2PSb)_2]$



$[Ter_2N_2PSbCl_2]$ (215 mg, 0.245 mmol) were dissolved in 5 ml benzene while stirring with a glas stirring bar. To the solution, KC_8 (70 mg, 0.518 mmol) was added. The solution adopted a dark green colour after 5 minutes. To ensure completion of the reaction, the suspension was stirred for 3 hours at ambient temperature. The suspension was filtered over a sinter padded with kieselguhr (Celite) and the residue was washed with another 2 ml benzene. The combined filtrate was concentrated to incipient crysallization (approx. 1 ml) and left undisturbed overnight. Orange block-shaped crystals were obtained. The supernatant was removed via syringe and the crystals were dried in vacuo (43 mg, 0.027 mmol, 22%).

Mp: 110 °C (dec.). **EA** for $C_{96}H_{100}N_4P_2Sb_2$ found (calc.): C 70.80 (70.98), H 6.98 (6.76), N 3.48 (3.45). **^{1}H NMR** (298 K, C_6D_6, 250.1 MHz): 2.03 (s, 48 H, o-CH_3), 2.25 (s, 24 H, p-CH_3), 6.72 (s, 16 H, m-CH_{Mes}), 6.80-6.93 (m, 12 H, *m*-/*p*-C*H*). **^{13}C{^{1}H} NMR** (298 K, C_6D_6, 62.9 MHz): 21.39 (s, *o*-CH_3), 21.71 (s, *p*-CH_3), 119.77 (s, C*H*), 128.31 (s, C*H*), 128.92 (s, C*H*),129.56 (s, C*H*), 135.31 (s), 136.01 (s), 136.83 (s), 137.18 (s), 137.43 (s), 137.89 (s), 138.52 (s), 141.86 (s). **^{31}P NMR** (298 K, C_6D_6, 121.5 MHz): 326.0 (s). **IR** (ATR, cm^{-1}): 551 (m), 559 (s), 599 (m), 624 (m), 649 (s), 657 (s), 675 (vs), 738 (s), 752 (s), 792 (vs), 813 (s), 842 (vs), 885 (m), 927 (m), 972 (m), 1006 (s), 1031 (m), 1085 (s), 1207 (s), 1263 (m), 1371 (s), 1400 (s), 1434 (s), 1479 (m), 1573 (w), 1610 (m), 2726 (w), 2852 (w), 2914 (m), 2946 (m), 2996 (w), 3033 (w). **Raman** (632 nm, cm^{-1}): 227 (64), 232 (64), 266 (61), 329 (12), 342 (7), 386 (24), 400 (18), 420 (35), 496 (7), 509 (17), 525 (19), 559 (80), 575 (64), 581 (48), 599 (10), 650 (8), 661 (9), 742 (49), 752 (5), 765 (4), 779 (5), 795 (6), 804 (4), 824 (3), 879 (3), 909 (4), 947 (10), 962 (4), 982 (31), 993 (33), 1004 (16), 1015 (5), 1031 (3), 1096 (61), 1158 (9), 1166 (10), 1184 (12), 1205 (67), 1237 (100), 1245 (81), 1266 (20), 1279 (38), 1297 (59), 1305 (94), 1372 (23), 1380 (24), 1402 (77), 1435 (14), 1444 (14), 1479 (17), 1577 (39), 1612 (51), 2727 (6), 2853 (17), 2913 (62), 2945 (19), 3016 (20), 3038 (20), 3061 (18).

2.6. Synthesis of [(Ter_2N_2PSb)(PhCCPh)]



[$Ter_2N_2PSbCl_2$] (180 mg, 0.205 mmol), diphenylacetylene (53 mg) and magnesium turnings (80 mg) were combined in a flask. To this mixture, 10 ml THF were added and the suspension was stirred overnight at ambient temperature with a glass stirring bar. The initially yellow solution quickly turned orange, but the formation of a black precipitate occurred as well. Volatiles were removed in vacuo. The residue was extracted with 5 ml benzene and washed with another 3 ml benzene. The extract was concentrated to incipient crystallization (approx. 1 ml) and left undisturbed overnight, affording orange crystals. The mother liquor was removed via syringe and the crystals were dried in vacuo (82 mg, 0.083 mmol, 40%).

Mp. 231 °C (dec.). **EA** for $C_{62}H_{60}N_2PSb$ found (calc.): C 68.93 (69.39), H 6.00 (5.64), N 2.86 (2.61). **^{1}H NMR** (298 K, C_6D_6, 250.1 MHz): 2.05 (s, 12 H, *o*-CH_3), 2.09 (s, 12 H, *o*-CH_3), 2.20 (s, 12 H, *p*-CH_3), 6.54 (s, 8 H, CH_{Mes}), 6.68 (s, 6 H, *m*-/*p*-C*H*), 6.82-7.23 (m, 10 H, CH_{Ph}). **^{13}C{^{1}H} NMR** (298 K, C_6D_6, 62.9 MHz): 21.76 (s, CH_3), 21.85 (s, CH_3), 21.96 (s, CH_3), 21.99 (s, CH_3), 118.47 (s, C*H*), 122.69 (s, C*H*), 124.29 (s), 127.02 (s, C*H*), 127.53 (s, C*H*), 129.09 (s, C*H*), 129.24 (s, C*H*), 139.65 (s, C*H*), 130.23 (s, C*H*), 131.04 (s, C*H*), 132.31 (s, C*H*), 134.15 (d, J_{CP} = 54.5 Hz), 137.20 (s), 137.47 (s, C*H*), 138.04 (s), 138.27 (s, C*H*), 138.32 (s, C*H*), 138.69 (s), 141.29 (d, J_{CP} = 54.5 Hz), 141.98 (d, J_{CP} = 54.5 Hz), 180.83 (d, J_{CP} = 54.5 Hz, P*C*), 183.95 (d, J_{CP} = 6.6 Hz, Sb*C*). **^{31}P NMR** (298 K, C_6D_6, 121.5 MHz): 219.0 (s). **IR** (ATR, cm^{-1}): 3061 (vw), 3053 (vw), 2968 (w), 2937 (w), 2912 (m), 2852 (w), 2725 (vw), 1610 (m), 1601 (m), 1579 (w), 1572 (w), 1497 (m), 1489 (m), 1441 (s), 1398 (s), 1373 (s), 1306 (w), 1289 (w), 1225 (s), 1180 (w), 1157 (vw), 1149 (vw), 1101 (vw), 1080 (m), 1070 (m), 1026 (m), 1007 (w), 985 (m), 955 (vw), 947 (vw), 916 (m), 881 (s), 845 (s), 810 (w), 800 (w), 791 (w), 773 (m), 750 (vs), 723 (m), 668 (vs), 665 (m), 646 (w), 627 (w), 609 (w), 604 (w), 590 (w), 571 (w), 550 (w), 536 (m). **Raman** (632 nm, cm^{-1}): 104 (10), 135 (8), 153 (36), 205 (10), 227 (12), 246 (24), 263 (8), 280 (6), 292 (11), 310 (8), 361 (7), 426 (33), 472 (2), 497 (3), 503 (3), 518 (4), 530 (10), 547 (12), 563 (26), 583 (39), 602 (14), 634 (4), 674 (4), 747 (9), 774 (4), 799 (3), 819 (2), 889 (4), 911 (7), 936 (9), 953 (6), 962 (4), 992 (5), 1006 (92), 1036 (18), 1099 (9), 1109 (9), 1157 (30), 1164 (29), 1188 (9), 1235 (17), 1243 (25), 1284 (19), 1312 (25), 1387 (16), 1407 (17), 1413 (18), 1445 (20), 1492 (7), 1529 (6), 1549 (100), 1594 (62), 2732 (24), 2737 (23), 2857 (4), 2920 (16), 2944 (6), 2977 (5), 3039 (8), 3063 (11), 3079 (5). **MS** (CI, pos., *iso*-butane) m/z (%): 330 (100) [$TerNH_3$]$^+$2AsAs, 386 (17) [$TerNH_2$+C_4H_9]$^+$, 687 (46) [$(TerNH)_2P$]$^+$, 705 (61) [$TerNH_3$]$^+$, 743 (16) [$TerNH_3$]$^+$, 806 (5) [Ter_2N_2PSb]$^+$, 987 (1) [M+H]$^+$.

3. Crystallographic Data

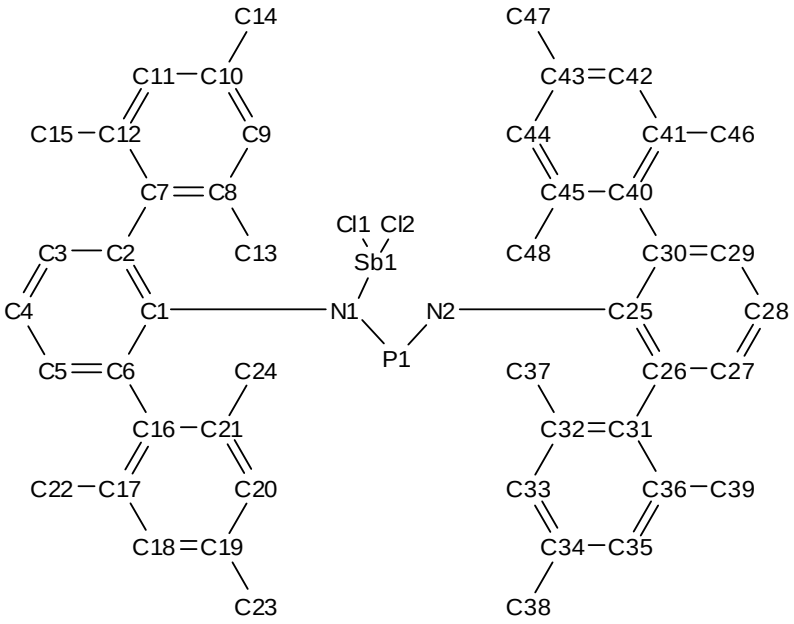
Table S1. Crystallographic data of **1**, **2** and **3**.

compound	**1**	**2**	**3**
sum formula	$C_{48}H_{50}N_2PK$	$C_{48}H_{50}N_2PSbCl_2$	$C_{48}H_{50}N_2PSbGaCl_5$
formular weight [g mol^{-1}]	724.97	878.52	1054.59
colour	yellow	yellow	red
crystal system	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$	$P2_1/c$
a [Å]	13.9771(9)	12.0987(9)	31.5546(10)
b [Å]	20.921(1)	22.5405(18)	16.1500(5)
c [Å]	14.604(1)	16.4923(14)	19.5721(6)
α [°]	90	90	90
β [°]	108.648(3)	106.879(3)	106.735(2)
γ [°]	90	90	90
V [Å^3]	4046.1(5)	4303.9(6)	9551.6(5)
Z	4	4	8
$\rho_{calc.}$ [g cm^{-3}]	1.190	1.356	1.467
μ [mm^{-1}]	0.206	0.837	1.478
$\lambda_{MoK\alpha}$ [Å]	0.71073	0.71073	0.71073
T [K]	173	173	173
measured reflexes	36804	56384	173701
independent reflexes	7525	8912	27774
reflexes $I > 2\sigma(I)$	3902	5362	17455
$R_{int.}$	0.1234	0.1256	0.0691
$2\Theta_{max.}$ [°]	51	53	60
$F(000)$	1544	1808	4272
R_1 (R [$F^2 > 2\sigma(F^2)$])	0.0572	0.0513	0.0565
wR_2 (all data)	0.1282	0.1354	0.1279
GooF	1.000	1.016	1.031
parameter	482	499	1096
CCDC #	1404259	1404260	1404261

Table S2. Crystallographic data of **4**, **5** and **6**.

compound	**4**	**5**	**6**
sum formula	$C_{52}H_{58}ClMgN_2OP$	$C_{62}H_{60}N_2PSb$	$C_{96}H_{100}N_4P_2Sb_2$
formular weight [g mol^{-1}]	817.73	985.84	1615.23
colour	yellow	orange	yellow
crystal system	monoclinic	monoclinic	orthorhombic
space group	$P2_1/c$	Cc	$Pnnn$
a [Å]	12.8983(9)	18.1642(6)	15.3403(5)
b [Å]	15.7209(11)	11.4249(4)	15.7088(7)
c [Å]	22.3241(15)	23.9813(8)	16.8844(6)
α [°]	90	90	90
β [°]	95.003(4)	99.487(2)	90
γ [°]	90	90	90
V [Å^3]	4509.5(5)	4908.6(3)	4068.8(3)
Z	4	4	2
$\rho_{calc.}$ [g cm^{-3}]	1.204	1.334	1.318
μ [mm^{-1}]	0.174	0.637	0.752
$\lambda_{MoK\alpha}$ [Å]	0.71073	0.71073	0.71073
T [K]	173	173	173
measured reflexes	43759	48308	37272
independent reflexes	8369	16881	6776
reflexes $I > 2\sigma(I)$	5311	14533	4081
$R_{int.}$	0.0633	0.0390	0.0670
$2\Theta_{max.}$ [°]	51	65	63
$F(000)$	1744	2048	1672
R_1 (R [$F^2 > 2\sigma(F^2)$])	0.0523	0.0425	0.0419
wR_2 (all data)	0.1489	0.1008	0.1077
GooF	1.023	1.048	1.020
parameter	560	573	242
CCDC #	1404262	1404263	1404264

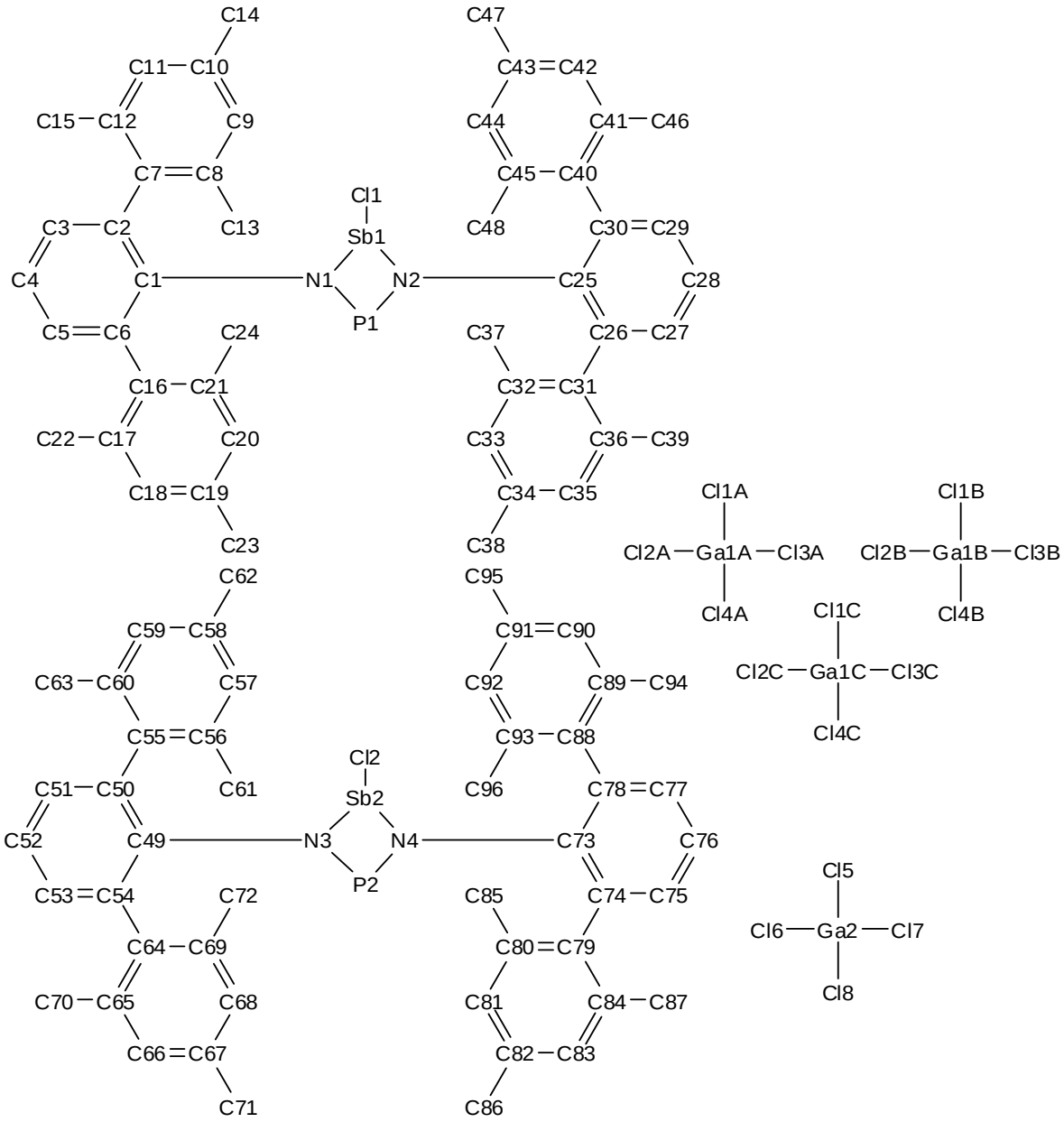
3.1. Numbering scheme of **2**



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

Sb1–N1	2.133(4)	**N1–Sb1–N2**	63.56(14)
Sb1–N2	2.392(4)	**Cl1–Sb1–Cl2**	88.21(5)
Sb1–Cl1	2.3582(15)	**N2–P1–N1**	96.0(2)
Sb1–Cl2	2.4509(14)	**P1–N1–Sb1**	105.12(19)
Sb1–P1	2.9978(15)	**P1–N2–Sb1**	95.33(18)
P1–N2	1.598(4)	**N2–Sb1–Cl2**	149.78(10)
P1–N1	1.623(4)	**N2–P1–N1–Sb1**	1.1(2)

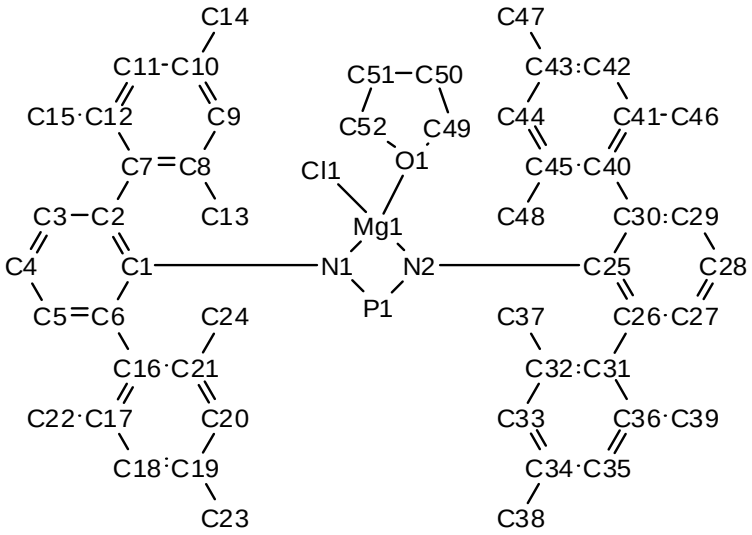
3.2. Numbering scheme of **3**



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

Sb1–N1	2.136(3)	**N1–Sb1–N2**	65.99(13)
Sb1–N2	2.171(3)	**N1–Sb1–Cl1**	100.97(9)
Sb1–Cl1	2.3417(11)	**N2–P1–N1**	91.74(17)
Sb1–P1	2.9430(11)	**P1–N1–Sb1**	101.52(16)
P1–N2	1.625(3)	**N2–P1–N1–Sb1**	–1.80(17)
P1–N1	1.643(4)	**N1–P1–N2–Sb1**	1.76(16)

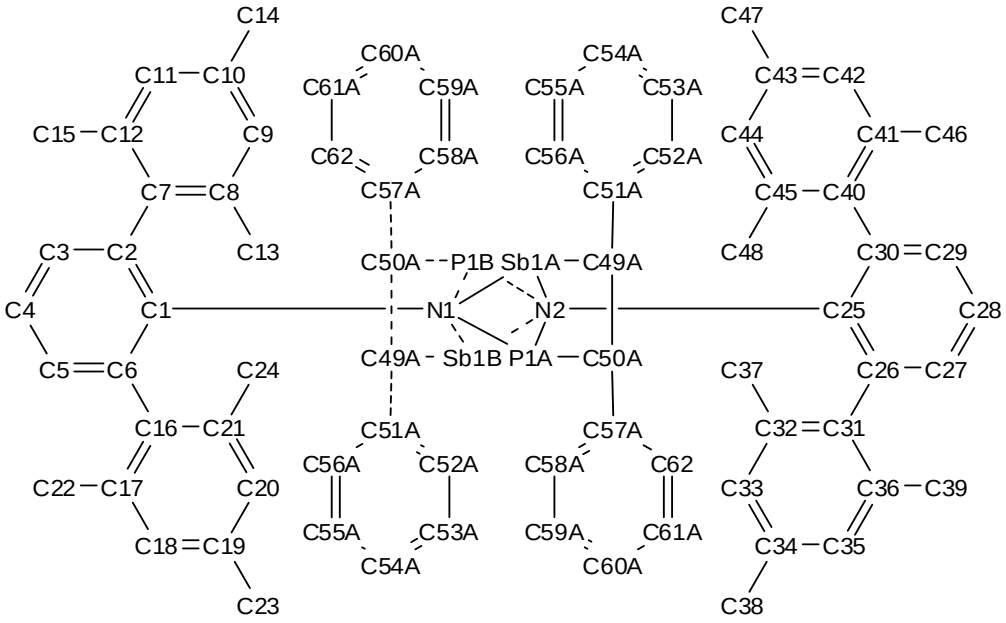
3.3. Numbering scheme of **4**



Selected bond lengths [Å] and angles [°] of **4**.

Cl1–Mg1	2.2685(11)	**N2–P1–N1**	98.26(11)
P1–N2	1.607(2)	**O1–Mg1–N2**	115.99(9)
P1–N1	1.615(2)	**N2–Mg1–N1**	71.12(8)
P1–Mg1	2.7576(12)	**O1–Mg1–Cl1**	102.94(7)
Mg1–O1	1.997(2)	**P1–N1–Mg1**	94.86(9)
Mg1–N2	2.088(2)	**N2–P1–N1–Mg1**	2.14(11)
Mg1–N1	2.102(2)	**N1–P1–N2–Mg1**	–2.16(11)

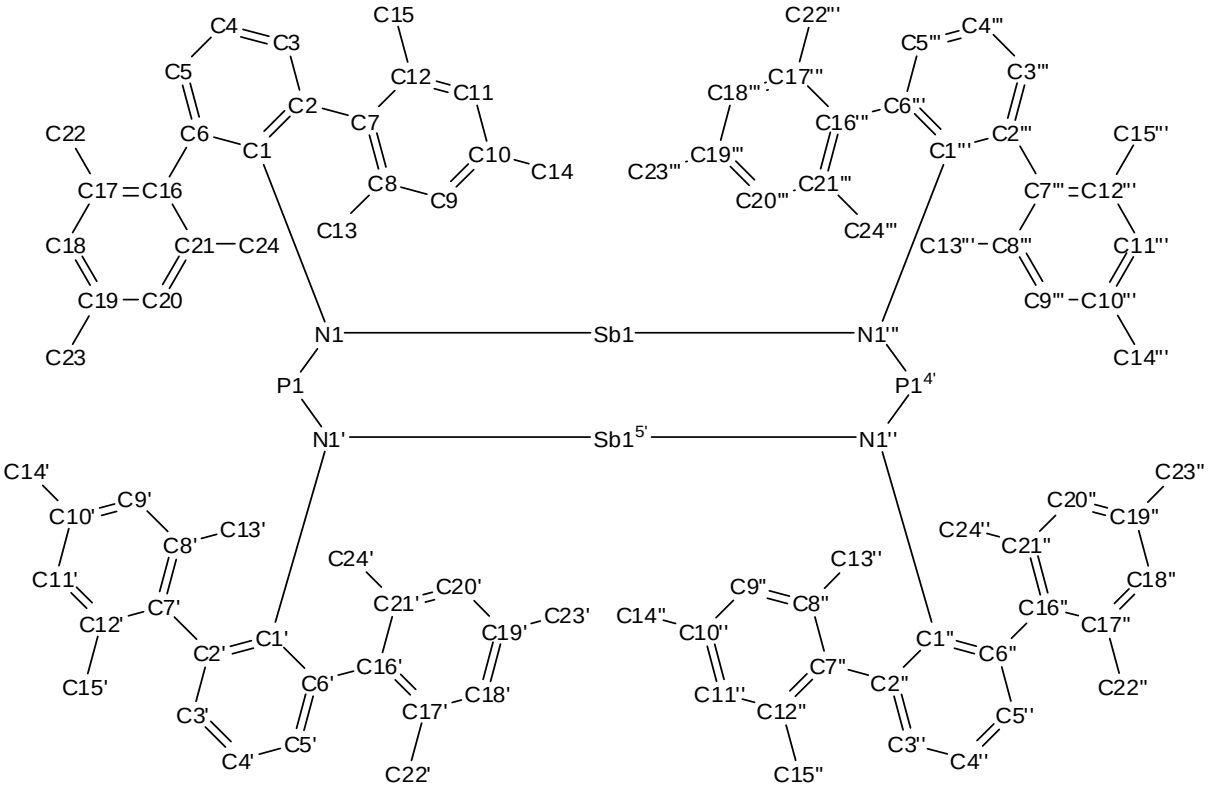
3.4. Numbering scheme of **5**



Selected bond lengths [Å] and angles [°] of **5**.

Sb1A–N1	2.163(3)	**N2–Sb1A–N1**	67.06(10)
Sb1A–N2	2.135(3)	**N2–Sb1A–C49A**	83.51(18)
Sb1A–C49A	2.228(8)	**C49A–Sb1A–P1A**	65.46(14)
Sb1A–P1A	2.8038(19)	**N1–P1A–N2**	89.05(16)
P1A–N1	1.682(3)	**C50A–P1A–Sb1A**	73.54(18)
P1A–N2	1.703(3)	**C50A–C49A–Sb1A**	107.7(4)
P1A–C50A	1.947(8)	**C49A–C50A–P1A**	113.3(4)
C49A–C50A	1.337(6)	**Sb1A–C49A–C50A–P1A**	–2.1(7)

3.5. Numbering scheme of **6**



Selected bond lengths [Å] and angles [°] of **6**.

Sb1–N1	2.372(2)	**N1–Sb1–N1'**	177.81(9)
Sb1–N1'	2.372(2)	**N1'–Sb1–Sb1''**	88.91(4)
Sb1–Sb1''	2.6438(4)	**N1–P1–N1'''**	104.61(14)
P1–N1	1.613(2)	**N1'''–P1–N1–Sb1**	–0.51(7)
P1–N1'''	1.613(2)	**N1'''–P1–N1–C1**	–169.4(2)

Symmetry code: (') 0.5-x, 0.5-y, z; ('') 0.5-x, y, 1.5-z; (''') x, 0.5-y, 1.5-z.

4. Computational Details

Utilizing the experimental structural data, all calculations were carried out with the Gaussian 09 package of molecular orbital programs.[8] The wave functions for the crystal structures were optimized with a 6-31G(d,p) basis set on the pbe1pbe level of density functional theory and the optimized structures were checked to be a minimum on the energy hypersurface. For Sb a relativistic pseudopotential was used, Sb: ECP46MDF 4 46.
ELF[9] and NBO/NRT[10–12] analyses were carried out to study the bonding, hybridization and polarization effects. For the ELF computations a full DZP basis was used for antimony instead of the above mentioned pseudopotential.

For **5** and **6** the ^{31}P NMR chemical shifts and coupling constants were calculated using the GIAO package implemented in Gaussian 09. The calculated absolute shifts (σ_{iso}) were referenced to the absolute chemical shift the standard (^{31}P: H_3PO_4, σ_{ref} =374.0604; ^{1}H, ^{13}C: $SiMe_4$, 31.665 and 196.4544 ppm, respecitvely), using the formula $\delta_{calc} = \sigma_{ref} - \sigma_{iso}$. Simulations of NMR spectra were performed with gNMR 5.06, which is obtainable free of charge from Peter H.M. Budzelaar via http://home.cc.umanitoba.ca/~budzelaa/gNMR/gNMR.html.

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

4.1. NPN salts (1, 4) – charge transfer

4.1.1. NBO analysis for $K[P(NPh)_2]$

```
Summary of Natural Population Analysis:
                                     Natural Population
                Natural  -----------------------------------------------
   Atom  No     Charge         Core      Valence    Rydberg      Total
 ------------------------------------------------------------------------
      N    1   -1.05614      1.99949     6.04222    0.01443     8.05614
      P    2    1.13767      9.99807     3.79444    0.06982    13.86233
      N    4   -1.05614      1.99949     6.04223    0.01442     8.05614
      K   22    0.90675     17.99501     0.09661    0.00164    18.09325

       (Occupancy)   Bond orbital/ Coefficients/ Hybrids
 --------------------------------------------------------------------------------
    1. (1.97852) BD ( 1) N   1 - P   2
               ( 73.64%)   0.8582* N   1 s( 30.78%)p 2.25( 69.12%)d 0.00(  0.10%)
                                          -0.0001  0.5548  0.0031 -0.0032  0.6162
                                           0.0150 -0.5426  0.0093 -0.1295  0.0056
                                          -0.0245 -0.0007  0.0036 -0.0057 -0.0188
               ( 26.36%)   0.5134* P   2 s( 15.76%)p 5.24( 82.55%)d 0.11(  1.68%)
                                           0.0000  0.0004  0.3830 -0.1044 -0.0013
                                          -0.0003 -0.6880  0.0523  0.0002  0.5758
                                          -0.0174  0.0000 -0.1326 -0.0012 -0.1067
                                           0.0389 -0.0124  0.0212 -0.0577
    4. (1.98021) BD ( 1) P   2 - N   4
               ( 26.42%)   0.5140* P   2 s( 15.97%)p 5.16( 82.47%)d 0.10(  1.56%)
                                           0.0000 -0.0005 -0.3855  0.1052  0.0012
                                          -0.0002 -0.6574  0.0498 -0.0002 -0.5787
                                           0.0175  0.0000 -0.2341 -0.0030 -0.1021
                                          -0.0282 -0.0207 -0.0220  0.0588
               ( 73.58%)   0.8578* N   4 s( 30.41%)p 2.29( 69.49%)d 0.00(  0.10%)
                                           0.0001 -0.5514 -0.0031  0.0033  0.6129
                                           0.0148  0.5315 -0.0096 -0.1907  0.0048
                                          -0.0245  0.0005  0.0057  0.0054  0.0186
    5. (1.87383) BD ( 2) P   2 - N   4
               ( 24.63%)   0.4963* P   2 s(  0.25%)p99.99( 97.91%)d 7.36(  1.84%)
                                           0.0000 -0.0008 -0.0482  0.0135 -0.0001
                                          -0.0005 -0.2535  0.0214 -0.0004 -0.0611
                                           0.0026  0.0008  0.9541  0.0170 -0.0375
                                           0.1032  0.0781 -0.0085  0.0139
               ( 75.37%)   0.8681* N   4 s(  0.55%)p99.99( 99.33%)d 0.22(  0.12%)
                                           0.0002 -0.0743  0.0009 -0.0003  0.0869
                                           0.0043  0.1734  0.0026  0.9776  0.0036
                                          -0.0027 -0.0060 -0.0336  0.0038  0.0030
   62. (1.89267) LP ( 1) N   1           s( 29.12%)p 2.43( 70.82%)d 0.00(  0.06%)
                                           0.0001  0.5396  0.0031  0.0017  0.2406
                                          -0.0168  0.7993 -0.0120  0.1045 -0.0021
                                          -0.0112  0.0029 -0.0027  0.0208  0.0079
   63. (1.97216) LP ( 1) P   2           s( 69.68%)p 0.43( 30.26%)d 0.00(  0.07%)
                                           0.0000 -0.0007  0.8343  0.0258  0.0005
                                           0.0000 -0.0019  0.0001 -0.0004 -0.5493
                                          -0.0289  0.0000  0.0060  0.0001 -0.0003
                                          -0.0029  0.0005 -0.0065  0.0249
   64. (1.89265) LP ( 1) N   4           s( 28.94%)p 2.45( 71.00%)d 0.00(  0.06%)
                                           0.0001  0.5379  0.0031  0.0017 -0.2388
                                           0.0169  0.8038 -0.0119 -0.0805  0.0023
                                           0.0112  0.0028  0.0019  0.0210  0.0080

Second Order Perturbation Theory Analysis of Fock Matrix in NBO Basis
  61. LP (   1) N   1               / 67. LP*(   1) K  22                    3.32
0.42    0.034
  61. LP (   1) N   1               / 68. LP*(   2) K  22                    0.78
0.46    0.017
  61. LP (   1) N   1               / 74. LP*(   8) K  22                    0.08
0.56    0.006
  61. LP (   1) N   1               /251. RY*(   2) K  22                    0.08
0.61    0.006
```

```
  61. LP (   1) N   1               /253. RY*(   4) K  22                    0.09
0.77    0.008
  62. LP (   2) N   1               / 71. LP*(   5) K  22                    0.36
0.23    0.009
  62. LP (   2) N   1               / 73. LP*(   7) K  22                    0.14
0.50    0.008
  63. LP (   1) P   2               / 67. LP*(   1) K  22                    3.21
0.51    0.037
  63. LP (   1) P   2               / 70. LP*(   4) K  22                    0.77
0.55    0.018
  63. LP (   1) P   2               / 74. LP*(   8) K  22                    0.05
0.65    0.005
  63. LP (   1) P   2               /251. RY*(   2) K  22                    0.11
0.70    0.008
  64. LP*(   2) P   2               / 73. LP*(   7) K  22                    0.16
0.42    0.012
  65. LP (   1) N   4               / 67. LP*(   1) K  22                    3.32
0.42    0.034
  65. LP (   1) N   4               / 68. LP*(   2) K  22                    0.78
0.46    0.017
  65. LP (   1) N   4               / 74. LP*(   8) K  22                    0.08
0.56    0.006
  65. LP (   1) N   4               /251. RY*(   2) K  22                    0.08
0.61    0.006
  65. LP (   1) N   4               /253. RY*(   4) K  22                    0.09
0.77    0.008
  66. LP (   2) N   4               / 71. LP*(   5) K  22                    0.36
0.23    0.009
  66. LP (   2) N   4               / 73. LP*(   7) K  22                    0.14
0.50    0.008
```

4.1.2. Optimized geometry for K[P(NPh)$_2$]

N	-1.27230500	0.38415400	0.10758800
P	0.00000100	-0.62032900	-0.00000300
C	-2.56981500	-0.10901100	0.02127900
N	1.27230400	0.38415100	-0.10764300
C	-3.57025400	0.45833300	0.83341800
C	-2.96291400	-1.12350300	-0.87380000
C	2.56981300	-0.10901100	-0.02130300
C	-4.88655900	0.02169700	0.77006000
C	-4.28102500	-1.56080900	-0.92875400
C	2.96291300	-1.12342600	0.87386100
C	3.57024800	0.45825900	-0.83349900
C	-5.25475800	-0.99419500	-0.11037800
C	4.28102400	-1.56073000	0.92884800
C	4.88655300	0.02162500	-0.77011000
C	5.25475400	-0.99419100	0.11041600
H	-5.63271700	0.47718500	1.41642900
H	-4.55117500	-2.34678900	-1.62950100
H	-6.28519100	-1.33238000	-0.16303900
H	4.55117500	-2.34664900	1.62966200
H	5.63270800	0.47705300	-1.41652400
H	6.28518600	-1.33237300	0.16310200
K	0.00000700	2.66561600	0.00000600
H	2.21924200	-1.55114100	1.54121600
H	3.28207100	1.23804800	-1.53461500
H	-2.21924200	-1.55127800	-1.54111500
H	-3.28208000	1.23818400	1.53446700

4.1.3. NBO analysis for Li[P(NPh)$_2$]

Summary of Natural Population Analysis:

		Natural	Natural Population			
Atom	No	Charge	Core	Valence	Rydberg	Total

```
     N    1   -1.08927      1.99948     6.07676    0.01303     8.08927
     P    2    1.18104      9.99794     3.75330    0.06773    13.81896
     N    4   -1.08926      1.99948     6.07676    0.01302     8.08926
    Li   22    0.82680      1.99839     0.17139    0.00342     2.17320

      (Occupancy)   Bond orbital/ Coefficients/ Hybrids
-------------------------------------------------------------------------------
    1. (1.96931) BD ( 1) N   1 - P   2
               ( 73.99%)   0.8602* N   1 s( 28.52%)p 2.50( 71.38%)d 0.00(  0.10%)
                                        -0.0002  0.5340  0.0034 -0.0030  0.6034
                                         0.0078 -0.5559 -0.0034  0.2014  0.0052
                                        -0.0236  0.0027 -0.0071 -0.0045 -0.0189
               ( 26.01%)   0.5100* P   2 s( 15.94%)p 5.17( 82.45%)d 0.10(  1.61%)
                                         0.0000  0.0003  0.3865 -0.0999 -0.0005
                                        -0.0003 -0.6871  0.0520  0.0002  0.5799
                                        -0.0153  0.0001  0.1150  0.0028 -0.1086
                                        -0.0074  0.0088  0.0226 -0.0609
    3. (1.96932) BD ( 1) P   2 - N   4
               ( 26.01%)   0.5100* P   2 s( 15.94%)p 5.17( 82.45%)d 0.10(  1.61%)
                                         0.0000 -0.0003 -0.3865  0.0999  0.0005
                                        -0.0003 -0.6873  0.0520 -0.0002 -0.5796
                                         0.0152  0.0001  0.1150  0.0028 -0.1086
                                         0.0074  0.0088 -0.0227  0.0609
               ( 73.99%)   0.8602* N   4 s( 28.53%)p 2.50( 71.37%)d 0.00(  0.10%)
                                         0.0002 -0.5341 -0.0034  0.0030  0.6034
                                         0.0078  0.5557  0.0034  0.2018  0.0052
                                        -0.0236 -0.0027 -0.0071  0.0045  0.0189
    53. (1.87325) LP ( 1) N   1           s( 27.31%)p 2.66( 72.65%)d 0.00(  0.04%)
                                        -0.0001  0.5225  0.0047  0.0029  0.2546
                                        -0.0258  0.8086 -0.0122  0.0845 -0.0027
                                        -0.0063  0.0027 -0.0016  0.0183  0.0047
    54. (1.54274) LP ( 2) N   1           s(  2.20%)p44.42( 97.70%)d 0.05(  0.11%)
                                         0.0003  0.1483  0.0025 -0.0017  0.1550
                                        -0.0013 -0.0427  0.0042 -0.9752 -0.0030
                                        -0.0065 -0.0060  0.0307  0.0013 -0.0053
    55. (1.97186) LP ( 1) P   2           s( 69.63%)p 0.44( 30.30%)d 0.00(  0.07%)
                                         0.0000 -0.0008  0.8341  0.0244  0.0002
                                         0.0000 -0.0001  0.0000 -0.0005 -0.5498
                                        -0.0281  0.0000 -0.0001  0.0000  0.0000
                                        -0.0031  0.0000 -0.0061  0.0251
    56. (0.73329) LP*( 2) P   2           s(  0.00%)p 1.00( 99.26%)d 0.01(  0.74%)
                                         0.0000  0.0000  0.0001  0.0000  0.0000
                                         0.0000  0.1620 -0.0048  0.0000 -0.0001
                                         0.0000  0.0000  0.9828  0.0185  0.0211
                                         0.0000  0.0834  0.0000  0.0000
    57. (1.87322) LP ( 1) N   4           s( 27.30%)p 2.66( 72.66%)d 0.00(  0.04%)
                                        -0.0001  0.5224  0.0047  0.0029 -0.2544
                                         0.0258  0.8087 -0.0122 -0.0844  0.0027
                                         0.0063  0.0027  0.0016  0.0183  0.0047
    58. (1.54272) LP ( 2) N   4           s(  2.20%)p44.46( 97.70%)d 0.05(  0.11%)
                                         0.0003  0.1482  0.0026 -0.0017 -0.1556
                                         0.0013 -0.0429  0.0042  0.9751  0.0030
                                         0.0065 -0.0060 -0.0307  0.0013 -0.0053
    59. (0.10939) LP*( 1)Li  22           s( 89.09%)p 0.12( 10.89%)d 0.00(  0.01%)
                                         0.0000  0.9439 -0.0029 -0.0003 -0.0001
                                         0.0000 -0.3292 -0.0233 -0.0002  0.0000
                                         0.0000 -0.0092  0.0000  0.0022 -0.0065


Second Order Perturbation Theory Analysis of Fock Matrix in NBO Basis
  54. LP (   2) N   1               / 56. LP*(   2) P   2                  138.75
0.11    0.120

  58. LP (   2) N   4               / 73. RY*(   1) P   2                    1.00
1.03    0.032
  53. LP (   1) N   1               / 59. LP*(   1)Li  22                   13.35
0.52    0.075
  57. LP (   1) N   4               / 59. LP*(   1)Li  22                   13.34
0.52    0.075
```

4.1.4. Optimized geometry for Li[P(NPh)$_2$]

N	-1.24418800	0.66168600	0.07918700
P	0.00000700	-0.38901800	0.00022000
C	-2.57521000	0.25681900	0.00821000
N	1.24417700	0.66169500	-0.07902000
C	-3.54200800	0.98380600	0.72264100
C	-3.01161800	-0.83134500	-0.76825900
C	2.57520500	0.25682900	-0.00820000
C	-4.88230400	0.62339200	0.68295400
C	-4.35354200	-1.19114800	-0.79821000
C	3.01169600	-0.83127400	0.76830400
C	3.54192500	0.98376400	-0.72279400
C	-5.29900200	-0.46957700	-0.07425600
C	4.35362500	-1.19106800	0.79814100
C	4.88222600	0.62335900	-0.68322200
C	5.29900500	-0.46955400	0.07402600
H	-5.60778900	1.20037500	1.25018400
H	-4.66410200	-2.03656700	-1.40632900
H	-6.34775100	-0.74831000	-0.10793600
H	4.66425200	-2.03643800	1.40629300
H	5.60765000	1.20030100	-1.25057300
H	6.34775900	-0.74828300	0.10761400
Li	-0.00001000	2.12824400	0.00009300
H	2.28865800	-1.38042100	1.36594600
H	3.21411900	1.82632700	-1.32616700
H	-2.28851600	-1.38054200	-1.36577600
H	-3.21426700	1.82641200	1.32599000

4.1.5. NBO analysis for MgCl[P(NPh)$_2$]

			Natural Population			
Atom	No	Natural Charge	Core	Valence	Rydberg	Total
P	1	1.21701	9.99795	3.72199	0.06305	13.78299
Cl	2	-0.69614	9.99987	7.69179	0.00448	17.69614
Mg	3	1.33915	9.99744	0.64661	0.01680	10.66085
N	4	-1.08417	1.99951	6.07029	0.01437	8.08417
N	5	-1.09810	1.99951	6.08448	0.01411	8.09810

(Occupancy) Bond orbital/ Coefficients/ Hybrids

```
    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
   81. (0.72509) LP*( 2) P   1          s(  0.12%)p99.99( 99.13%)d 6.33(  0.75%)
                                        0.0000  0.0000  0.0343  0.0003  0.0007
                                        0.0000 -0.0835 -0.0040  0.0000  0.3327
                                       -0.0016  0.0000 -0.9345 -0.0207 -0.0073
                                        0.0044 -0.0685 -0.0233 -0.0466
   82. (1.98531) LP ( 1)Cl   2          s( 61.10%)p 0.64( 38.88%)d 0.00(  0.02%)
                                        0.0000 -0.0002  0.7817 -0.0028  0.0007
                                        0.0000  0.0274  0.0003  0.0000  0.3047
                                       -0.0024  0.0000  0.5433 -0.0037 -0.0006
                                       -0.0009 -0.0107  0.0031 -0.0086
   83. (1.95414) LP ( 2)Cl   2          s(  0.19%)p99.99( 99.77%)d 0.19(  0.04%)
                                        0.0000  0.0000  0.0437 -0.0001  0.0001
                                        0.0000 -0.1294 -0.0004  0.0000  0.8387
                                        0.0020  0.0000 -0.5268 -0.0029  0.0001
                                        0.0026 -0.0091  0.0081  0.0144
   84. (1.95144) LP ( 3)Cl   2          s(  0.00%)p 1.00( 99.96%)d 0.00(  0.04%)
                                        0.0000  0.0000  0.0019  0.0008  0.0000
                                       -0.0001 -0.9908 -0.0030  0.0000 -0.0912
                                       -0.0006  0.0000  0.0984  0.0005  0.0094
                                        0.0160  0.0007 -0.0001 -0.0029
   85. (1.80502) LP ( 4)Cl   2          s( 38.70%)p 1.58( 61.18%)d 0.00(  0.12%)
                                        0.0000  0.0002  0.6221  0.0039 -0.0009
                                        0.0000 -0.0223 -0.0013  0.0001 -0.4412
                                        0.0036  0.0002 -0.6455  0.0035  0.0012
                                        0.0017  0.0276 -0.0094  0.0182
   86. (0.30302) LP*( 1)Mg   3          s( 97.90%)p 0.02(  1.91%)d 0.00(  0.19%)
                                        0.0000  0.0000  0.9894 -0.0042  0.0007
                                        0.0000  0.0256 -0.0027  0.0000 -0.0057
                                        0.0261  0.0000  0.1297  0.0302  0.0005
                                        0.0003  0.0396 -0.0119  0.0140
   87. (0.13791) LP*( 2)Mg   3          s(  1.24%)p79.31( 98.24%)d 0.42(  0.52%)
                                        0.0000  0.0000  0.0632  0.0912 -0.0084
                                        0.0000  0.1339  0.0002  0.0000 -0.8329
                                        0.0123  0.0000 -0.5199 -0.0137  0.0159
                                       -0.0041 -0.0506  0.0472 -0.0135
   88. (0.11292) LP*( 3)Mg   3          s(  0.15%)p99.99( 99.48%)d 2.36(  0.36%)
                                        0.0000  0.0000  0.0280  0.0272 -0.0025
                                        0.0000 -0.9873  0.0056  0.0000 -0.1395
                                        0.0001  0.0000 -0.0221  0.0055 -0.0311
                                       -0.0506 -0.0088  0.0022 -0.0021
   89. (0.09661) LP*( 4)Mg   3          s(  1.41%)p69.63( 98.27%)d 0.23(  0.32%)
                                        0.0000  0.0000  0.1149  0.0292 -0.0072
                                        0.0000 -0.0516  0.0098  0.0000  0.5258
                                       -0.0100  0.0000 -0.8386 -0.0084  0.0027
                                        0.0014  0.0086 -0.0295 -0.0475
   90. (1.84251) LP ( 1) N   4          s( 28.45%)p 2.51( 71.52%)d 0.00(  0.02%)
                                       -0.0003  0.5333  0.0102  0.0030 -0.3715
                                        0.0320  0.6873 -0.0124  0.3220 -0.0099
                                        0.0079 -0.0004 -0.0054  0.0106 -0.0008
   91. (1.55352) LP ( 2) N   4          s(  0.73%)p99.99( 99.18%)d 0.12(  0.09%)
                                        0.0001  0.0852  0.0028 -0.0017 -0.1760
                                       -0.0008  0.2790  0.0072 -0.9396 -0.0066
                                        0.0046  0.0051  0.0254  0.0089  0.0114
   92. (1.84333) LP ( 1) N   5          s( 28.71%)p 2.48( 71.27%)d 0.00(  0.02%)
                                       -0.0003  0.5357  0.0103  0.0032  0.2124
                                       -0.0274  0.7626 -0.0203  0.2912 -0.0056
                                       -0.0022 -0.0004 -0.0054  0.0129 -0.0012
   93. (1.56851) LP ( 2) N   5          s(  0.40%)p99.99( 99.52%)d 0.21(  0.08%)
                                        0.0000  0.0629  0.0051 -0.0007 -0.0404
                                       -0.0017  0.3267  0.0050 -0.9417 -0.0060
                                        0.0039 -0.0090  0.0217  0.0081  0.0144


 Second Order Perturbation Theory Analysis of Fock Matrix in NBO Basis
  91. LP (   2) N   4               / 81. LP*(   2) P   1                143.40
0.10    0.115
  93. LP (   2) N   5               / 81. LP*(   2) P   1                133.07
0.10    0.112
```

```
  90. LP (   1) N   4               / 86. LP*(   1)Mg   3                   28.02
0.47    0.106
  92. LP (   1) N   5               / 86. LP*(   1)Mg   3                   27.23
0.47    0.105
  92. LP (   1) N   5               / 87. LP*(   2)Mg   3                   11.42
0.57    0.073
  92. LP (   1) N   5               / 88. LP*(   3)Mg   3                   12.59
0.52    0.073
  90. LP (   1) N   4               / 87. LP*(   2)Mg   3                   13.57
0.57    0.079
  80. LP (   1) P   1               / 87. LP*(   2)Mg   3                   11.46
0.67    0.080
```

4.1.6. Optimized geometry for $MgCl[P(NPh)_2]\cdot THF$

```
0 1
 P                  0.43298800   -1.86518200   -0.13286400
 Cl                 0.21119400    2.02479300    2.63318700
 Mg                 0.13841100    0.73796200    0.77976000
 N                  1.52455100   -0.67793200    0.09911500
 N                 -0.90097500   -1.00933300    0.26456100
 C                  2.90147500   -0.80730800   -0.09334600
 C                  3.46239400   -1.66299300   -1.05472500
 C                  4.84101700   -1.75161700   -1.20143200
 H                  5.25530100   -2.42014800   -1.95106400
 C                  5.68868700   -0.98096500   -0.40946400
 H                  6.76528400   -1.04758300   -0.53265100
 C                  5.13951600   -0.11615400    0.53469000
 H                  5.78815000    0.49309900    1.15777900
 C                  3.76256100   -0.02617800    0.69253400
 C                 -2.20698900   -1.49807200    0.21966000
 C                 -3.15451000   -0.96197700    1.10679600
 C                 -4.47177900   -1.40199700    1.08830300
 H                 -5.18506200   -0.97748800    1.78924100
 C                 -4.87828600   -2.38285100    0.18623600
 H                 -5.90870600   -2.72424400    0.17259900
 C                 -3.94858200   -2.91426500   -0.70415600
 H                 -4.25330200   -3.67152600   -1.42129000
 C                 -2.63069300   -2.47397100   -0.69821500
 O                 -0.42995600    2.03924500   -0.70753900
 C                 -0.38071400    3.48488400   -0.55321600
 H                  0.64304100    3.81525700   -0.74916500
 H                 -0.62950600    3.70138100    0.48823600
 C                 -1.39303600    4.03964500   -1.55357000
 H                 -1.93064400    4.90063200   -1.14999800
 H                 -0.89222700    4.35731300   -2.47376200
 C                 -2.30275700    2.84348700   -1.83501600
 H                 -2.82034500    2.91374600   -2.79468100
 H                 -3.05253800    2.72642000   -1.04570400
 C                 -1.31899400    1.69244700   -1.78905000
 H                 -1.75866500    0.72082600   -1.55565800
 H                 -0.73633200    1.61645100   -2.71579900
 H                  3.33227400    0.63445400    1.44126800
 H                  2.80807800   -2.24481700   -1.69891800
 H                 -2.83154700   -0.21380200    1.82665800
 H                 -1.92055400   -2.87505700   -1.41704000
```

4.2. Isomers of 2

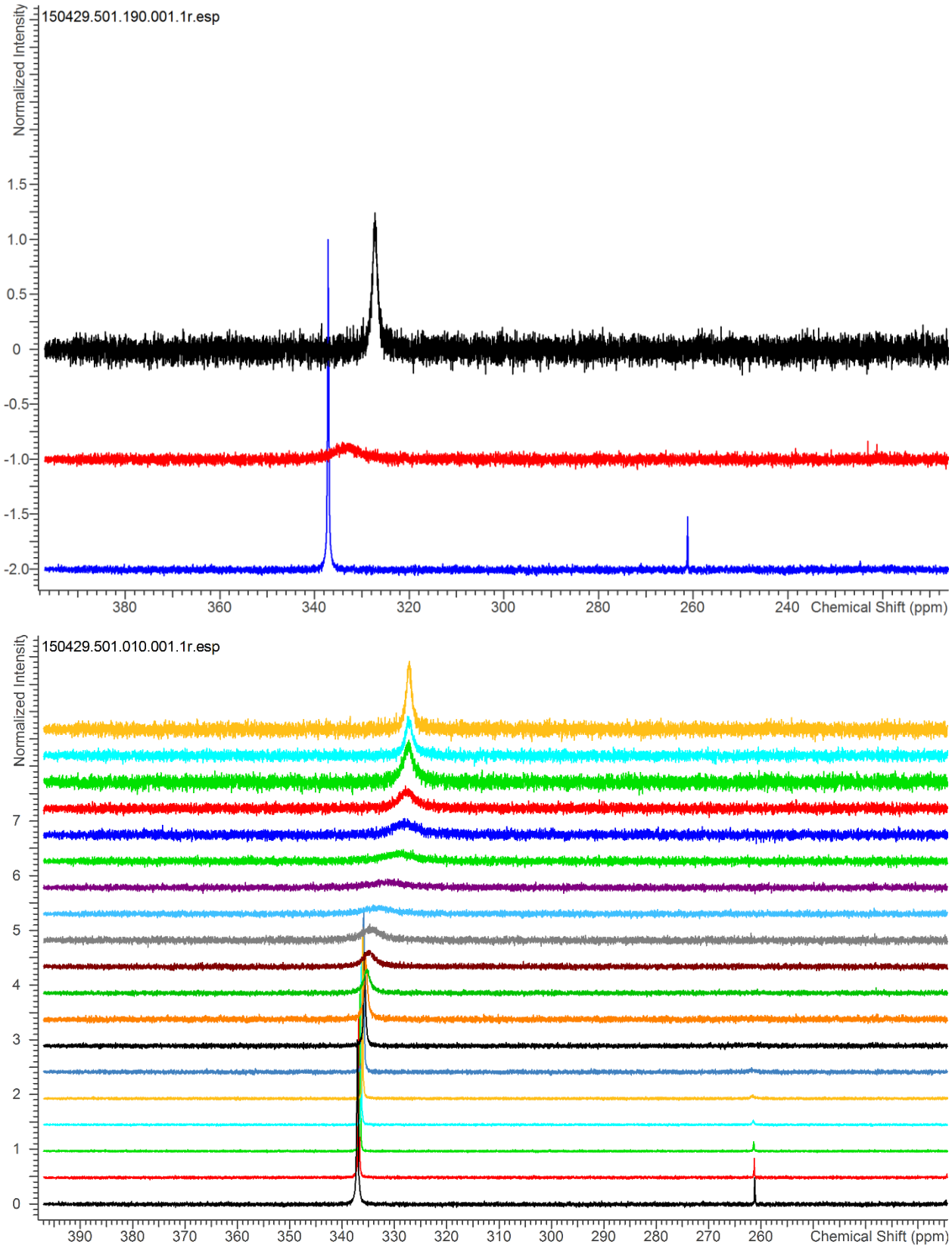


Figure S2. Observed ^{31}P NMR spectra of **2** in [D_8]-toluene at different temperatures (top: –80, +20, +100 °C; bottom: from –80 °C to +100 °C in 10 K steps). Integral ratio at –80 °C: 18:1.

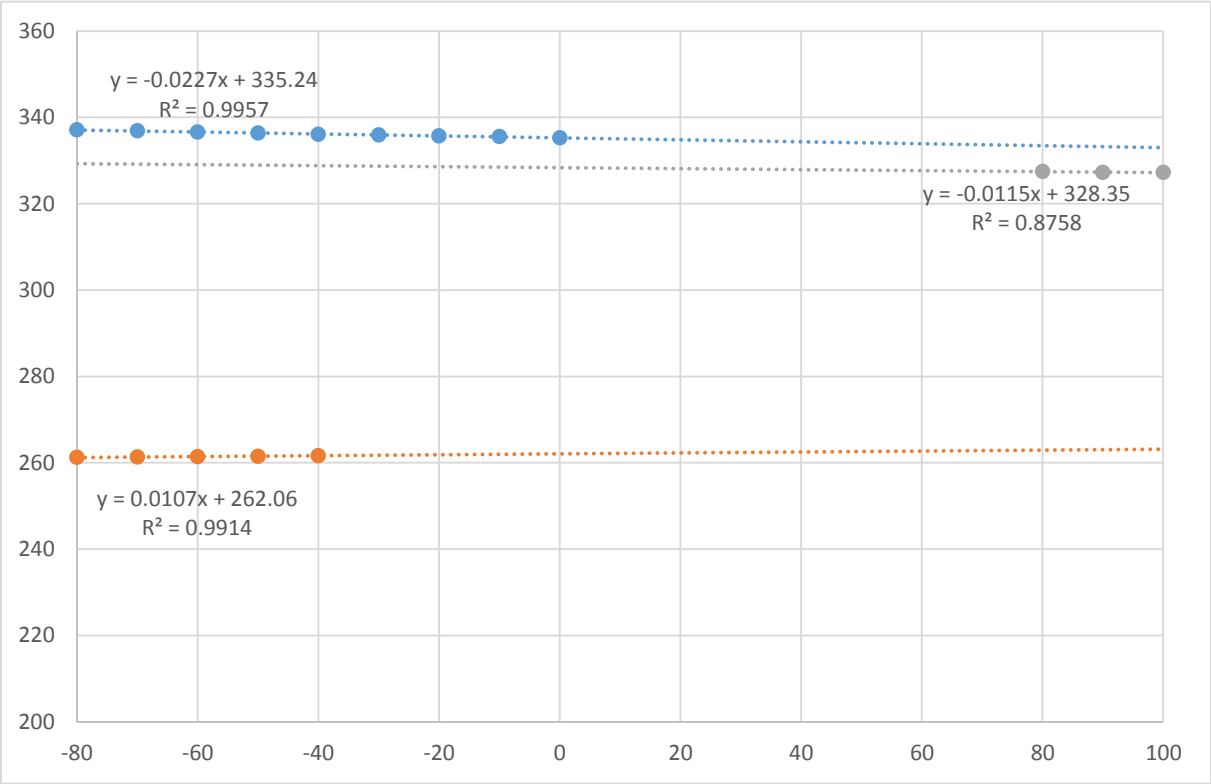


Figure S3. Observed ^{31}P NMR data at different temperatures (δ vs T).

Table S3. Temperature-variable NMR data of **2**.

T [°C]	δ_1	δ_2	δ_3
–80	337.1	261.22	
–70	336.88	261.3	
–60	336.59	261.43	
–50	336.33	261.51	
–40	336.1	261.65	
–30	335.89		
–20	335.69		
–10	335.51		
0	335.28		
10			
20			
30			
40			
50			
60			
70			
80			327.45
90			327.26
100			327.22

To calculate the NMR shift of the coalesced signal the formula below was used. To compensate temperature dependent solvent effects, the values extrapolated to +100 °C were used.

$$\delta_3 = x_1\delta_1 + x_2\delta_2 = \frac{1}{19}332.97 + \frac{18}{19}260.99 = 327.2 \text{ ppm}$$

Approximation for the Gibbs activation energy in kJ mol^{-1} (T_c: coalescence temperature in K, Δν: difference between both resonances in Hz):

$$\Delta G_c = -0.0191 \cdot T_c \left(10.32 + \log\frac{T_c}{\Delta v \cdot 2.22}\right) = 49.5 \text{ kJ mol}^{-1}$$

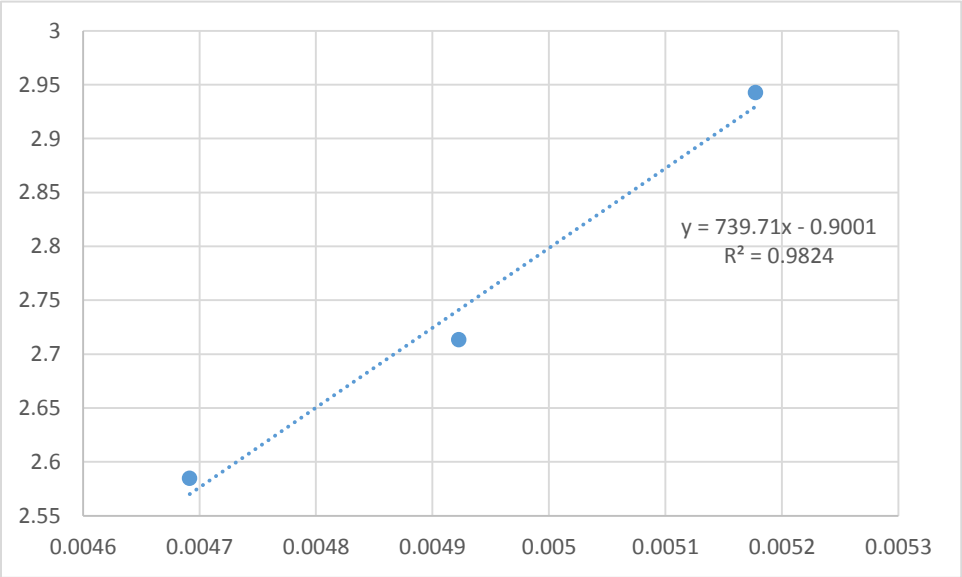


Figure S4. Van't Hoff plot (ln K vs 1/T). Only the values for –80, –70, and –60 °C were used, because at higher temperatures the integral of the resonance at 261 ppm is strongly influences by line broadening.

Table S4. Temperature-variable NMR data of **2** for Van't Hoff plot.

T [K]	Integral1	Integral2	K	1/T	ln K
193.15	16184620	307005376	18.9689579	0.00517732	2.94280385
203.15	19081684	287723744	15.07853	0.00492247	2.71327188
213.15	20185022	267673104	13.2609766	0.00469153	2.58482563
223.15	18916354	251695568	13.3057125	0.00448129	2.58819345
233.15	15240096	234753088	15.4036489	0.00428908	2.73460442

Relative Energy of the isomers

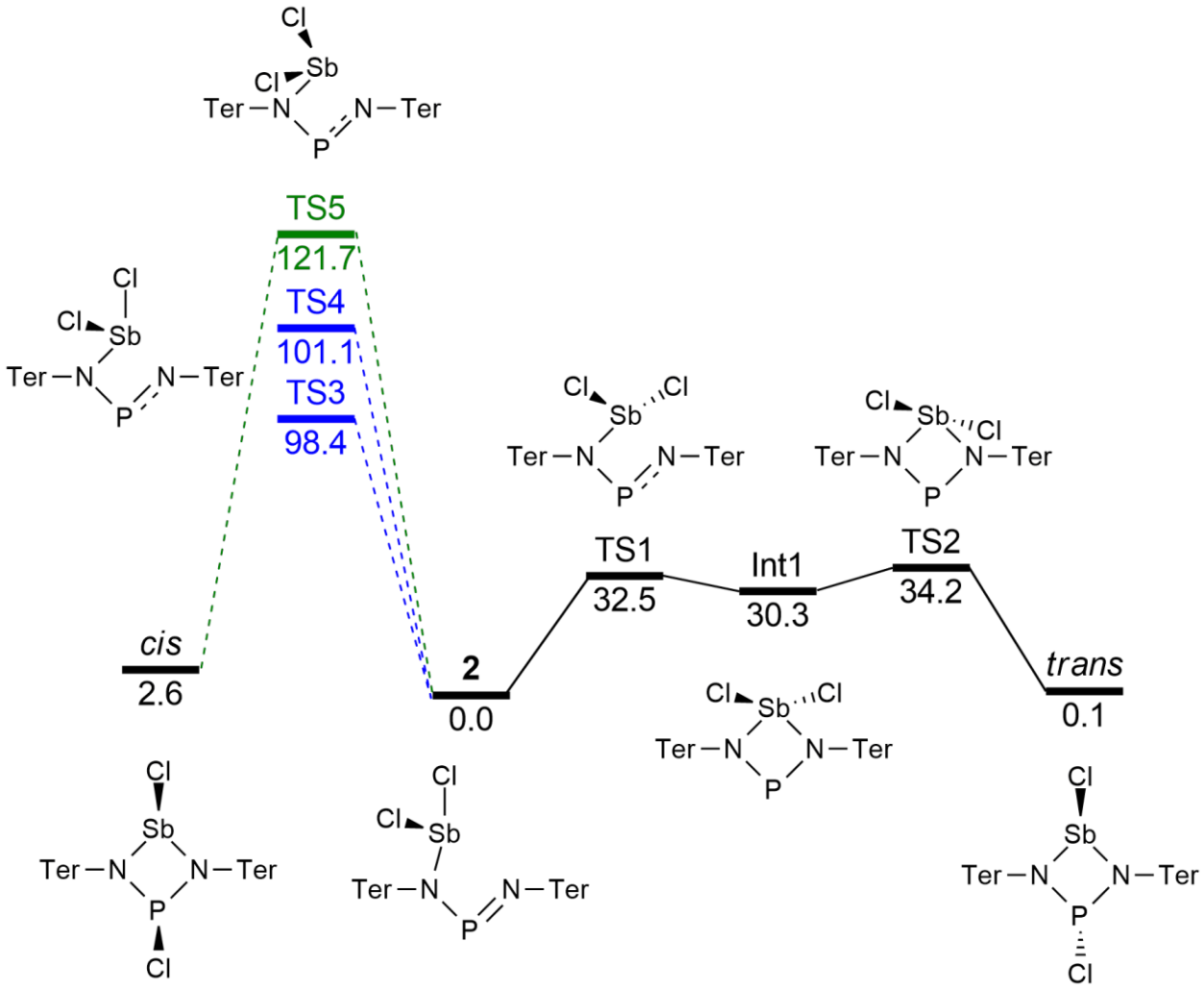


Figure S5. Isomerization pathways for **2** at the model of $Ph_2N_2PSbCl_2$ (E in kJ mol^{-1}). Blue: self-isomerization 2→TS→2' (flipping of N–Sb bond). Green: Isomerisation 2→TS5→cis. Black: Two-step rearrangement 2→TS1→Int1→TS2→trans.

Table S5. Isomers and transition states for $Ph_2N_2PSbCl_2$.

	E [a.u.]	ΔE [a.u.]	ΔE [kJ mol^{-1}]	δ(^{31}P) calc	δ(^{31}P) obs. –80°C
trans	-1838.92678061	0.00004002	0.1	+262	+261.2
2	-1838.92682063	0.00000000	0.0	+333	+337.1
cis	-1838.92581966	0.00100097	2.6	+242	
Int1	-1838.91526687	0.01155376	30.3	+391	
TS1	-1838.91443786	0.01238277	32.5		
TS2	-1838.91378746	0.01303317	34.2		
TS3	-1838.88934306	0.03747757	98.4		
TS4	-1838.88832716	0.03849347	101.1		
TS5	-1838.88046570	0.04635493	121.7		

4.2.1. Optimized geometry for **2**

```
0 1
 N                  1.48043400    0.56799400    0.00543700
 N                 -0.91308900    0.69263500   -0.20283200
 Cl                -2.30981200   -2.18249400   -0.64785800
 Cl                 0.24354900   -1.85292900    1.78913100
 C                  2.86822600    0.71337200   -0.03092800
 C                  3.49280600    1.76724400   -0.71421100
 C                  3.65875800   -0.24350400    0.62171100
 C                  4.87818000    1.87455600   -0.71842600
 H                  2.88437800    2.48507500   -1.25882900
 C                  5.04307300   -0.13066400    0.60558700
 H                  3.16839200   -1.04968700    1.15943900
 C                  5.65917100    0.92765600   -0.06015400
 H                  5.34958300    2.69543600   -1.25109100
 H                  5.64500900   -0.87352100    1.12081800
 H                  6.74173200    1.00899300   -0.07321000
 C                 -2.25701200    1.09006700    0.00620300
 C                 -3.17181600    1.07092400   -1.04964000
 C                 -2.66412000    1.52603600    1.27074400
 C                 -4.47884600    1.49193200   -0.83956400
 H                 -2.85081600    0.72278600   -2.02596300
 C                 -3.97129200    1.95766500    1.47007200
 H                 -1.95511700    1.50376800    2.09374700
 C                 -4.88096300    1.94044700    0.41706500
 H                 -5.18636400    1.47179300   -1.66297100
 H                 -4.27968000    2.29732900    2.45426500
 H                 -5.90353900    2.26943400    0.57555700
 Sb                -0.05801800   -1.22397500   -0.51203300
 P                  0.36289500    1.71698200    0.07275000
```

4.2.2. Optimized geometry for Int1

```
0 1
 Sb                -0.00000300    0.87888900    0.94237500
 N                  1.18348600   -0.30983500   -0.38432300
 N                 -1.18349200   -0.30983900   -0.38431800
 C                  2.57618700   -0.46403200   -0.50261400
 C                  3.15479700   -1.73661600   -0.48671000
 C                  3.38095200    0.67367400   -0.62573300
 C                  4.53314500   -1.86736000   -0.61830200
 H                  2.52443200   -2.60873700   -0.33913500
 C                  4.75823800    0.52975500   -0.73873400
 H                  2.91369200    1.65404900   -0.66671600
 C                  5.33783200   -0.73801200   -0.74096800
 H                  4.97948000   -2.85712800   -0.60444200
 H                  5.38063200    1.41396700   -0.83800600
 H                  6.41449600   -0.84416500   -0.83138600
 C                 -2.57619400   -0.46403400   -0.50260900
 C                 -3.15480600   -1.73661700   -0.48669700
 C                 -3.38095700    0.67367200   -0.62573600
 C                 -4.53315400   -1.86735900   -0.61828800
 H                 -2.52444200   -2.60873800   -0.33911800
 C                 -4.75824200    0.52975500   -0.73873500
 H                 -2.91369400    1.65404700   -0.66672400
 C                 -5.33783900   -0.73801100   -0.74096100
 H                 -4.97949100   -2.85712600   -0.60442200
 H                 -5.38063400    1.41396800   -0.83801300
 H                 -6.41450400   -0.84416200   -0.83137800
 P                 -0.00000300   -1.08432600   -1.20602500
 Cl                 0.00000700    2.66625000   -0.89373800
 Cl                 0.00002400   -1.16658000    2.45406900
```

4.2.3. Optimized geometry for trans-[ClSb(μ-NTer)$_2$PCl]

```
0 1
 Sb                 0.00007400   -1.28062500    0.66514100
 N                 -1.17372000    0.32512600    0.27406800
 N                  1.17365600    0.32537800    0.27420800
 C                 -2.56759300    0.46983300    0.26376700
 C                 -3.17148000    1.67530200    0.64208000
```

C	-3.37500000	-0.60769400	-0.11706900
C	-4.55609200	1.79414900	0.62978300
H	-2.55257400	2.51206300	0.95421900
C	-4.76012000	-0.48628100	-0.10007300
H	-2.91378500	-1.53010700	-0.46380200
C	-5.35898800	0.71487200	0.26882900
H	-5.00994000	2.73727400	0.92034100
H	-5.37171400	-1.33307700	-0.39763900
H	-6.44017200	0.81086500	0.27073000
C	2.56753900	0.46996700	0.26379300
C	3.17149800	1.67525300	0.64263100
C	3.37484100	-0.60742300	-0.11757400
C	4.55609300	1.79406700	0.63034500
H	2.55255500	2.51184100	0.95517200
C	4.75998500	-0.48604300	-0.10063300
H	2.91359600	-1.52968400	-0.46465700
C	5.35890600	0.71490200	0.26878800
H	5.01000700	2.73702900	0.92131200
H	5.37155700	-1.33270100	-0.39864800
H	6.44010000	0.81080000	0.27061800
P	-0.00012000	1.55965000	0.02208600
Cl	0.00015100	-2.48929800	-1.43448500
Cl	-0.00007400	1.79776100	-2.07769700

4.2.4. Optimized geometry for cis-[ClSb(μ-NTer)$_2$PCl]

0 1

Sb	0.00007400	-1.28062500	0.66514100
N	-1.17372000	0.32512600	0.27406800
N	1.17365600	0.32537800	0.27420800
C	-2.56759300	0.46983300	0.26376700
C	-3.17148000	1.67530200	0.64208000
C	-3.37500000	-0.60769400	-0.11706900
C	-4.55609200	1.79414900	0.62978300
H	-2.55257400	2.51206300	0.95421900
C	-4.76012000	-0.48628100	-0.10007300
H	-2.91378500	-1.53010700	-0.46380200
C	-5.35898800	0.71487200	0.26882900
H	-5.00994000	2.73727400	0.92034100
H	-5.37171400	-1.33307700	-0.39763900
H	-6.44017200	0.81086500	0.27073000
C	2.56753900	0.46996700	0.26379300
C	3.17149800	1.67525300	0.64263100
C	3.37484100	-0.60742300	-0.11757400
C	4.55609300	1.79406700	0.63034500
H	2.55255500	2.51184100	0.95517200
C	4.75998500	-0.48604300	-0.10063300
H	2.91359600	-1.52968400	-0.46465700
C	5.35890600	0.71490200	0.26878800
H	5.01000700	2.73702900	0.92131200
H	5.37155700	-1.33270100	-0.39864800
H	6.44010000	0.81080000	0.27061800
P	-0.00012000	1.55965000	0.02208600
Cl	0.00015100	-2.48929800	-1.43448500
Cl	-0.00007400	1.79776100	-2.07769700

4.2.5. Optimized geometry for TS1

0 1

Sb	0.11138900	1.03161200	0.76976700
N	1.29652400	-0.43074100	-0.28961300
N	-1.06498600	-0.36426400	-0.42468300
C	2.69018900	-0.59265500	-0.36711700
C	3.27637500	-1.85407900	-0.21695200
C	3.49861500	0.52886000	-0.58254400
C	4.65723600	-1.98996500	-0.30394500
H	2.64732800	-2.71563000	-0.01097900
C	4.87928800	0.38386900	-0.64866300
H	3.03638100	1.50204300	-0.72782800
C	5.46304000	-0.87404100	-0.51511400
H	5.10509800	-2.97248200	-0.18860300
H	5.50024200	1.25846100	-0.81765500

H	6.54164800	-0.98325100	-0.57068000
C	-2.45224700	-0.59184400	-0.51651400
C	-2.98849200	-1.82142800	-0.12122700
C	-3.29077900	0.42074500	-0.99533500
C	-4.35668800	-2.04484100	-0.23019600
H	-2.33269000	-2.57487400	0.30484600
C	-4.65770700	0.18903800	-1.08511200
H	-2.85622600	1.36461300	-1.31014700
C	-5.19399200	-1.04193300	-0.70988000
H	-4.76932000	-3.00011800	0.08004100
H	-5.30723200	0.97402400	-1.46082800
H	-6.26333500	-1.21511600	-0.78405500
P	0.11638300	-1.30227100	-1.02666200
Cl	-0.35482100	2.59156300	-1.18204000
Cl	-0.79213500	-0.43986400	2.61635600

4.2.6. Optimized geometry for TS2

0 1

Sb	-0.00000100	0.83292600	0.96231800
N	1.18638800	-0.10044500	-0.51589400
N	-1.18638800	-0.10044800	-0.51589300
C	2.57630700	-0.33427800	-0.56196000
C	3.10939500	-1.60624000	-0.33030300
C	3.42257400	0.74459600	-0.84001600
C	4.48571000	-1.79738400	-0.40753100
H	2.44715500	-2.42161000	-0.05392400
C	4.79582700	0.54334100	-0.89692600
H	2.98793500	1.72285400	-1.02536200
C	5.33051800	-0.72748800	-0.68798200
H	4.89774900	-2.78603400	-0.22865100
H	5.45105300	1.38118900	-1.11590600
H	6.40433600	-0.88050600	-0.73759500
C	-2.57630800	-0.33428000	-0.56196000
C	-3.10939600	-1.60624300	-0.33030300
C	-3.42257400	0.74459400	-0.84001500
C	-4.48571100	-1.79738600	-0.40753100
H	-2.44715600	-2.42161400	-0.05392500
C	-4.79582800	0.54333900	-0.89692500
H	-2.98793500	1.72285200	-1.02536100
C	-5.33051800	-0.72748900	-0.68798100
H	-4.89775000	-2.78603600	-0.22865000
H	-5.45105400	1.38118800	-1.11590500
H	-6.40433700	-0.88050700	-0.73759300
P	0.00000100	-1.09607600	-1.08747800
Cl	-0.00000200	2.99867500	-0.22478200
Cl	0.00000600	-1.85362000	1.72336700

4.2.7. Optimized geometry for TS3

0 1

N	-1.22232700	-0.75710100	0.03446000
N	1.17174300	-0.79714200	-0.13182500
Cl	0.02963500	3.66959900	-0.44980700
Cl	0.18799500	1.30577100	1.97149500
C	-2.60291100	-0.98923300	-0.02513600
C	-3.15123600	-2.00188500	-0.82337900
C	-3.45345100	-0.17489800	0.73453700
C	-4.52511100	-2.21572800	-0.83181300
H	-2.49816300	-2.60393000	-1.45021100
C	-4.82594100	-0.38459800	0.70450600
H	-3.02220500	0.59948300	1.36308900
C	-5.36712600	-1.40791100	-0.07244000
H	-4.93947600	-3.00549200	-1.45153100
H	-5.47614400	0.25111800	1.29804100
H	-6.44070300	-1.56764200	-0.09315600
C	2.54670800	-1.03771700	-0.08591700
C	3.41472300	-0.22553900	-0.82641400
C	3.08033900	-2.06382800	0.70652500
C	4.78616200	-0.44247900	-0.78192400
H	3.00722500	0.56398200	-1.45369800
C	4.45181200	-2.28395900	0.73059600

H	2.41751500	-2.66379400	1.32422200
C	5.31125800	-1.47630500	-0.01031300
H	5.44628200	0.19811400	-1.35895400
H	4.85197800	-3.08058200	1.35087100
H	6.38319300	-1.64357400	0.02283300
Sb	-0.00861100	1.09438100	-0.40344700
P	-0.04182100	-1.88921600	-0.04505300

4.2.8. Optimized geometry for TS4

0 1

N	-1.22232700	-0.75710100	0.03446000
N	1.17174300	-0.79714200	-0.13182500
Cl	0.02963500	3.66959900	-0.44980700
Cl	0.18799500	1.30577100	1.97149500
C	-2.60291100	-0.98923300	-0.02513600
C	-3.15123600	-2.00188500	-0.82337900
C	-3.45345100	-0.17489800	0.73453700
C	-4.52511100	-2.21572800	-0.83181300
H	-2.49816300	-2.60393000	-1.45021100
C	-4.82594100	-0.38459800	0.70450600
H	-3.02220500	0.59948300	1.36308900
C	-5.36712600	-1.40791100	-0.07244000
H	-4.93947600	-3.00549200	-1.45153100
H	-5.47614400	0.25111800	1.29804100
H	-6.44070300	-1.56764200	-0.09315600
C	2.54670800	-1.03771700	-0.08591700
C	3.41472300	-0.22553900	-0.82641400
C	3.08033900	-2.06382800	0.70652500
C	4.78616200	-0.44247900	-0.78192400
H	3.00722500	0.56398200	-1.45369800
C	4.45181200	-2.28395900	0.73059600
H	2.41751500	-2.66379400	1.32422200
C	5.31125800	-1.47630500	-0.01031300
H	5.44628200	0.19811400	-1.35895400
H	4.85197800	-3.08058200	1.35087100
H	6.38319300	-1.64357400	0.02283300
Sb	-0.00861100	1.09438100	-0.40344700
P	-0.04182100	-1.88921600	-0.04505300

4.2.9. Optimized geometry for TS5

0 1

N	-1.22232700	-0.75710100	0.03446000
N	1.17174300	-0.79714200	-0.13182500
Cl	0.02963500	3.66959900	-0.44980700
Cl	0.18799500	1.30577100	1.97149500
C	-2.60291100	-0.98923300	-0.02513600
C	-3.15123600	-2.00188500	-0.82337900
C	-3.45345100	-0.17489800	0.73453700
C	-4.52511100	-2.21572800	-0.83181300
H	-2.49816300	-2.60393000	-1.45021100
C	-4.82594100	-0.38459800	0.70450600
H	-3.02220500	0.59948300	1.36308900
C	-5.36712600	-1.40791100	-0.07244000
H	-4.93947600	-3.00549200	-1.45153100
H	-5.47614400	0.25111800	1.29804100
H	-6.44070300	-1.56764200	-0.09315600
C	2.54670800	-1.03771700	-0.08591700
C	3.41472300	-0.22553900	-0.82641400
C	3.08033900	-2.06382800	0.70652500
C	4.78616200	-0.44247900	-0.78192400
H	3.00722500	0.56398200	-1.45369800
C	4.45181200	-2.28395900	0.73059600
H	2.41751500	-2.66379400	1.32422200
C	5.31125800	-1.47630500	-0.01031300
H	5.44628200	0.19811400	-1.35895400
H	4.85197800	-3.08058200	1.35087100
H	6.38319300	-1.64357400	0.02283300
Sb	-0.00861100	1.09438100	-0.40344700
P	-0.04182100	-1.88921600	-0.04505300

4.3. Phosphenium ion vs. stibenium ion (3)

Table S6. Relative Energy of the isomers of **3**.

	E [a.u.]	ΔE [a.u.]	ΔE [kJ mol^{-1}]
P^+	-2773.07009115	0.0	0.0
Sb^+	-2773.04749254	+0.02259861	+59.3

4.3.1. Optimized geometry for $[ClSb(\mu\text{-}NTer)_2P]^+$

```
1 1
 Sb                -1.58986300    0.22119000    0.13095400
 Cl                -1.99394400    0.68547800   -2.18310200
 P                  1.32937000   -0.18785900   -0.22931100
 N                  0.00816000   -1.18782900   -0.03325300
 N                  0.35562400    1.14483600   -0.10448000
 C                  0.00345400   -2.56051900    0.27742500
 C                 -1.13022400   -3.32698500   -0.05436900
 C                 -1.15436600   -4.68546800    0.26530700
 H                 -2.03263000   -5.26648000   -0.00173000
 C                 -0.08305200   -5.28802000    0.91247600
 H                 -0.11176800   -6.34612500    1.15251000
 C                  1.01614400   -4.51693300    1.27181200
 H                  1.84495100   -4.96534800    1.81243200
 C                  1.07760900   -3.15416200    0.97537500
 C                 -2.32387500   -2.71878700   -0.70784000
 C                 -2.43418500   -2.71137300   -2.11553200
 C                 -3.61256200   -2.25528700   -2.69468500
 H                 -3.69707300   -2.25549700   -3.77898700
 C                 -4.68462200   -1.77999400   -1.93033300
 C                 -4.55824100   -1.78888000   -0.54501900
 H                 -5.38762600   -1.44580000    0.06990000
 C                 -3.40312800   -2.27085000    0.08782100
 C                 -1.29504900   -3.17948200   -2.97414000
 H                 -1.57381400   -3.17768300   -4.02996600
 H                 -0.97453400   -4.19025700   -2.70373100
 H                 -0.42464100   -2.52383500   -2.85570200
 C                 -5.92448100   -1.26331200   -2.59953700
 H                 -6.73117000   -1.09690800   -1.88164800
 H                 -6.28446700   -1.96350800   -3.35951200
 H                 -5.72239000   -0.31308000   -3.10660700
 C                 -3.38228500   -2.40281500    1.58891800
 H                 -4.07469400   -1.69626800    2.05493100
 H                 -2.38594900   -2.24805500    2.01487400
 H                 -3.69097100   -3.41179700    1.88549600
 C                  2.24551600   -2.36554100    1.45996500
 C                  3.49694400   -2.48070300    0.82435000
 C                  4.58596400   -1.78887700    1.35300200
 H                  5.55317800   -1.88454800    0.86459200
 C                  4.47492600   -0.98585000    2.48855900
 C                  3.22387600   -0.87843900    3.09880700
 H                  3.11978900   -0.27046700    3.99534100
 C                  2.11045700   -1.56744000    2.61791200
 C                  3.66270000   -3.31475000   -0.41509500
 H                  2.94818600   -3.02088300   -1.19255400
 H                  3.49149200   -4.37764300   -0.21682300
 H                  4.66918700   -3.20746800   -0.82566400
 C                  5.67447000   -0.29255400    3.06820100
 H                  6.45628100   -0.14435000    2.31844000
 H                  6.11064500   -0.88848300    3.87828900
 H                  5.41244600    0.68225600    3.48944900
 C                  0.79812500   -1.47726300    3.34484200
 H                  0.89980500   -0.90008900    4.26678100
 H                  0.41649100   -2.47078500    3.60174400
 H                  0.02532200   -0.99333200    2.73206600
 C                  0.62442200    2.51149500   -0.27811400
```

C	1.75502800	2.96660900	-0.98842000
C	1.93708700	4.33928900	-1.15571700
H	2.80829900	4.67999700	-1.70820000
C	1.03574300	5.25974500	-0.63202600
H	1.19789500	6.32397100	-0.76990200
C	-0.07065900	4.80591700	0.07488300
H	-0.77602000	5.51333200	0.50132600
C	-0.29107400	3.44126800	0.26253400
C	2.75214200	2.00722400	-1.53561300
C	2.54968900	1.42066400	-2.80258400
C	3.47894200	0.48884900	-3.26566800
H	3.32229900	0.03430900	-4.24174400
C	4.61742700	0.15231500	-2.53055700
C	4.81373200	0.77643100	-1.29897200
H	5.70454300	0.54268500	-0.72045200
C	3.90161000	1.69804600	-0.78415900
C	1.37535200	1.80805800	-3.65606900
H	1.38883700	2.88134200	-3.87417100
H	0.41952200	1.59721200	-3.16618000
H	1.39065300	1.27120100	-4.60737000
C	5.62514900	-0.81771500	-3.07855400
H	5.13991000	-1.65865600	-3.58272500
H	6.27053900	-1.21560300	-2.29091200
H	6.27260800	-0.32955000	-3.81598500
C	4.14798400	2.33623100	0.55516800
H	4.17067900	3.42805300	0.48339400
H	5.09985700	2.00380500	0.97492700
H	3.36028300	2.08288800	1.27493100
C	-1.47267800	2.97614800	1.04036000
C	-2.78048100	3.10372100	0.51058600
C	-3.86243200	2.63155900	1.26545100
H	-4.86300400	2.71488100	0.84705700
C	-3.69937900	2.08268700	2.53653800
C	-2.40483000	2.01640000	3.06382500
H	-2.26150900	1.62531400	4.06877200
C	-1.29190200	2.46314800	2.35226400
C	-3.04014100	3.76173200	-0.81508700
H	-3.97881900	3.40878600	-1.24807600
H	-2.23897200	3.58239900	-1.53417300
H	-3.12466000	4.84688600	-0.68479400
C	-4.88204600	1.62756400	3.34145300
H	-5.25670700	2.44655900	3.96625900
H	-4.62079600	0.80363200	4.01094700
H	-5.70609200	1.30579800	2.69947300
C	0.06925000	2.42972900	2.98857300
H	0.55182900	3.40975400	2.92412600
H	0.73707100	1.71474800	2.49544100
H	-0.00355700	2.15073900	4.04209200

4.3.2. Optimized geometry for $[Sb(\mu\text{-}NTer)_2PCl]^+$

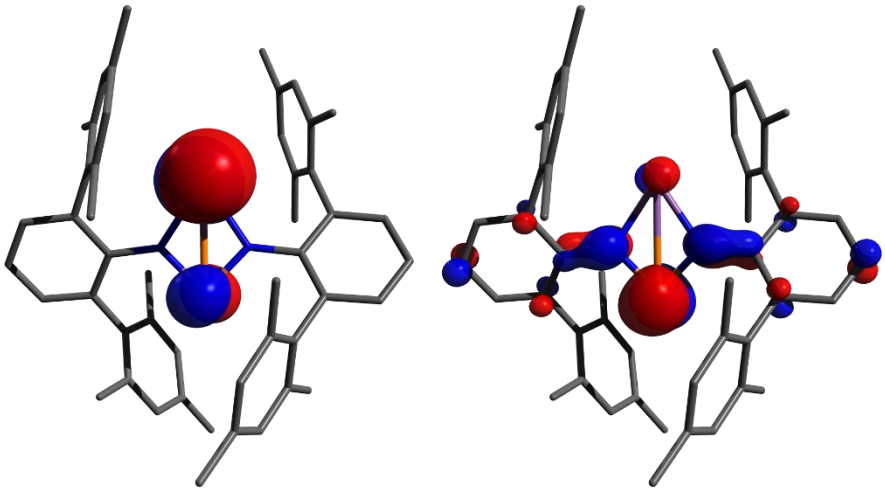
P	-1.26600300	0.21973200	0.00872900
Cl	-1.85664700	0.70974300	-1.94504000
Sb	1.61601000	-0.28962000	-0.22139400
N	-0.23629400	-1.17280000	-0.16774500
N	0.23025300	1.16471400	-0.02579500
C	-0.58836500	-2.46605100	0.27911300
C	-1.85558900	-3.02952200	0.02077200
C	-2.14471200	-4.29933100	0.53251300
H	-3.12351300	-4.71990900	0.31959100
C	-1.22022600	-5.02635000	1.26910000
H	-1.46858100	-6.01373700	1.64484000
C	0.03225300	-4.47526200	1.50899100
H	0.77446800	-5.02238500	2.08390400
C	0.35417700	-3.20761000	1.02806200
C	-2.90565700	-2.36317300	-0.80030600
C	-2.84208000	-2.45560000	-2.20414600
C	-3.88766500	-1.93681900	-2.96288200
H	-3.83950500	-2.01494400	-4.04701000
C	-4.99223600	-1.32134200	-2.37205700

C	-5.04029500	-1.25283900	-0.98096700
H	-5.90165800	-0.79305400	-0.50115300
C	-4.02565000	-1.77682200	-0.17877100
C	-1.66640000	-3.09991200	-2.88296100
H	-1.82744800	-3.16993900	-3.96127200
H	-1.48041800	-4.10888600	-2.50015800
H	-0.75197500	-2.51633400	-2.71836500
C	-6.08823600	-0.73400300	-3.21436300
H	-7.03697200	-0.69976200	-2.67215800
H	-6.24021800	-1.30977600	-4.13157200
H	-5.84260700	0.29240400	-3.51193700
C	-4.15895900	-1.72620500	1.31942400
H	-5.07183400	-1.19878500	1.60615900
H	-3.31466000	-1.20614800	1.78510100
H	-4.20083400	-2.73000600	1.75514300
C	1.69818600	-2.64752600	1.32922100
C	2.83374900	-3.08786700	0.61345700
C	4.08611300	-2.55698300	0.93959800
H	4.95830000	-2.90338000	0.38959700
C	4.25274200	-1.60519600	1.94677400
C	3.11946900	-1.18113200	2.64754100
H	3.22980000	-0.45988300	3.45440100
C	1.84577500	-1.69885600	2.37716500
C	2.71168700	-4.11738000	-0.47506400
H	1.84718400	-3.93113100	-1.11904500
H	2.56976200	-5.11658500	-0.04957000
H	3.61180800	-4.14384400	-1.09355600
C	5.61550800	-1.08850600	2.30557500
H	6.30596000	-1.15065900	1.46050200
H	6.04525300	-1.68198900	3.12068300
H	5.57681800	-0.05088900	2.64839800
C	0.66956000	-1.30452800	3.22364200
H	0.95914500	-0.57522800	3.98280000
H	0.25549300	-2.18430600	3.72697900
H	-0.14601000	-0.87555000	2.63100100
C	0.33069200	2.55966100	-0.14823800
C	1.46219500	3.10851900	-0.79340900
C	1.56105100	4.48662800	-0.97057200
H	2.43546400	4.88902200	-1.47466000
C	0.56097200	5.33521000	-0.50967500
H	0.64166800	6.40769200	-0.65489600
C	-0.52853500	4.79784100	0.16370600
H	-1.29736400	5.45206800	0.56430900
C	-0.66152900	3.42264700	0.37016700
C	2.57371800	2.22259500	-1.23332000
C	2.53394100	1.58395500	-2.49709700
C	3.57974300	0.72155200	-2.84883900
H	3.54616600	0.22947100	-3.81850400
C	4.68504300	0.51675700	-2.01755400
C	4.72298200	1.18976200	-0.79586000
H	5.58370000	1.05830900	-0.14415900
C	3.68749900	2.03477800	-0.38167000
C	1.42072000	1.86303100	-3.46411300
H	1.44043200	2.91567600	-3.76596800
H	0.43543200	1.68016000	-3.02584800
H	1.51831500	1.25012500	-4.36275200
C	5.82103400	-0.36393700	-2.45129300
H	5.48204400	-1.15683000	-3.12303200
H	6.32212200	-0.82502200	-1.59583700
H	6.57354900	0.22118000	-2.99218600
C	3.77926500	2.74887600	0.93884900
H	3.94611900	3.82062000	0.78839500
H	4.60723100	2.36166500	1.53711700
H	2.85574900	2.66031300	1.51965300
C	-1.80850400	2.91396700	1.17251300
C	-3.12246200	2.96834300	0.67143000
C	-4.16403300	2.47242700	1.46220900
H	-5.17646100	2.49825800	1.06500800
C	-3.94880600	1.96450900	2.73912900

C	-2.64188300	1.97178700	3.23770700
H	-2.45750500	1.61667500	4.24991800
C	-1.57259300	2.44329700	2.48485000
C	-3.44679600	3.57118000	-0.66761100
H	-4.33917200	3.10693900	-1.09500900
H	-2.62994300	3.46109300	-1.38282900
H	-3.65356400	4.64361300	-0.56763100
C	-5.08342200	1.45247800	3.57969400
H	-5.20399400	2.05584600	4.48599400
H	-4.90544700	0.42100300	3.90207200
H	-6.03007500	1.47792000	3.03444600
C	-0.19499400	2.47895300	3.08839500
H	0.24659200	3.47825500	3.01344600
H	0.48826900	1.78685600	2.58181100
H	-0.22891700	2.20343000	4.14547300

4.4. Biradical character of [P(μ-NPh)$_2$Sb]

4.4.1. Frontier orbitals of [P(μ-NPh)$_2$Sb]



HOMO **LUMO**

Figure S6. Frontier orbitals of [P(μ-NTer)$_2$Sb].

Computed UVvis excitations:

```
Excited State   1:      Singlet-A      1.9991 eV  620.20 nm  f=0.0150  <S**2>=0.000
     159 ->187        -0.01032
     176 ->187         0.01261
     177 ->188        -0.01078
     186 ->187        -0.38628
     186 ->188         0.58475
     186 ->190         0.08259
     186 ->192        -0.02954
     186 ->196         0.04673
     186 ->199         0.03102
     186 ->206        -0.01583
     186 <-187         0.05615
     186 <-188        -0.02544
     186 <-190        -0.01399
     186 <-200         0.01495
 This state for optimization and/or second-order correction.
 Total Energy, E(TD-HF/TD-KS) =  -2313.10432843
 Copying the excited state density for this state as the 1-particle RhoCI density.

 Excited State   2:      Singlet-A      2.1057 eV  588.81 nm  f=0.0460
<S**2>=0.000
     149 ->188         0.01250
     158 ->188         0.01604
     159 ->188        -0.01257
     171 ->188         0.01298
     173 ->189         0.01057
     173 ->201        -0.01832
     176 ->187        -0.01875
     177 ->187         0.01264
```

```
     179 ->187         0.01992
     184 ->189        -0.01167
     184 ->201         0.01233
     185 ->201         0.01589
     186 ->187         0.59510
     186 ->188         0.37663
     186 ->190         0.07901
     186 ->192         0.02128
     186 ->199         0.02963
     186 ->200        -0.03467
     186 ->203         0.03065
     186 ->204         0.01292
     186 ->235        -0.01226
     186 <-187        -0.09771
     186 <-188        -0.02441
     186 <-192         0.01264
     186 <-196        -0.01185
     186 <-200        -0.02124
     186 <-203         0.01586

 Excited State   3:      Singlet-A      2.8472 eV  435.47 nm  f=0.0004
<S**2>=0.000
     184 ->187        -0.01275
     185 ->187         0.03085
     186 ->189         0.68798
     186 ->191         0.15052
     186 ->193        -0.03002
     186 ->195        -0.01065
     186 ->197        -0.01411
     186 ->198        -0.01023
     186 ->201        -0.02578
     186 ->205        -0.01316

 Excited State   4:      Singlet-A      3.0952 eV  400.56 nm  f=0.0073
<S**2>=0.000
     186 ->187        -0.02519
     186 ->188        -0.11326
     186 ->190         0.67572
     186 ->192         0.13508
     186 ->194         0.03667
     186 ->196         0.08339
     186 ->199         0.04410
     186 ->204         0.02320
     186 <-188        -0.01036

 Excited State   5:      Singlet-A      3.2057 eV  386.76 nm  f=0.0125
<S**2>=0.000
     173 ->187         0.01463
     184 ->187        -0.04514
     185 ->187        -0.33159
     186 ->189        -0.10903
     186 ->191         0.58303
     186 ->193         0.16914
     186 ->195        -0.02574
     186 ->197        -0.04701
     186 ->198        -0.04754
     186 ->201        -0.01110
     186 ->202        -0.01579
     186 ->205        -0.01156
     185 <-187         0.01464
```

4.4.2. CASSCF computations

```
Configurations
1 10
2 01
EIGENVALUES AND  EIGENVECTORS OF CI MATRIX
(    1) 0.9714936 (   2)-0.1990032
```

4.4.3. Optimized geometry for [Sb(μ-NTer)$_2$P]

```
0 1
 P                 -1.29409200   -0.00025500   -0.00031400
 N                 -0.09261500   -1.17311200    0.07120000
 N                 -0.09303900    1.17307000   -0.07151700
 C                 -0.25453700    2.54632500   -0.27617900
 C                  0.75828800    3.42762700    0.16947500
 C                 -1.38168800    3.08502200   -0.94382600
 C                  0.61736600    4.80273500   -0.02072700
 C                 -1.48365500    4.46793800   -1.11084400
 C                 -0.50109100    5.33420700   -0.64932000
 H                  1.40681900    5.45634800    0.34119200
 H                 -2.35460600    4.85602000   -1.63292700
 H                 -0.59975600    6.40639800   -0.78928200
 C                 -0.25378700   -2.54640300    0.27595500
 C                 -1.38079400   -3.08526600    0.94371400
 C                  0.75916100   -3.42754700   -0.16972300
 C                 -1.48253500   -4.46819600    1.11077200
 C                  0.61843700   -4.80267900    0.02048000
 C                 -0.49988900   -5.33432100    0.64915800
 H                 -2.35337800   -4.85639800    1.63294300
 H                  1.40796500   -5.45617500   -0.34149700
 H                 -0.59838500   -6.40652900    0.78912200
 Sb                 1.69024300    0.00034800    0.00001700
 C                  1.99625100   -2.93921100   -0.84432100
 C                  1.97365600   -2.62770700   -2.22242400
 C                  3.21407300   -2.89799900   -0.13501300
 C                  3.16067000   -2.27870500   -2.85888900
 C                  4.37603100   -2.50958200   -0.80931600
 C                  4.37038600   -2.19689300   -2.16656700
 H                  3.13787800   -2.04412600   -3.92117900
 H                  5.31136900   -2.46195800   -0.25523600
 C                 -2.45132500   -2.23394400    1.53869600
 C                 -2.21433300   -1.58779600    2.76902100
 C                 -3.70822700   -2.12350400    0.91736900
 C                 -3.23388100   -0.83327600    3.34541800
 C                 -4.70042400   -1.35681700    1.52955200
 C                 -4.48372300   -0.69998400    2.73925900
 H                 -3.04781300   -0.33900900    4.29726600
 H                 -5.66935000   -1.26798200    1.04190500
 C                 -2.45211400    2.23351300   -1.53871700
 C                 -2.21522800    1.58762400   -2.76918100
 C                 -3.70884500    2.12261700   -0.91710200
 C                 -3.23469900    0.83287600   -3.34544400
 C                 -4.70095000    1.35571600   -1.52913800
 C                 -4.48433600    0.69910400   -2.73899400
 H                 -3.04870600    0.33879700   -4.29740400
 H                 -5.66972800    1.26652100   -1.04126400
 C                  1.99540400    2.93944300    0.84414800
 C                  1.97266800    2.62799800    2.22229400
 C                  3.21335300    2.89845000    0.13504600
 C                  3.15963500    2.27927300    2.85896000
 C                  4.37528200    2.51025700    0.80956300
 C                  4.36947000    2.19760900    2.16681000
 H                  3.13673200    2.04475000    3.92126000
 H                  5.31070700    2.46273200    0.25562100
 C                 -5.55718400    0.14508500    3.36652000
 H                 -5.54472800    0.06307100    4.45767200
 H                 -5.41791700    1.20459100    3.11966500
```

H	-6.55155800	-0.14506400	3.01557800
C	-3.97808800	-2.76641200	-0.41507500
H	-3.72594100	-3.83063900	-0.42025400
H	-5.03106000	-2.66113400	-0.68996900
H	-3.37794500	-2.29018800	-1.20014000
C	-0.87456300	-1.68523800	3.44298600
H	-0.10059300	-1.17434600	2.85542400
H	-0.90180700	-1.22656400	4.43495300
H	-0.55488900	-2.72663500	3.55307100
C	3.29055400	-3.29166700	1.31609700
H	3.27479600	-4.38189300	1.42965200
H	4.21480700	-2.92203400	1.76792200
H	2.44736600	-2.89661300	1.88905100
C	0.68476000	-2.66800800	-2.99130400
H	0.00139800	-1.88935900	-2.63307100
H	0.85938700	-2.50262400	-4.05739300
H	0.17262900	-3.62754300	-2.86685300
C	5.62624300	-1.76181800	-2.86789000
H	6.51984600	-2.05680800	-2.31103900
H	5.69207000	-2.19206600	-3.87199200
H	5.65099300	-0.67157700	-2.98011300
C	5.62526100	1.76257500	2.86827200
H	6.51890800	2.05724000	2.31132800
H	5.69117700	2.19305300	3.87227000
H	5.64977200	0.67235300	2.98076700
C	0.68364400	2.66809200	2.99097200
H	0.85813300	2.50266300	4.05707700
H	0.17142200	3.62757600	2.86650100
H	0.00042700	1.88938400	2.63259300
C	3.29021900	3.29235500	-1.31597000
H	3.27866500	4.38271600	-1.42894500
H	4.21274100	2.91940800	-1.76862500
H	2.44512700	2.90090500	-1.88852200
C	-3.97855300	2.76528500	0.41548800
H	-3.72705300	3.82966800	0.42061800
H	-5.03134800	2.65934700	0.69080400
H	-3.37780600	2.28938700	1.20028600
C	-5.55768300	-0.14628800	-3.36601300
H	-6.55222300	0.14490400	-3.01639200
H	-5.54418500	-0.06588100	-4.45726500
H	-5.41923000	-1.20550500	-3.11745000
C	-0.87565400	1.68557200	-3.44346300
H	-0.10137600	1.17485600	-2.85616000
H	-0.90299700	1.22701400	-4.43547900
H	-0.55634200	2.72708800	-3.55350200

4.5. Bonding situation in the distibenium dication (6)

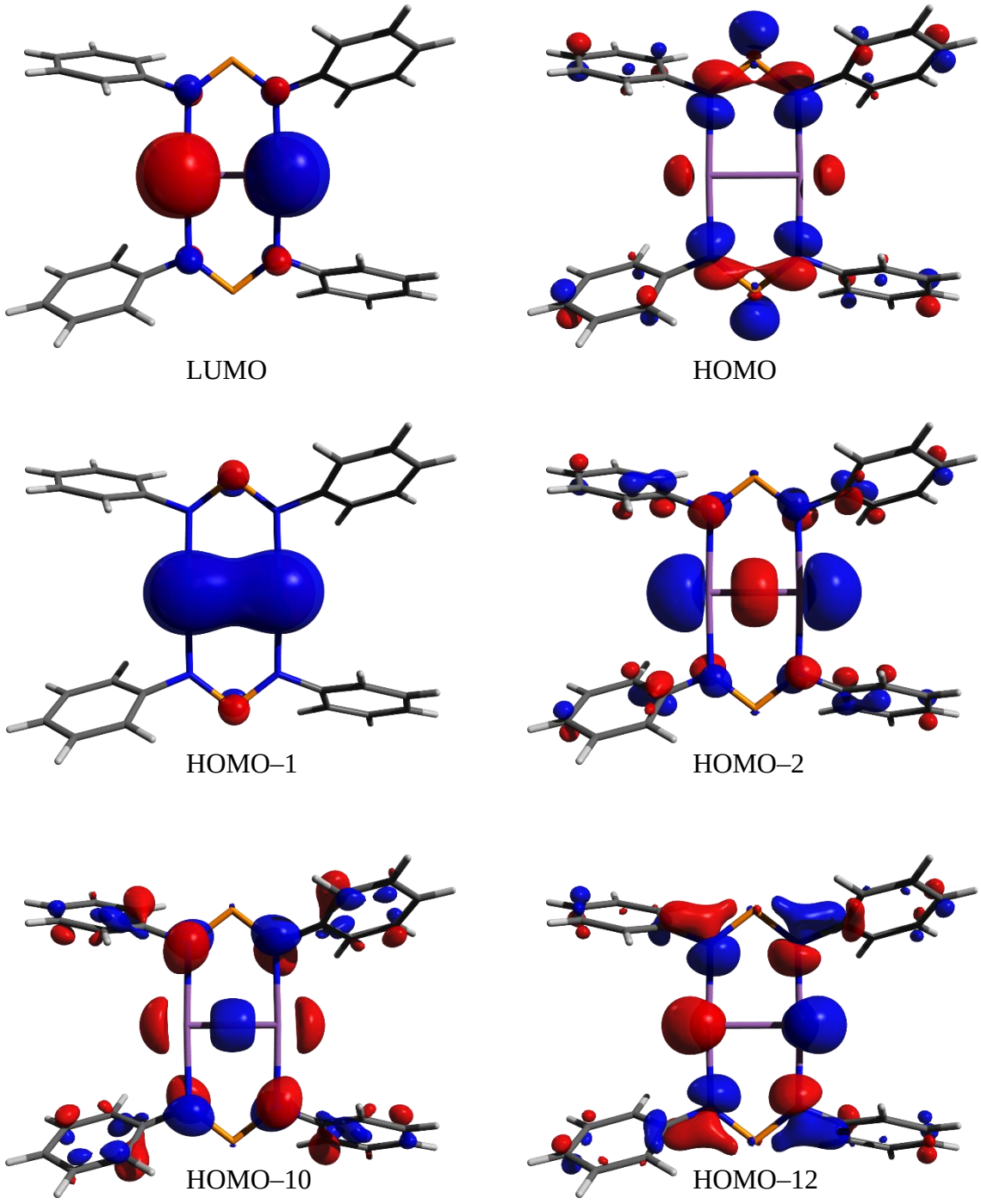
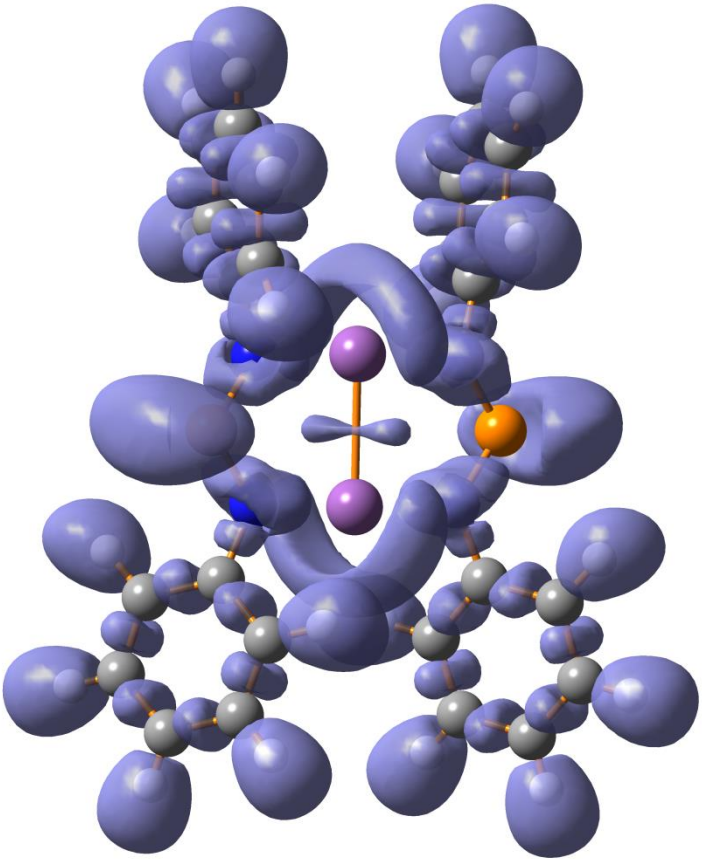


Figure S7. Frontier orbitals of $[P(\mu\text{-}NTer)_2Sb]_2$.



ELF at 0.75

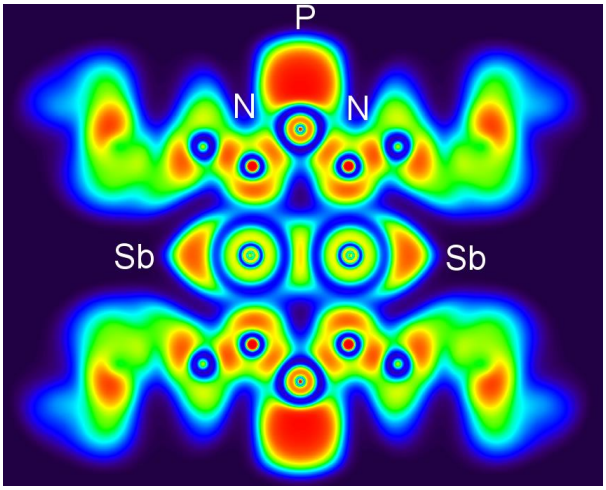


Figure S8. ELF representations of $[P(\mu\text{-}NTer)_2Sb]_2$.

4.5.1. NBO analysis for $[Sb(\mu\text{-}NPh)_2P]_2$

Summary of Natural Population Analysis:

Atom	No	Natural Charge	Natural Population: Core	Valence	Rydberg	Total
Sb	1	0.54271	46.00000	4.44002	0.01727	50.45729
N	2	-1.04470	1.99945	6.02984	0.01541	8.04470
N	3	-1.04470	1.99945	6.02984	0.01541	8.04470
Sb	4	0.54271	46.00000	4.44002	0.01727	50.45729
P	5	1.23775	9.99811	3.69185	0.07230	13.76225
N	6	-1.04470	1.99945	6.02984	0.01541	8.04470
N	13	-1.04470	1.99945	6.02984	0.01541	8.04470
P	15	1.23775	9.99811	3.69185	0.07230	13.76225

Wiberg bond index matrix in the NAO basis:

Atom	1	2	3	4	5	6	7	8	9
1. Sb	0.0000	0.3510	0.3510	1.7535	0.0516	0.0239	0.0072	0.0093	0.0114
2. N	**0.3510**	0.0000	0.0272	0.0239	0.0050	0.0058	0.0013	0.0011	0.0012
3. N	**0.3510**	**0.0272**	0.0000	0.0239	1.1700	0.0922	1.0392	0.0286	0.0287
4. Sb	**1.7535**	**0.0239**	**0.0239**	0.0000	0.0516	0.3510	0.0020	0.0027	0.0042
5. P	**0.0516**	**0.0050**	**1.1700**	**0.0516**	0.0000	1.1700	0.0136	0.0189	0.0176
6. N	**0.0239**	**0.0058**	**0.0922**	**0.3510**	**1.1700**	0.0000	0.0064	0.0058	0.0043
7. C	0.0072	0.0013	1.0392	0.0020	0.0136	0.0064	0.0000	1.3861	1.3639
8. C	0.0093	0.0011	0.0286	0.0027	0.0189	0.0058	1.3861	0.0000	0.0118
9. C	0.0114	0.0012	0.0287	0.0042	0.0176	0.0043	1.3639	0.0118	0.0000
10. C	0.0015	0.0001	0.0078	0.0013	0.0018	0.0007	0.0127	0.1081	1.4436
11. C	0.0035	0.0006	0.0084	0.0018	0.0060	0.0023	0.0999	0.0122	0.0122
12. C	0.0013	0.0002	0.0090	0.0013	0.0012	0.0006	0.0130	1.4237	0.1095
13. N	**0.0239**	**0**.0922	0.0058	0.3510	0.0050	0.0272	0.0002	0.0004	0.0003
14. C	0.0020	0.0002	0.0064	0.0072	0.0136	1.0392	0.0008	0.0001	0.0002
15. P	**0.0516**	**1.1700**	**0.0050**	**0.0516**	**0.0045**	**0.0050**	0.0003	0.0003	0.0003

(Occupancy) Bond orbital/ Coefficients/ Hybrids

1. (1.98721) BD (1)Sb 1-Sb 4
   (50.00%) 0.7071*Sb 1 s(11.48%)p 7.71(88.52%)
   -0.3339 0.0552 -0.0157 -0.0033 0.0000
   0.0000 0.0000 0.0000 0.9399 -0.0422
   0.0018 -0.0005 0.0000 0.0000 0.0000
   0.0000
   (50.00%) 0.7071*Sb 4 s(11.48%)p 7.71(88.52%)
   -0.3339 0.0552 -0.0157 -0.0033 0.0000
   0.0000 0.0000 0.0000 -0.9399 0.0422
   -0.0018 0.0005 0.0000 0.0000 0.0000
   0.0000
2. (1.93061) BD (2)Sb 1-Sb 4
   (50.00%) 0.7071*Sb 1 s(0.00%)p 1.00(100.00%)
   0.0000 0.0000 0.0000 0.0000 0.9999
   0.0079 0.0016 -0.0030 0.0000 0.0000
   0.0000 0.0000 0.0062 -0.0007 0.0026
   0.0000
   (50.00%) 0.7071*Sb 4 s(0.00%)p 1.00(100.00%)
   0.0000 0.0000 0.0000 0.0000 0.9999
   0.0079 0.0016 -0.0030 0.0000 0.0000
   0.0000 0.0000 -0.0062 0.0007 -0.0026
   0.0000
3. (1.97462) BD (1) N 2- P 15
   (75.25%) 0.8675* N 2 s(28.64%)p 2.49(71.17%)d 0.01(0.19%)
   -0.0002 0.5351 0.0015 0.0353 -0.0085
   -0.6499 -0.0185 0.5362 -0.0138 -0.0017
   0.0054 -0.0355 -0.0211 0.0130
   (24.75%) 0.4975* P 15 s(16.71%)p 4.87(81.46%)d 0.11(1.84%)
   0.0000 0.0005 0.3919 -0.1163 -0.0001

```
                                    0.0545  0.0112  0.0004  0.6931 -0.0537
                                   -0.0003 -0.5724  0.0219  0.0033 -0.0023
                                   -0.1165 -0.0675  0.0145
  5. (1.97463) BD ( 1) N  3- P  5
             ( 75.25%)   0.8675* N  3 s( 28.64%)p 2.49( 71.17%)d 0.01(  0.19%)
                                   -0.0002  0.5351  0.0015 -0.0353  0.0085
                                   -0.6499 -0.0185 -0.5362  0.0138  0.0017
                                    0.0054  0.0355 -0.0211  0.0130
             ( 24.75%)   0.4975* P  5 s( 16.71%)p 4.87( 81.46%)d 0.11(  1.84%)
                                    0.0000  0.0005  0.3919 -0.1163  0.0001
                                   -0.0545 -0.0112  0.0004  0.6931 -0.0537
                                    0.0003  0.5724 -0.0219 -0.0033 -0.0023
                                    0.1165 -0.0675  0.0145
  7. (1.97463) BD ( 1) P  5- N  6
             ( 24.75%)   0.4975* P  5 s( 16.71%)p 4.87( 81.46%)d 0.11(  1.84%)
                                    0.0000  0.0005  0.3919 -0.1163 -0.0001
                                    0.0545  0.0112 -0.0004 -0.6931  0.0537
                                    0.0003  0.5724 -0.0219 -0.0033  0.0023
                                   -0.1165 -0.0675  0.0145
             ( 75.25%)   0.8675* N  6 s( 28.64%)p 2.49( 71.17%)d 0.01(  0.19%)
                                   -0.0002  0.5351  0.0015  0.0353 -0.0085
                                    0.6499  0.0185 -0.5362  0.0138  0.0017
                                   -0.0054 -0.0355 -0.0211  0.0130
 23. (1.97462) BD ( 1) N 13- P 15
             ( 75.25%)   0.8675* N 13 s( 28.64%)p 2.49( 71.17%)d 0.01(  0.19%)
                                   -0.0002  0.5351  0.0015 -0.0353  0.0085
                                    0.6499  0.0185  0.5362 -0.0138 -0.0017
                                   -0.0054  0.0355 -0.0211  0.0130
             ( 24.75%)   0.4975* P 15 s( 16.71%)p 4.87( 81.46%)d 0.11(  1.84%)
                                    0.0000  0.0005  0.3919 -0.1163  0.0001
                                   -0.0545 -0.0112 -0.0004 -0.6931  0.0537
                                   -0.0003 -0.5724  0.0219  0.0033  0.0023
                                    0.1165 -0.0675  0.0145
105. (1.98007) LP ( 1)Sb  1             s( 88.75%)p 0.13( 11.25%)
                                    0.9420  0.0099 -0.0026 -0.0006  0.0000
                                    0.0000  0.0000  0.0000  0.3349  0.0178
                                   -0.0052 -0.0007  0.0000  0.0000  0.0000
                                    0.0000
106. (1.74936) LP ( 1) N  2             s( 33.92%)p 1.95( 66.05%)d 0.00(  0.03%)
                                    0.0005  0.5824 -0.0047 -0.1984 -0.0009
                                   -0.1666  0.0019 -0.7700  0.0205  0.0023
                                   -0.0088 -0.0077 -0.0072 -0.0123
107. (1.57532) LP ( 2) N  2             s(  0.12%)p99.99( 99.78%)d 0.84(  0.10%)
                                    0.0000  0.0342 -0.0045  0.9734  0.0045
                                   -0.0889  0.0004 -0.2059  0.0032 -0.0101
                                    0.0286 -0.0020  0.0031 -0.0082
108. (1.74935) LP ( 1) N  3             s( 33.92%)p 1.95( 66.05%)d 0.00(  0.03%)
                                    0.0005  0.5824 -0.0047  0.1984  0.0009
                                   -0.1666  0.0019  0.7700 -0.0205 -0.0023
                                   -0.0088  0.0077 -0.0072 -0.0123
109. (1.57532) LP ( 2) N  3             s(  0.12%)p99.99( 99.78%)d 0.84(  0.10%)
                                    0.0000  0.0342 -0.0045 -0.9734 -0.0045
                                   -0.0889  0.0004  0.2059 -0.0032  0.0101
                                    0.0286  0.0020  0.0031 -0.0082
110. (1.98007) LP ( 1)Sb  4             s( 88.75%)p 0.13( 11.25%)
                                    0.9420  0.0099 -0.0026 -0.0006  0.0000
                                    0.0000  0.0000  0.0000 -0.3349 -0.0178
                                    0.0052  0.0007  0.0000  0.0000  0.0000
                                    0.0000
111. (1.96703) LP ( 1) P  5             s( 68.65%)p 0.46( 31.27%)d 0.00(  0.08%)
                                    0.0000 -0.0007  0.8280  0.0296  0.0000
                                    0.0000  0.0000  0.0000  0.0000  0.0000
                                   -0.0005 -0.5585 -0.0275 -0.0009  0.0000
                                    0.0000  0.0268 -0.0109
112. (1.74935) LP ( 1) N  6             s( 33.92%)p 1.95( 66.05%)d 0.00(  0.03%)
                                    0.0005  0.5824 -0.0047 -0.1984 -0.0009
                                    0.1666 -0.0019  0.7700 -0.0205 -0.0023
                                    0.0088 -0.0077 -0.0072 -0.0123
113. (1.57532) LP ( 2) N  6             s(  0.12%)p99.99( 99.78%)d 0.84(  0.10%)
```

```
                                     0.0000  0.0342 -0.0045  0.9734  0.0045
                                     0.0889 -0.0004  0.2059 -0.0032  0.0101
                                    -0.0286 -0.0020  0.0031 -0.0082
 114. (1.74936) LP ( 1) N 13          s( 33.92%)p 1.95( 66.05%)d 0.00(  0.03%)
                                     0.0005  0.5824 -0.0047  0.1984  0.0009
                                     0.1666 -0.0019 -0.7700  0.0205  0.0023
                                     0.0088  0.0077 -0.0072 -0.0123
 115. (1.57532) LP ( 2) N 13          s(  0.12%)p99.99( 99.78%)d 0.84(  0.10%)
                                     0.0000  0.0342 -0.0045 -0.9734 -0.0045
                                     0.0889 -0.0004 -0.2059  0.0032 -0.0101
                                    -0.0286  0.0020  0.0031 -0.0082
 116. (1.96703) LP ( 1) P 15          s( 68.65%)p 0.46( 31.27%)d 0.00(  0.08%)
                                     0.0000 -0.0007  0.8280  0.0296  0.0000
                                     0.0000  0.0000  0.0000  0.0000  0.0000
                                     0.0005  0.5585  0.0275  0.0009  0.0000
                                     0.0000  0.0268 -0.0109
 117. (0.40556) LP*( 2)Sb  1          s(  0.00%)p 1.00(100.00%)
                                     0.0000  0.0000  0.0000  0.0000 -0.0061
                                    -0.0064 -0.0041 -0.0004  0.0000  0.0000
                                     0.0000  0.0000  0.9993  0.0352 -0.0079
                                     0.0096
 118. (0.40556) LP*( 2)Sb  4          s(  0.00%)p 1.00(100.00%)
                                     0.0000  0.0000  0.0000  0.0000  0.0061
                                     0.0064  0.0041  0.0004  0.0000  0.0000
                                     0.0000  0.0000  0.9993  0.0352 -0.0079
                                     0.0096
 119. (0.73358) LP*( 2) P  5          s(  0.00%)p 1.00( 99.39%)d 0.01(  0.61%)
                                     0.0000  0.0000  0.0000  0.0000  0.0000
                                     0.9937  0.0217  0.0000  0.0762 -0.0158
                                     0.0000  0.0000  0.0000  0.0000  0.0778
                                     0.0082  0.0000  0.0000
 120. (0.73358) LP*( 2) P 15          s(  0.00%)p 1.00( 99.39%)d 0.01(  0.61%)
                                     0.0000  0.0000  0.0000  0.0000  0.0000
                                     0.9937  0.0217  0.0000 -0.0762  0.0158
                                     0.0000  0.0000  0.0000  0.0000 -0.0778
                                     0.0082  0.0000  0.0000

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106. LP ( 1) N 2          117. LP*( 2)Sb 1            69.29    0.38    0.150
114. LP ( 1) N13          118. LP*( 2)Sb 4            69.29    0.38    0.150
107. LP ( 2) N 2          120. LP*( 2) P15           118.36    0.11    0.112
115. LP ( 2) N13          120. LP*( 2) P15           118.36    0.11    0.112
108. LP ( 1) N 3          117. LP*( 2)Sb 1            69.29    0.38    0.150
112. LP ( 1) N 6          118. LP*( 2)Sb 4            69.29    0.38    0.150
109. LP ( 2) N 3          119. LP*( 2) P 5           118.36    0.11    0.112
113. LP ( 2) N 6          119. LP*( 2) P 5           118.36    0.11    0.112
```

4.5.2. Isomers of $[Sb(\mu\text{-}NPh)_2P]_2$ and $[P_4(NPh)_4]$

Table S7. Isomers of $[Sb(\mu\text{-}NPh)_2P]_2$ (relative energies referenced to the dication).

	E	G	ΔE	ΔG
alpha 1	-1837.64632	-1837.32287	-51.9	-50.6
alpha 2	-1837.63964	-1837.31707	-34.4	-35.4
beta 1	-1837.64787	-1837.32257	-56.0	-49.8
beta 2	-1837.65935	-1837.33363	-86.1	-78.9
beta 3	-1837.65398	-1837.32906	-72.0	-66.9
chain	-1837.60244	-1837.28266	63.3	55.0
dication	-1837.62654	-1837.30359	0.0	0.0

Table S8. Isomers of $[P_4(NPh)_4]$ (relative energies referenced to the dication).

	E	G	ΔE	ΔG
alpha 1	-2509.18891	-2508.8742	-453.3	-222.9
beta 1	-2509.00602	-2508.88682	26.9	-256.1
chain	-2509.00639	-2508.7949	25.9	-14.7
dication	-2509.01627	-2508.78928	0.0	0.0

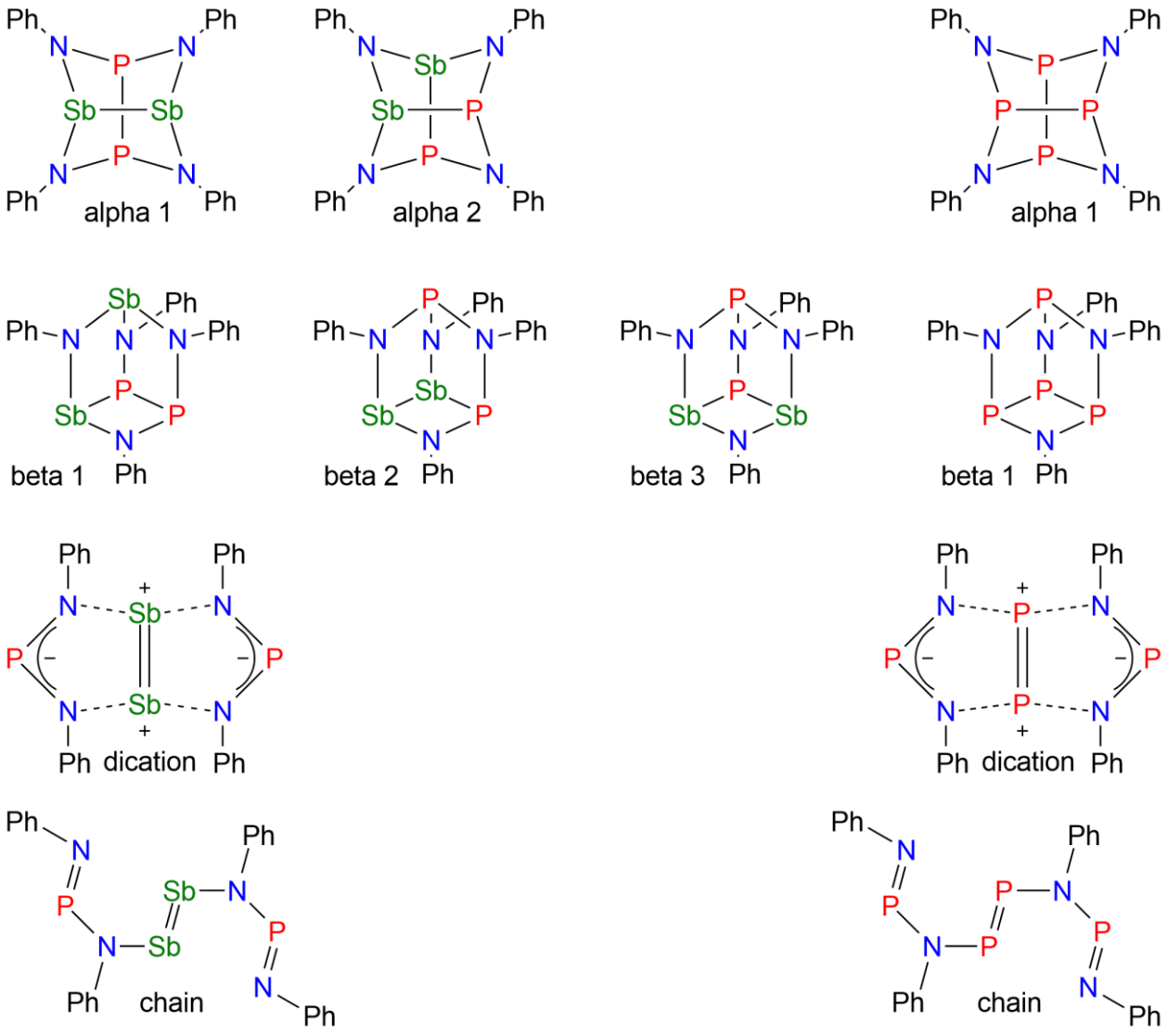

Figure S9. Computed isomers of **6** and $[P_4(NPh)_4]$.

4.5.3. Geometry for $[Sb(\mu\text{-}NPh)_2P]_2$

```
0 1
 Sb                 0.00000000    1.32188000   -0.00000300
 N                 -0.01587000    1.27663000    2.37145700
 N                  0.01587000    1.27663000   -2.37145300
 Sb                 0.00000000   -1.32188000   -0.00000300
 P                  0.00000000    0.00000000   -3.35799300
 N                 -0.01587000   -1.27663000   -2.37145300
 C                 -0.19495000    2.59446000   -2.89072300
 C                 -1.38834000    2.92809000   -3.55634300
 C                  0.76926000    3.60077000   -2.64773300
 C                  0.46498000    4.91758000   -2.98261300
 C                 -0.74146000    5.25814000   -3.55894300
 C                 -1.64911000    4.26905000   -3.85808300
 N                  0.01587000   -1.27663000    2.37145700
 C                  0.19495000   -2.59446000   -2.89072300
 P                  0.00000000    0.00000000    3.35799700
 C                 -0.19495000   -2.59446000    2.89072700
 C                 -0.76926000   -3.60077000   -2.64773300
 C                  1.38834000   -2.92809000   -3.55634300
 C                  0.76926000   -3.60077000    2.64773700
 C                 -1.38834000   -2.92809000    3.55634700
 C                 -0.46498000   -4.91758000   -2.98261300
 C                  1.64911000   -4.26905000   -3.85808300
 C                  0.19495000    2.59446000    2.89072700
 C                  0.46498000   -4.91758000    2.98261700
 C                 -1.64911000   -4.26905000    3.85808700
 C                  0.74146000   -5.25814000   -3.55894300
 C                 -0.76926000    3.60077000    2.64773700
 C                  1.38834000    2.92809000    3.55634700
 C                 -0.74146000   -5.25814000    3.55894700
 C                 -0.46498000    4.91758000    2.98261700
 C                  1.64911000    4.26905000    3.85808700
 C                  0.74146000    5.25814000    3.55894700
 H                  1.10433000    5.59887000   -2.81034300
 H                 -0.94253000    6.16787000   -3.74610300
 H                 -2.46942000    4.50138000   -4.27840300
 H                 -1.10433000   -5.59887000   -2.81034300
 H                  2.46942000   -4.50138000   -4.27840300
 H                  1.10433000   -5.59887000    2.81034700
 H                 -2.46942000   -4.50138000    4.27841700
 H                  0.94253000   -6.16787000   -3.74610300
 H                 -0.94253000   -6.16787000    3.74610700
 H                 -1.10433000    5.59887000    2.81034700
 H                  2.46942000    4.50138000    4.27841700
 H                  0.94253000    6.16787000    3.74610700
 H                 -2.08804700    2.16571000   -3.82853200
 H                  1.71589800    3.35424000   -2.21414500
 H                  2.08804700   -2.16571000   -3.82853200
 H                 -1.71589800   -3.35424000   -2.21414500
 H                 -1.71589800    3.35424000    2.21414800
 H                  2.08804700    2.16571000    3.82853500
 H                  1.71589800   -3.35424000    2.21414800
 H                 -2.08804700   -2.16571000    3.82853500
```

5. References

[1] A. Hinz, A. Schulz, A. Villinger, *Angew. Chem. Int. Ed.* **2014**, *54*, 668–672.

[2] D. Savoia, C. Trombini, A. Umani-Ronchi, *Pure Appl. Chem.* **1985**, *57*, 1887–1896.

[3] C. B. Fischer, S. Xu, H. Zipse, *Chem. Eur. J.* **2006**, *12*, 5779–5784.

[4] G. R. Fulmer, A. J. M. Miller, N. H. Sherden, H. E. Gottlieb, A. Nudelman, B. M. Stoltz, J. E. Bercaw, K. I. Goldberg, *Organometallics* **2010**, *29*, 2176–2179.

[5] G. M. Sheldrick, **2013**, SHELXS–2013.

[6] G. M. Sheldrick, **2013**, SHELXL–2013.

[7] G. M. Sheldrick, **2004**, SADABS 2.

[8] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian 09, *Gaussian, Inc., Wallingford CT, 2009.*

[9] T. Lu, F. Chen, *J. Comput. Chem.* **2012**, *33*, 580–592.

[10] E. D. Glendening, C. R. Landis, F. Weinhold, *J. Comput. Chem.* **2013**, *34*, 1429–1437.

[11] E. D. Glendening, F. Weinhold, *J. Comput. Chem.* **1998**, *19*, 593–609.

[12] E. D. Glendening, F. Weinhold, *J. Comput. Chem.* **1998**, *19*, 610–627.