Supporting Information

Zwitterionic And Biradicaloid Heteroatomic Cyclopentane Derivatives Containing Different Group 15 Elements

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1. General Information

All manipulations were carried out under oxygen- and moisture free conditions using standard Schlenk and Drybox techniques. \([P(\mu\text{-NTer})]_2\), \([\text{As}(\mu\text{-NTer})]_2\), \([E(\mu\text{-NTer})_2N]\) (E = P, As, Sb), \([\text{Sb}(\mu\text{-NTer})_2P]\) and CNDmp\[5\] 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.

**NMR:** \(^{31}\text{P}\{^1\text{H}\}\), \(^{13}\text{C}\{^1\text{H}\}\) and \(^1\text{H}\) NMR spectra were recorded on BRUKER spectrometers AVANCE 250, AVANCE 300 and AVANCE 500, respectively. The \(^1\text{H}\) and \(^{13}\text{C}\) NMR chemical shifts were referenced to the solvent signals.\[6\] The \(^{31}\text{P}\) NMR chemical shifts are referred to \(\text{H}_3\text{PO}_4\) (85\%) respectively. \(\text{C}_6\text{D}_6\) 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 \(\mu\text{m}\)) 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\(_\alpha\) radiation (\(\lambda = 0.71073\)). The structures were solved by direct methods (\textit{SHELXS-2013})\[7\] and refined by full-matrix least squares procedures (\textit{SHELXL-2013}).\[8\] Semi-empirical absorption corrections were applied (SADABS).\[9\] 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 Ter$_2$N$_3$AsCNDmp (2NA)

To a solution of [As(µ-NTer)$_2$N] (165 mg, 0.222 mmol) in benzene (4 ml), a solution CNDmp (30 mg, 0.229 mmol) in benzene (2 ml) was added dropwise at ambient temperature. Immediately, a change of colour from yellow to red occurred. After the addition, the solution was concentrated to approx. 1 ml and left undisturbed at 4 °C, affording red needle-shaped crystals. The supernatant was removed via syringe and the crystals were dried in vacuo (161 mg, 0.184 mmol, 83%).

Mp. 141 °C (dec.). EA for C$_{63}$H$_{65}$AsN$_4$ found (calc.) C 79.11 (79.39), H 6.67 (6.87), N 5.74 (5.88). $^1$H NMR (298 K, C$_6$D$_6$, 250.1 MHz): 1.66 (s, 6 H, CH$_3$), 1.72 (s, 6 H, CH$_3$), 1.85 (s, 12 H, CH$_3$), 2.15 (s, 6 H, CH$_3$), 2.21 (s, 6 H, CH$_3$), 2.27 (s, 6 H, CH$_3$), 6.88 (s, 4 H, CH$_{Mes}$), 6.72 (s, 4 H, CH$_{Mes}$), 6.76-7.02 (m, 9 H). $^{13}$C($^1$H) NMR (298 K, C$_6$D$_6$, 62.9 MHz): 19.26 (s, CH), 21.23 (s, CH), 21.42 (s, CH), 21.52 (s, CH), 21.66 (s, CH), 21.96 (s, CH), 122.78 (s, CH), 128.92 (s, CH), 129.09 (s, CH), 129.21 (s, CH), 129.25 (s, CH), 129.45 (s, CH), 129.86 (s, CH), 132.53 (s, CH), 132.65 (s, CH), 136.31 (s), 136.56 (s), 136.81 (s), 136.94 (s), 137.11 (s), 137.42 (s), 137.84 (s), 137.94 (s), 138.10 (s), 138.34 (s), 141.10 (s), 142.09 (s), 152.43 (s), 181.05 (s, AsCN). UV/vis ($\lambda_{max}$, nm): 350 (br), 523. IR (ATR, cm$^{-1}$): 536 (m), 543 (m), 551 (m), 559 (m), 574 (m), 586 (m), 594 (m), 613 (s), 638 (m), 655 (m), 676 (m), 730 (s), 742 (m), 759 (vs), 767 (s), 786 (m), 808 (m), 848 (s), 879 (w), 908 (w), 919 (w), 966 (m), 1031 (m), 1054 (m), 1095 (m), 1157 (s), 1201 (s), 1222 (s), 1257 (m), 1274 (m), 1295 (s), 1375 (m), 1411 (m), 1450 (s), 1481 (m), 1535 (vs), 1556 (m), 1594 (w), 1610 (w), 2730 (w), 2854 (w), 2914 (m), 2944 (m), 2998 (w). Raman (632 nm, cm$^{-1}$): 231 (43), 246 (51), 264 (36), 279 (27), 331 (23), 368 (5), 386 (17), 404 (13), 423 (23), 435 (12), 468 (9), 478 (13), 492 (11), 499 (12), 512 (15), 521 (39), 552 (43), 559 (55), 575 (100), 613 (16), 638 (13), 654 (15), 700 (11), 742 (12), 756 (11), 765 (7), 774 (7), 804 (6), 833 (7), 855 (19), 911 (4), 944 (11), 991 (7), 1004 (19), 1054 (9), 1076 (12), 1083 (11), 1162 (21), 1188 (8), 1201 (16), 1222 (6), 1258 (8), 1286 (37), 1304 (59), 1380 (14), 1414 (10), 1456 (36), 1481 (18), 1523 (9), 1535 (9), 1574 (13), 1585 (15), 1612 (21), 2730 (1), 2854 (1), 2918 (4), 2949 (2), 3008 (1). MS (Cl, pos., isobutane) m/z (%): 132 (49) [CNDmp]$^+$, 716 (13), 743 (100) [Ter$_2$N$_3$As]$^+$, 874 (<1) [M]$^+$. 
2.2. Synthesis of Ter$_2$N$_2$PAsCNDmp (2PAs)

To a violet solution of [P(µ-NTer)$_2$As] (181 mg, 0.246 mmol) in 4 ml benzene, a colourless solution of CNDmp (33 mg, 0.252 mmol) in 2 ml was added within 5 minutes. The solution turned grey and finally green within 10 minutes. Afterwards, volatiles were removed in vacuo until crystallization commenced (approx. 0.5 ml). The solution was left undisturbed overnight, resulting in the deposition of a green precipitate. The supernatant was filtered off (sintered glass frit) and the solid was dried in vacuo (150 mg, 0.168 mmol, 68%).

Mp. 122 °C (dec.). EA for C$_{57}$H$_{59}$N$_3$AsP found (calc.): C 76.20 (76.75), H 6.93 (6.67), N 4.38 (4.71). $^1$H NMR (298 K, C$_6$D$_6$, 300 MHz): 1.71 (s, 6 H, CH$_3$), 1.72 (s, 6 H, CH$_3$), 1.95 (s, 12 H, CH$_3$), 2.08 (s, 6 H, CH$_3$), 2.16 (s, 6 H, CH$_3$), 2.17 (s, 12 H, CH$_3$), 2.25 (s, 6 H, CH$_3$), 2.28 (s, 6 H, CH$_3$), 2.30 (s, 6 H, CH$_3$), 2.50 (s, 6 H, CH$_3$), 6.58 (s, 1 H, CHMes), 6.70-6.96 (m, 12 H, CH). $^{13}$C($^1$H) NMR (298 K, C$_6$D$_6$, 62.9 MHz): 19.00 (s, C$_5$H$_3$), 19.08 (s, C$_5$H$_3$), 20.64 (s, C$_5$H$_3$), 21.37 (s, C$_5$H$_3$), 21.50 (s, C$_5$H$_3$), 21.66 (s, C$_5$H$_3$), 21.71 (s, C$_5$H$_3$), 21.74 (s, C$_5$H$_3$), 21.80 (s, C$_5$H$_3$), 21.93 (s, C$_5$H$_3$), 122.59 (s, C$_5$H), 128.21 (s, C$_5$H), 128.24 (s, C$_5$H), 129.08 (s, C$_5$H), 129.18 (s, C$_5$H), 129.45 (s, C$_5$H), 129.53 (s, C$_5$H), 130.20 (s, C$_5$H), 131.71 (s, C$_5$H), 132.61 (s, C$_5$H), 135.24 (s), 135.43 (d, $J_{CP} = 12.7$ Hz), 136.39 (s), 136.80 (s), 137.18 (s), 137.39 (s), 137.56 (s), 137.88 (s), 138.36 (s), 139.92 (d, $J_{CP} = 12.1$ Hz), 141.20 (d, $J_{CP} = 5.0$ Hz), 151.43 (s), 184.98 (d, $J_{CP} = 9.9$ Hz). $^{31}$P NMR (298 K, C$_6$D$_6$, 121.5 MHz): 269.0 (s). Raman (632 nm): 3067 (5), 3044 (7), 3018 (3), 2858 (8), 2731 (3), 1681 (8), 1633 (88), 1616 (34), 1594 (100), 1584 (48), 1467 (16), 1422 (15), 1406 (17), 1382 (17), 1307 (55), 1269 (16), 1256 (16), 1222 (7), 1178 (43), 1118 (2), 109 (17), 1087 (35), 1073 (36), 1010 (7), 947 (8), 903 (2), 874 (21), 852 (6), 843 (11), 812 (6), 794 (6), 774 (7), 767 (3), 744 (9), 691 (4), 660 (1), 643 (8), 616 (35), 598 (3), 579 (81), 564 (37), 557 (34), 529 (22), 508 (21), 487 (4), 474 (7), 448 (16), 415 (20), 400 (22), 390 (12), 380 (5), 360 (38), 345 (14), 310 (5), 262 (25), 237 (28), 217 (7). IR (ATR, cm$^{-1}$): 2967 (w), 2943 (w), 2912 (m), 2850 (m), 2727 (w), 1630 (w), 1610 (m), 1574 (w), 1531 (vs), 1443 (s), 1406 (s), 1371 (m), 1335(vw), 1309 (vw), 1286 (w), 1273 (vw), 1240 (w), 1221 (m), 1192 (s), 1163 (w), 1138 (w), 1097 (m), 1088 (m), 1080 (m), 1024 (s), 990 (w), 957 (vvw), 945 (vw), 937 (vvw), 908 (w), 867 (w), 847 (vs), 827 (w), 806 (w), 798 (s), 773 (w), 762 (s), 746 (s), 698 (w), 690 (w), 673 (m), 654 (vw), 644 (w), 600 (m), 573 (m), 559 (w), 546 (vw), 528 (vw). MS (Cl, pos., isobutane) m/z (%): 132 (57) [CNDmp]$^+$, 188 (10), 330 (100) [TerNH$_3$]$^+$, 372 (11), 386 (24) [TerNH$_2$+C$_4$H$_9$]$^+$, 459 (35) [TerNCNDmp]$^+$, 687 (71) [Ter$_2$N$_2$PH$_2$]$^+$, 705 (31) [Ter$_2$N$_2$PAs]$^+$, 743 (14), 760 (11) [Ter$_2$N$_2$PAs]$^+$, 793 (26), 829 (9).
To a solution of [Ter₂N₂PAs(CNDmp)] (121 mg, 0.134 mmol) in benzene (3 ml), PC'Bu (20 μl) was added via microliter syringe. After shaking of the reaction mixture, the solution turned yellow within 30 minutes. The yellow solution was concentrated until crystallization commenced and left undisturbed at ambient temperature overnight, affording yellow crystals. The supernatant was removed via syringe and the crystals were dried in vacuo (93 mg, 0.094 mmol, 70%).

Mp. 118 °C (dec.). EA for C₆₂H₈₈As₃P₂ found (calc.): C 75.20 (75.06), H 6.93 (6.91), N 4.38 (4.24). ¹H NMR (298 K, C₆D₆, 300 MHz): 1.00 (s, 9 H, 'Bu), 1.72 (s, 3 H, CH₃), 2.02 (s, 3 H, CH₃), 2.06 (s, 9 H, CH₃), 2.11 (s, 3 H, CH₃), 2.21 (s, 3 H, CH₃), 2.28 (s, 3 H, CH₃), 2.30 (s, 3 H, CH₃), 2.34 (s, 3 H, CH₃), 2.36 (s, 3 H, CH₃), 2.37 (s, 3 H, CH₃), 2.38 (s, 3 H, CH₃), 2.47 (s, 3 H, CH₃), 6.45 (dd, J_HH = 2.1, J_HH = 7.2 Hz, 1 H, CH₃), 6.58 (s, 1 H, CH₃), 6.61 (s, 1 H, CH), 6.65 (dd, J_HH = 1.7, J_HH = 7.5 Hz, 1 H, CH), 6.70-6.73 (m, 3H), 6.79-6.94 (m, 9 H), 6.97 (t, J_HH = 7.4, 1 H, CH). ¹³C{¹H} NMR (298 K, C₆D₆, 62.9 MHz): 17.88 (s, CH₃), 20.64 (s, CH₃), 20.68 (s, CH₃), 20.79 (s, CH₃), 21.09 (s, CH₃), 21.53 (s, CH₃), 21.67 (s, CH₃), 21.68 (s, CH₃), 22.37 (d, J_CP = 6.4 Hz, CH₃), 21.45 (d, J_CP = 12.7 Hz, CH₃), 22.49 (s, CH₃), 22.68 (s, CH₃), 22.80 (s, CH₃), 23.02 (s, CH₃), 23.05 (s, CH₃), 24.39 (d, J_CP = 7.5 Hz, CH₃), 33.49 (d, J_CP = 11.8 Hz, C(CH₃)₃), 41.69 (d, J_CP = 9.7 Hz, C(CH₃)₃), 122.68 (s, CH), 123.14 (s, CH), 127.18 (s, CH), 127.54 (s, CH), 127.80 (s, CH), 128.30 (s, CH), 128.49 (s, CH), 128.68 (s, CH), 128.92 (s, CH), 129.11 (s, CH), 129.18 (s, CH), 129.26 (s, CH), 129.41 (s, CH), 129.54 (s, CH), 130.22 (s, CH), 130.71 (s, CH), 131.68 (s, CH), 131.98 (s, CH), 132.63 (s, CH), 133.18 (s, CH), 133.23 (d, J_CP = 10.1 Hz), 135.45 (s), 135.72 (d, J_CP = 3.2 Hz), 136.02 (s), 136.15 (s), 136.26 (s), 137.14 (s), 137.20 (s), 137.26 (s), 137.37 (s), 137.42 (s), 137.46 (s), 137.57 (s), 137.64 (s), 137.85 (s), 137.93 (d, J_CP = 14.0 Hz), 137.98 (s), 138.05 (s), 138.15 (s), 138.78 (d, J_CP = 5.3 Hz), 138.79 (s), 139.05 (d, J_CP = 1.3 Hz), 129.27 (d, J_CP = 2.1 Hz), 139.55 (s), 139.60 (s), 140.29 (s), 141.05 (d, J_CP = 11.8 Hz), 142.37 (d, J_CP = 3.2 Hz), 143.28 (d, J_CP = 7.5 Hz), 149.03 (s), 174.31 (d, J_CP = 9.6 Hz), 220.03 (d, J_CP = 81.7 Hz). ³¹P NMR (298 K, C₆D₆, 121.5 MHz): 331.8 (J_PP = 260 Hz, P=P), 156.8 (J_PP = 260 Hz, PNP). IR (ATR, cm⁻¹): 2956 (m), 2916 (m), 2854 (w), 2729 (vw), 1608 (s), 1574 (s), 1444 (s), 1398 (s), 1373 (m), 1360 (w), 1259 (s), 1232 (m), 1196 (s), 1165 (vw), 1092 (s), 1070 (sh), 1026 (s), 976 (m), 881 (w), 847 (s), 795 (vs), 764 (w), 750 (m), 675 (w), 640 (vw), 594 (vw), 577 (vw), 567 (ww), 552 (ww). Raman (632 nm, cm⁻¹): 3065 (14), 3042 (26), 3008 (20), 2951 (27), 2915 (75), 2854 (21), 2767 (2), 2724 (6), 2700 (2), 1612 (36), 1578 (39), 1481 (16), 1462 (13), 1437 (20), 1417 (11), 1399 (28), 1379 (26), 1373 (23), 1303 (100), 1282 (27), 1258 (12), 1251 (14), 1227 (29), 1211 (20), 1198 (26), 1188 (20), 1160 (15), 1102 (38), 1096 (34), 1071 (29), 1025 (7), 1005 (16), 995 (31), 985 (5), 946 (9), 926 (5), 922 (5), 881 (3), 848 (5), 834 (5), 819 (3), 808 (1), 797 (3), 789 (4), 771 (7), 742 (29), 682 (10), 655 (5), 605 (3), 595 (16), 580 (71), 552 (51), 539 (12), 526 (53), 515 (24), 489 (17), 432 (29), 418 (61), 399 (21), 387 (10), 375 (7), 357 (22), 335 (23), 314 (3), 281 (9), 270 (12), 263 (11), 234 (32), 210 (13). MS (Cl, pos., isobutane) m/z (%): 132 (40) [CNDmp]+, 330 (52) [TerNH₃]+, 358 (19) [TerNP]+, 459 (69) [TerNCNDmp+H]+, 533 (84) [M–TerNCNDmp]+, 687 (32) [(TerNH)₂P]+, 705 (27), 760 (10) [Ter₂N₂PAs]+, 860 (9) [M–CNDmp]+, 893 (1) [M–PC'Bu]+, 992 (26) [M+H]+.
2.4. Attempted synthesis of Ter$_2$N$_3$PCNDmp (2NP)

To a solution of [P(µ-NTer)$_2$N] (ca. 30% purity, 70% Ter$_2$N$_3$H; 150 mg) in benzene (3 ml), a solution of CNDmp (28 mg, 0.213 mmol) in benzene (2 ml) was added. The initially yellow solution turned red. Various attempts of crystallization failed and the product could not be isolated.

$^{31}$P NMR (298 K, C$_6$D$_6$, 121.5 MHz): 167.3 (s). UV/vis ($\lambda_{max}$, nm): 490.
### 3. Crystallographic Data

#### Table S1. Crystallographic data of 2NAs, 2PAs and 3PAs.

| compound | 2NAs | 2PAs | 2’PAs | 3PAs |
|----------|------|------|-------|------|
| sum formula | C\textsubscript{72}H\textsubscript{74}AsN\textsubscript{4} | C\textsubscript{65}H\textsubscript{71}AsN\textsubscript{3}P | C\textsubscript{60}H\textsubscript{62}AsN\textsubscript{3}P | C\textsubscript{65.25}H\textsubscript{71.25}AsN\textsubscript{3}P\textsubscript{2} |
| formular weight [g mol\textsuperscript{-1}] | 1070.27 | 931.01 | 931.01 | 1034.36 |
| colour | red | green | green | yellow |
| crystal system | triclinic | triclinic | triclinic | monoclinic |
| space group | P-1 | P-1 | P-1 | P\textsubscript{2}\textsubscript{1}/c |
| a [Å] | 10.8398(18) | 10.6316(9) | 10.6707(5) | 24.123(2) |
| b [Å] | 16.340(3) | 12.8458(10) | 12.7933(6) | 12.4043(9) |
| c [Å] | 17.690(3) | 20.4651(17) | 20.5386(9) | 39.140(3) |
| α [°] | 85.439(6) | 85.732(4) | 85.861(3) | 90 |
| β [°] | 75.150(5) | 82.704(5) | 82.563(3) | 106.871(3) |
| γ [°] | 82.111(6) | 66.749(4) | 67.099(2) | 90 |
| V [Å\textsuperscript{3}] | 2996.9(9) | 2546.3(4) | 2560.3(2) | 11207.6(15) |
| Z | 2 | 2 | 2 | 8 |
| \(\rho_{\text{calc.}}\) [g cm\textsuperscript{-3}] | 1.186 | 1.214 | 1.214 | 1.226 |
| \(\mu\) [mm\textsuperscript{-1}] | 0.612 | 0.740 | 0.736 | 0.706 |
| \(\lambda_{\text{MoK}α}\) [Å] | 0.71073 | 0.71073 | 0.71073 | 0.71073 |
| T [K] | 173 | 123 | 123 | 173 |
| measured reflexes | 46291 | 20662 | 25244 | 72808 |
| independent reflexes | 10440 | 14001 | 14381 | 31138 |
| reflexes \(I > 2\sigma(I)\) | 5013 | 10531 | 8482 | 21139 |
| \(R_{\text{int.}}\) | 0.1198 | 0.0549 | 0.0667 | 0.0502 |
| 2\(\Theta_{\text{max.}}\) [°] | 50 | 60 | 60 | 60 |
| \(F(000)\) | 1134 | 982 | 982 | 4374 |
| \(R_1\) (\(R[F^2 > 2\sigma(F^2)]\)) | 0.0596 | 0.0576 | 0.0465 | 0.0511 |
| \(wR_2\) (all data) | 0.1470 | 0.1486 | 0.1013 | 0.1204 |
| Goof | 0.965 | 1.008 | 0.877 | 1.005 |
| parameter | 685 | 613 | 625 | 1286 |
| CCDC # | 1421413 | 1421414 | 1421415 | 1421416 |
**3.1. Numbering scheme of 2NAs**

| Bond/Angle | Length/ Angle [Å/°] |
|------------|-------------------|
| As1–N1     | 1.875(3)          |
| As1–N2     | 1.316(4)          |
| N2–N1–As1  | 119.4(2)          |
| N2–N3–C49  | 123.4(3)          |
| N2–N3–N3   | 119.4(3)          |
| N2–N3–C25  | 123.4(3)          |
| N3–C49     | 1.428(5)          |
| N3–C49–C50 | 116.3(4)          |
| N4–C49     | 1.293(5)          |
| N4–C50     | 1.428(5)          |
| N1–As1–C49 | 82.71(16)         |
| N1–N2–N3–C49 | −1.3(5)    |

Selected bond lengths [Å] and angles [°] of 2.
3.2. Numbering scheme of 2PAs

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

| Bond                  | Length [Å]   | Angle [°]    |
|-----------------------|--------------|--------------|
| AsIB–N1               | 1.8740(19)   | P1B–N1–AsIB  | 120.45(10)   |
| AsIB–C49              | 1.937(2)     | N1–AsIB–C49  | 88.51(8)     |
| P1B–N1                | 1.6356(19)   | N1–P1B–N2    | 97.69(9)     |
| P1B–N2                | 1.6909(19)   |              |              |
### 3.3. Numbering scheme of 2'PAs

![Diagram of 2'PAs]

> Selected bond lengths [Å] and angles [°] of 2'PAs

| Bond/Angle | Distance/Angle |
|------------|---------------|
| As1A–N1    | 1.9696(14)    | N1–C1 | 1.447(2)  |
| As1A–C49   | 2.0105(17)    | N2–C49| 1.393(2)  |
| As1A–P1A   | 2.2920(7)     | N2–C25| 1.441(2)  |
| P1A–N1     | 1.6917(16)    | N3–C49| 1.252(2)  |
| P1A–N2     | 1.8009(15)    | N3–C50| 1.422(2)  |
| N1–As1A–C49| 87.16(7)      | N2–P1A–As1A| 81.94(5) |
| N1–P1A–N2  | 95.12(7)      | P1A–N1–As1A| 77.10(6) |
| N1–P1A–As1A| 56.89(5)      | N1–As1A–P1A| 46.01(5) |
### 3.4. Numbering scheme of 3PAs

![Diagram of 3PAs]

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

| Bond or Angle | Length [Å] (E) | Bond or Angle | Length [Å] (E) |
|---------------|----------------|---------------|----------------|
| As1–N1        | 1.8950(18)     | As1–C58       | 1.996(2)       |
| As1–C49       | 2.007(2)       | N2–C25        | 1.452(3)       |
| P1–N1         | 1.7378(18)     | N3–C49        | 1.270(3)       |
| P1–N2         | 1.756(2)       | P1–P2         | 2.2822(8)      |
| P2–C58        | 1.673(2)       | N2–C49        | 1.392(3)       |
| N3–C50        | 1.415(3)       | N1–As1–C49    | 88.96(8)       |
| C58–P2–P1     | 96.42(8)       | N1–P1–N2      | 93.94(9)       |
| C49–N2–P1     | 117.97(14)     | P1–N1–As1     | 106.81(9)      |
4. Computational Details

Utilizing the experimental structural data, all calculations were carried out with the Gaussian 09 package of molecular orbital programs. 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\[^{12-14}\] analyses were carried out to study the bonding, hybridization and polarization effects.

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 (\(\sigma_{iso}\)) were referenced to the absolute chemical shift the standard (\(^{31}\)P: H\(_3\)PO\(_4\), \(\sigma_{ref} = 374.0604\); \(^1\)H, \(^{13}\)C: SiMe\(_4\), 31.665 and 196.4544 ppm, respectively), 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/~budzelaar/gNMR/gNMR.html.

\emph{It should be emphasized that the computation was carried out for a single, isolated (gas-phase) molecule.}
4.1. Optimized geometries

4.1.1. Ter$_2$N$_3$PCNDmp

P          0.30046800  -0.77023100  -1.68519700
N          0.57308300  0.75125700  -0.89061200
N          0.20281200  0.89971200  0.34856900
N         -0.33739900  -0.23952500  0.77558800
N         -0.73783700  -2.50246300  0.27678600
C          1.19267900  1.85654900  -1.58214300
C          2.45419100  1.64474900  -2.18242300
C          3.05655700  2.70349500  -2.86699800
H          4.03405000  2.53246700  -3.30828500
C          2.43968900  3.93946100  -2.97801500
H          2.92357800  4.75215600  -3.51517000
C          1.18540000  4.11645400  -2.41794000
H          0.66564700  5.06359800  -2.52892400
C          0.52795400  3.08879500  -1.72916100
C          3.22735500  0.36820400  -2.13503500
C          3.25618700  -0.48053800  -3.25759900
C          4.02705800  -1.63914000  -3.20091000
C          4.03591900  -2.30521700  -4.06064100
C          4.78229300  -1.96194400  -2.07440300
C          4.78063800  -1.08267900  -1.00026900
C          5.39061900  -1.30043000  -0.12582200
C          4.02336800  0.08977000  -1.01507100
H          2.47880700  -0.15908400  -4.50408600
H          1.41406500  -0.01831900  -4.28924700
H          2.56802400  -0.96644700  -5.23500600
H          2.83390100  0.76397100  -4.97511300
C          5.56722200  -3.24954700  -2.02392500
H          6.00814200  -3.48804700  -2.99654200
H          4.92268500  -4.09169300  -1.74550400
H          6.37430300  -3.19597900  -1.28799100
C          4.08772000  1.05092000  0.13448900
H          4.27331700  2.07228600  -0.21427300
H          4.88592600  0.77378900  0.82410900
H          3.15498900  1.07058500  0.70793200
C         -0.86356800  3.43152200  -1.30451000
C         -1.94875300  3.05766600  -2.12040100
C         -3.20570900  3.60198700  -1.85904600
H         -4.03872900  3.32155400  -2.50077100
C         -3.42003100  4.50635700  -0.81933100
H         -2.33327400  4.85440300  -0.02068300
C         -2.47573700  5.55770600  0.79756900
H         -1.05607200  4.34103100  -0.25043600
C         -1.76501500  2.13464700  -3.29248400
H         -0.97752600  2.49462700  -3.96351800
H         -2.68967800  2.04997000  -3.86663300
H         -1.47744400  1.12705200  -2.97161400
C         -4.79062900  5.06032500  -0.54912400
H         -4.73888700  6.02919500  -0.04729000
H         -5.36856400  4.38756600  0.09696500
H         -5.36000600  5.18771900  -1.47446500
C          0.99661500  4.80954900  0.59460700
H          0.65681100  5.60965100  0.09592100
H          0.80406800  4.00196600  0.79710000
H         -0.25878500  5.20461700  1.55009700
C         -0.78136800  -0.33740600  2.14206700
C          0.12069300  -0.11108000  3.19849700
C         -0.33884400  -0.25723000  4.51376000
H          0.36707100  -0.08000500  5.32006300
C         -1.64214800  -0.63032300  4.79356300
H         -1.97502900  -0.74279700  5.82114100
C         -2.51727800  -0.84845400  3.74175200
H         -3.55162900  -1.11524300  3.93596100
C         -2.11819800  -0.70590900  2.41002800
C          1.56457300  0.26691700  3.10737700
C          1.93683200  1.60001400  3.35966800
4.1.2. Ter2N₃AsCNdmp

0 1
As -1.06624800  1.24586400  -0.95845900
N  -0.84880100  -0.59435500  -0.65316900
N  0.01969700  -0.97924400  0.23096400
N  0.62170600  0.06748800  0.78267100
N  0.79404800  2.40138700  0.92316000
C  1.54216000  -1.59832700  -1.40129600
C  -2.88600000  -1.35413300  -1.77063800
4.1.3. Ter$_2$N$_3$SbCNDmp

Sb  -0.8335500  1.17602000  -1.49681100
N   -0.82682700 -0.74018000  -0.59494400
N   -0.10742300 -0.93272300  0.46382500
N   0.55576900  0.14954900  0.86266700
N   1.13226900  2.39647500  0.54066400
C   -1.54961200 -1.87728700  -1.09362600
C   -2.89097800 -1.67912100  -1.50367600
C   -3.66533800 -2.77917700 -1.87623300
H   -4.69895500 -2.60131800  -2.15887100
C   -3.13631100 -4.05996700  -1.90274400
H   -3.74886400 -4.90922600 -2.19023000
C   -1.79160600 -4.22458200 -1.62069500
C   -1.33200000 -5.20205300 -1.73068500
C   -0.96431800 -3.15820100 -1.23778500
C   -3.55840100 -0.35131500 -1.65776200
C   -3.67655000  0.19715000  -2.95128600
C   -4.35006800  1.40885300  -3.10815500
H   -4.42347200  1.84262300  -4.10333100
C   -4.93111400  2.07942600  -2.02980300
C   -4.85231500  1.47976400  -0.76996100
H   -5.32559900  1.96718500  0.08005100
4.1.4. Ter$_2$N$_3$PAsCNDmp

```
  As  -0.71111400  0.90506400  -1.40253100
  N   -0.90804400  -0.85617100  -0.77096900
  P   -0.18120200  -1.29626200  -0.85617100  -0.77096900
  N   0.55985400  0.19196200  0.95450200
  N   1.05129900  2.38513300  0.29480400
  N  -1.60394400  -1.82772700  -1.55969500
  N  -2.87103900  -1.50570900  -1.59177600
  N  -3.55383100  -2.45960400  -2.85139100
  N  -4.07325200  -2.19739500  -3.24173300
  N  -3.00759700  -3.71098800  -3.09639300
  N  -3.55088000  -4.44319400  -3.68934300
  N  -1.74881300  -4.00518200  -2.59989400
  N  -1.28495000  -4.96313200  -2.81685000
  N  -1.02154100  -3.08272100  -1.83779600
  N  -3.52063900  -0.18178700  -1.88526400
  N  -3.51205100  -0.78055100  -2.91163600
  N  -4.07995400  -2.02828200  -2.66199200
  N  -4.04485500  -2.78567200  -3.44223400
  N  -4.67063400  -2.33877400  -1.43780600
  N  -4.71259300  1.34904000  -0.45702700
  H  -5.19509000  1.56135800  0.49513500
  H  -4.14789400  0.09158100  -0.65974100
  H  -2.82079000  0.52167900  -4.22186500
  H  -1.73768200  0.44046000  -4.06426200
  H  -2.99649700  1.34142400  -4.92273200
  H  -3.15177000  -0.40920500  -4.69091600
  C  -5.28758600  3.68832700  -1.20105500
  H  -6.33391800  3.70773900  -1.52918400
  H  -4.75795400  4.47003900  -1.75276200
  H  -5.27307900  3.95327700  -0.14011900
  C  -4.25108600  -0.96634900  0.40184900
  H  -4.60050400  -1.91457200  -0.01934600
  H  -4.94707200  -0.66099900  1.18581000
```
4.1.5. Ter$_2$N$_3$PSbCNdmp

0 1

Sb 0.86514700 -1.32233600 -1.25685900
N 1.07247500 0.70866000 -0.66807700
P 0.14209400 1.30391200 0.55958600
N -0.77988200 0.06647000 0.93820900
N -1.39672400 2.29259200 0.55901600
C 1.95488000 1.62960100 1.31895000
C 3.28383900 1.24137700 1.61760600
C 4.16179400 2.16983100 2.18214300
H 5.18032700 1.84834500 2.38135600
C 3.76080800 3.46142100 2.48654600
C 4.45723100 4.17046700 2.92392300
C 2.44232600 3.81713300 2.25536500
C 2.08520800 4.80293700 2.53995300
C 1.52127200 2.92699800 1.68909000
C 3.83319500 1.30643000 4.11985000
C 4.01507900 0.96766700 2.53082000
C 4.57963900 2.22911700 2.34273700
C 4.69979200 2.88365600 3.20367700
C 4.99043100 2.67332400 1.08686500
C 4.84619100 1.80706200 0.00360700
C 5.18582400 2.12372900 0.98065800
C 4.27556100 0.54067600 -0.14332300
C 3.60375000 -0.53739700 -3.93952000
C 2.59265200 -0.11782600 -3.92499700
C 3.62387200 -1.38598900 -4.60241300
C 4.27177700 0.23436000 -4.31245800
C 5.55839900 -0.05216700 -0.90178900
C 6.29865700 -0.07566000 -0.09657800
C 6.03636700 -4.41538300 -1.81605200
C 4.76789200 -4.76525000 -0.64001500
C 4.14426900 0.36317400 1.04401900
C 4.55286000 1.35754500 0.83481700
C 4.66580700 -0.04997400 1.91048000
C 3.09565700 0.49722500 1.32865100
C 0.11712600 3.44625600 -1.64181900
C -0.79429900 3.05132300 -2.64218400
C -2.01413700 3.71959300 -2.74811300
C -2.70607200 3.42071100 -3.53319900
C -2.36051200 4.76824500 -1.89708300
C -1.45190600 5.13213600 -0.90422600
C -1.70712100 5.94578300 -0.22577200
C -0.21646900 4.49876200 -0.76641700
C -0.45264800 1.96046700 -3.61756200
C 0.49230400 2.16986000 -4.13139200
C -1.23532700 1.85379000 -4.37290800
H -0.33675100 0.99280600 -3.11548900
4.1.6. Ter$_2$N$_2$As$_3$CNDmp

0 1
As -0.03792700 1.70783800 -0.69986000
N -1.22941800 0.26868400 -0.78270100
As -0.88809700 -1.22560100 0.14704000
N 0.70159300 -0.56161000 0.78080500
C 2.25214800 1.20554100 0.84310600
C -2.38357800 0.32606900 -1.61431900
C -3.12521200 1.52411200 -1.73122300
C -4.26100300 1.54683600 -2.54279900
H -4.82427000 2.47378000 -2.60465200
C -4.66980700 0.42666100 -3.25217800
H -5.55337500 0.46418600 -3.88208700
C -3.92363900 -0.73866900 -3.15514600
H -4.20464600 -1.62050500 -3.72401800
C -2.78576500 -0.81187500 -2.34716400
C -2.74453800 2.77047000 -1.01168000
C -2.12312300 3.82616700 -1.70429400
C -1.69998100 4.93989800 -0.98356400
H -1.18212900 5.73915000 -1.50959400
C -1.87543500 5.03526800 0.39701000
C -2.54062600 4.00006500 1.05133800
H -2.70780600 4.06784100 2.12448600
C -2.97583600 2.86561500 0.36988300
C -1.76014100 3.69954100 -3.15702800
H -0.93853220 2.97659300 -3.25288700
C -1.41488700 4.65501000 -3.55943500
H -2.58764600 3.34055100 -3.77409500
C -1.32920600 6.21174700 1.15449300
H -1.54965400 7.15542200 0.64557300
C -0.23887700 6.13497600 1.24021300
H -1.74081200 6.26554100 2.16595000
C -3.66437900 1.75000700 1.10012700
H -4.63930000 1.52113800 0.65618600
H -3.81793400 2.00569500 2.15062700
H -3.06945200 0.83099100 1.06089800
C -2.02413600 -2.09531000 -2.37280700
C -0.81940400 -2.16427000 -3.10243100
C -0.19846500 -3.40107400 -3.25548000
H 0.71749500 -3.45764500 -3.84017000
C -0.70846300 -4.56173900 -2.67161600
C -1.87288400 -4.45951300 -1.91251100
H -2.27436500 -5.34898200 -1.43119400
C -2.54310700 -3.24718900 -1.75240100
C -0.21205500 -0.92800800 -3.70045300
H -0.89267000 -0.44743100 -4.41184200
H 0.72147100 -1.16044500 -4.21817500
H 0.00508400 -0.19139400 -2.91755200
C 0.00045600 -5.87719000 -2.82856600
H -0.67841000 -6.71955500 -2.67045100
H 0.81699400 -5.97325400 -2.10277400
H 0.44012100 -5.97689600 -3.82540500
C -3.74993100 -3.16782200 -0.85802100
H -4.60493400 -2.69263400 -1.34605700
H -3.51387700 -2.56858700 0.03234800
H -4.05348000 -4.16194700 -0.52039700
C 1.37192500 -1.32529500 1.78757700
C 0.62212800 -1.75393100 2.90481500
C 1.26561000 -2.42821100 3.94697200
H 0.67459300 -2.73156600 4.80649100
C 2.62236100 -2.70445200 3.89195000

S22
4.1.7. Ter$_2$N$_3$PAsCNDmpPCBu

0 1
As 0.77823100 0.67177600 1.27553800
P -1.33578200 0.17963200 -0.68141400
P -2.33391400 0.11104300 1.37243600
4.1.8. Ter$_2$N$_3$PAsCNDmpPC'Bu – isomeric species

\[
\begin{align*}
0 & \quad 1 \\
As & \quad -1.73881100 \quad 0.46559200 \quad -0.08619200
\end{align*}
\]
4.19. CNDmp

C
-2.32292600  -0.00252700   0.00001900
|Element| X       | Y       | Z       |
|--------|---------|---------|---------|
|C       | -1.62926700 | -1.20780400 | -0.00000600 |
|C       | -0.23593300  | -1.23341300  | -0.00002000 |
|C       | 0.43456100   | 0.00047400   | 0.00002800 |
|C       | -0.23866400  | 1.32290300   | -0.00008000 |
|C       | -1.63188700  | 1.20424800   | 0.00002000 |
|H       | -3.40886300  | -0.00371500  | 0.00003800 |
|H       | -2.17253000  | -2.14864600  | -0.00001800 |
|H       | -2.17719800  | 2.14390500   | 0.00003400 |
|C       | 0.52935700   | 2.51985000   | -0.00001000 |
|H       | -0.14747700  | 3.37687200   | -0.00018200 |
|H       | 1.17939300   | 2.59380500   | 0.87834300 |
|H       | 1.17966000   | 2.59365200   | -0.87817700 |
|C       | 0.53490400   | -2.51864000  | -0.00001000 |
|H       | 1.18560700   | -2.59086200  | -0.87799700 |
|H       | 1.18487300   | -2.59124600  | 0.87851900 |
|N       | -0.13998600  | -3.37719400  | -0.00044500 |
|C       | 1.81517600   | 0.00195500   | -0.00004200 |
|C       | 2.99496300   | 0.00319900   | 0.00006300 |
### 4.2. Analysis of Cyclopentane-1,3-diyl derivatives

**Table S2. Computational data for the cyclopentanediyls 2.**

| synthesis? | NP | NAs | NSb | PAs | PSb | AsAs |
|------------|----|-----|-----|-----|-----|------|
| E\text{ex}(1) [a.u.] | -2362.3807537 | -4254.64879047 | -2026.60465092 | -4541.22621168 | -2313.17811000 | -6433.48904378 |
| E\text{ex}(2, s) [a.u.] | -2765.06124362 | -4657.31655534 | -2429.24994777 | -4943.88643318 | -2715.82179945 | -6836.14788714 |
| E\text{ex}(2, t) [a.u.] | -2765.00454611 | -4657.26602338 | -2429.20469891 | -4943.85769934 | -2715.79410710 | -6836.13099469 |
| \(\Delta E_{\text{res}}\) [kJ mol\(^{-1}\)] \(^a\) | -148.0 | -114.6 | -55.6 | -94.8 | -51.4 | 91.2 |
| S–T gap [kJ mol\(^{-1}\)] \(^a\) | -148.9 | -132.7 | -118.8 | -75.4 | -72.7 | -44.4 |
| \(\beta\) (6,6) \(^b\) | 13% | 11% | 4% | 24% | 7% | 38% |
| \(c_1\) | 0.946 | 0.956 | 0.961 | 0.916 | 0.982 | 0.889 |
| \(c_2\) | -0.250 | -0.229 | -0.132 | -0.339 | -0.185 | -0.433 |
| e \(p_z\) (N1) | 1.29633 | 1.34073 | 1.45787 | 1.2979 | 1.44315 | 1.22819 |
| e \(p_z\) (N2) | 1.48432 | 1.45477 | 1.43699 | 1.58679 | 1.56992 | 1.56856 |
| e \(p_z\) (C) | 1.54945 | 1.54784 | 1.55258 | 1.63894 | 1.63915 | 1.63620 |
| e \(p_z\) (C\exo) | 1.38723 | 1.37707 | 1.35582 | 1.37496 | 1.35444 | 1.38402 |
| \(\pi\) e cpd-ring (NBO) | 6.51 | 6.51 | 6.55 | 6.49 | 6.53 | 6.50 |
| \(\lambda_{\text{max}}\) calc. E–E BO (WBI) | 0.3129 | 0.2875 | 0.2615 | 0.3889 | 0.3432 | 0.4337 |
| HOMO | -0.017495 | -0.17161 | -0.16343 | -0.15961 | -0.15204 | -0.15380 |
| LUMO | -0.05435 | -0.05990 | -0.05810 | -0.07163 | -0.07009 | -0.07582 |
| NICS(0) [ppm] | -8.32 | -7.45 | -6.40 | -5.62 | -4.84 | -4.66 |
| NICS(1) [ppm] | -6.65 | -6.10 | -5.51 | -3.24 | -3.18 | -2.90 |

\(^a\) E(CNDmp): -402.624107815 a.u.; \(^b\); \(^c\).
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LUMO

HOMO
Table S3. Computed energies and energy differences for the formation of the
cyclopentanediyls 2 (red: accessible, grey: no formation observed, green: E2 lighter than E1,
formation not observed, blue: not attempted in lieu of suitable precursors).

|      | E2 = | E1 = | ΔE 4ring-int | ΔE int-5ring | ΔE 4ring-5ring |
|------|------|------|--------------|--------------|---------------|
|      | P    | As   | Sb           |              |               |
| E2 = |      |      |              |              |               |
| E1 = |      |      |              |              |               |
| 4ring| -2362.38075537 | -4254.64879047 | -2026.60465092 |              |               |
|      | -2764.97362419 | -4657.24897956 | -2429.18047044 |              |               |
| intermediate | -2765.06124362 | -4657.31655534 | -2429.24994477 |              |               |
| 5ring |      |      |              |              |               |
|     | ΔE 4ring-int | 82.0 | 62.8 | 126.8 |              |
|     | ΔE int-5ring | -230.0 | -177.4 | -182.4 |              |
|     | ΔE 4ring-5ring | -148.0 | -114.6 | -55.6 |              |

|      | E2 = | E1 = | ΔE 4ring-int | ΔE int-5ring | ΔE 4ring-5ring |
|------|------|------|--------------|--------------|---------------|
|      | N    | P    | As           |              |               |
| E2 = |      |      |              |              |               |
| E1 = |      |      |              |              |               |
| 4ring| -2362.38075537 | -2648.95984829 | -4541.22621168 |              | -2313.17811000 |
|      | -2764.97362419 | -3051.60297046 | -4943.87650537 |              | -2715.81322120 |
|      | -2765.09987684 | -3051.62831340 | -4943.88825952 |              | -2715.81589049 |
| intermediate |      |      |              |              |               |
| 5ring | ΔE 4ring-int | 82.0 | -49.9 | -68.8 | -28.9 |
|     | ΔE int-5ring | -331.5 | -66.5 | -30.9 | -7.0 |
|     | ΔE 4ring-5ring | -249.5 | -116.5 | -99.6 | -35.9 |

|      | E2 = | E1 = | ΔE 4ring-int | ΔE int-5ring | ΔE 4ring-5ring |
|------|------|------|--------------|--------------|---------------|
|      | N    | P    | As           |              |               |
| E2 = |      |      |              |              |               |
| E1 = |      |      |              |              |               |
| 4ring| -4254.64879047 | -4541.22621168 | -6434.48904378 | -4205.05946650 |              |
|      | -4657.24897956 | -4943.87650537 | -6836.14264078 | -4607.70112786 |              |
|      | -4657.36155483 | -4943.88643325 | -6836.14788719 | -4607.70330624 |              |
| intermediate |      |      |              |              |               |
| 5ring | ΔE 4ring-int | 62.8 | -68.8 | -77.4 | -46.1 |
|     | ΔE int-5ring | -295.6 | -26.1 | -13.8 | -5.7 |
|     | ΔE 4ring-5ring | -232.8 | -94.8 | -91.2 | -51.8 |

|      | E2 = | E1 = | ΔE 4ring-int | ΔE int-5ring | ΔE 4ring-5ring |
|------|------|------|--------------|--------------|---------------|
|      | N    | P    | As           |              |               |
| E2 = |      |      |              |              |               |
| E1 = |      |      |              |              |               |
| 4ring| -2026.60465092 | -2313.17811000 | -4205.05946650 |              |              |
|      | -2429.18047044 | -2715.81322120 | -4607.70112786 |              |              |
|      | -2429.29010829 | -2715.82179943 | -4607.70445746 |              |              |
| intermediate |      |      |              |              |               |
| 5ring | ΔE 4ring-int | 126.8 | -28.9 | -46.1 |              |
|     | ΔE int-5ring | -287.9 | -22.5 | -8.7 |              |
|     | ΔE 4ring-5ring | -161.1 | -51.4 | -54.8 |              |
5. References

[1] T. Beweries, R. Kuzora, U. Rosenthal, A. Schulz, A. Villinger, Angew. Chem. Int. Ed. 2011, 50, 8974–8978.
[2] S. Demeshko, C. Godemann, R. Kuzora, A. Schulz, A. Villinger, Angew. Chem. Int. Ed. 2013, 52, 2105–2108.
[3] A. Hinz, A. Schulz, A. Villinger, J.-M. Wolter, J. Am. Chem. Soc. 2015, 137, 3975–3980.
[4] A. Hinz, J. Rothe, A. Schulz, A. Villinger, Dalton Trans. 2015, 2, 10.1039/C5DT02711J.
[5] W. P. Weber, G. W. Gokel, Tetrahedron Lett. 1972, 13, 1637–1640.
[6] 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.
[7] G. M. Sheldrick, 2013, SHELXS–2013.
[8] G. M. Sheldrick, 2013, SHELXL–2013.
[9] G. M. Sheldrick, 2004, SADAB 2.
[10] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, Gaussian 09, Gaussian, Inc., Wallingford CT, 2009.
[11] T. Lu, F. Chen, J. Comput. Chem. 2012, 33, 580–592.
[12] E. D. Glendening, C. R. Landis, F. Weinhold, J. Comput. Chem. 2013, 34, 1429–1437.
[13] E. D. Glendening, F. Weinhold, J. Comput. Chem. 1998, 19, 593–609.
[14] E. D. Glendening, F. Weinhold, J. Comput. Chem. 1998, 19, 610–627.