Cyano(triphenylsilyl)phosphanide as a Building Block for P,C,N Conjugated Molecules
Grégoire Le Corre, Juan José Gamboa-Carballo, Zhongshu Li, and Hansjörg Grützmacher*

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Experimental Procedures

General remarks

All experiments were performed under Ar atmosphere using standard Schlenk and vacuum-line techniques or in an MBraun glove box. Glassware was flame dried on a Schlenk line prior to use. Solvents were purified using an Innovative Technologies Pure-Solve solvent purification system and stored over 4 Å molecular sieves under Ar except for 1,2-difluorobenzene (DFB, 99%, Fluorochem), which was distilled over calcium hydride and stored under 4 Å molecular sieves. Deuterated solvents were purchased from Eurisotop, degassed and distilled from the proper drying agent, and stored over 4 Å molecular sieves under Ar. The argon was provided by PANGAS and further purified with an MBraun >99 HP gas purification system. Air-sensitive compounds were handled in a glovebox (MBraun lab master 130 or 150B-G). Small scale reactions were performed inside a glovebox.

Triphenyltin chloride (> 96.7 %) was purchased from Tokyo Chemical Industry. Chlorotriphenylsilane (95 %) was purchased from Acros Organics. Chlorotriphenylgermane (99 %), 1,3-di-p-tolylcarbodiimide (96 %), mesityl isocyanate (98 %) and sodium bis(trimethylsilyl)amide (95%) were purchased from Sigma Aldrich. Triphenylboron (97.8 %) was purchased from Alfa Aesar. Na[OCP](dioxane)2 and Ph3EPCO (E = Ge, Sn) were prepared via literature procedures.

NMR measurements were carried out on Bruker Avance 300, 400, 500 MHz and 500 MHz Cryoprobe spectrometers at 298 K (unless indicated otherwise). Chemical shifts δ are given as dimensionless numbers and the absolute values of the coupling constants are given in Hertz (Hz), the first atom mentioned in the subscript always refers to the atom that was used to observe the coupling. Multiplicities are abbreviated as singlet (s), doublet (d), triplet (t), quartet (q), virtual triplet (vt), virtual doublet of doublets (vdd), and broad (br). NMR spectra were referenced to TMS (1H, 13C, and 29Si), H3PO4 (31P), Me4Sn (119Sn), and BF3 etherate (11B).

IR measurements were carried out on a Bruker ATR device under inert atmosphere. Signals are reported as follows: weak (w), medium (m), strong (s), broad (br).

X-ray single crystals suitable for X-ray diffraction were coated with perfluoroalkylether oil in a glovebox, transferred to a nylon loop, and then transferred to the goniometer of an Oxford XCalibur diffractometer or Bruker D8-Venture diffractometer equipped with a copper X-ray tube (λ = 1.5406 Å) or a molybdenum tube (λ = 0.7107 Å). Preliminary data was collected to determine the crystal system. The space group was identified, and the data was processed using the Bruker SAINT+ or Crystals program and corrected for absorption using SADABS or the SCALE3 ABSPACK on CrysAlis absorption correction. The structures were solved using direct methods (XT) on OLEX2 completed by Fourier transformation and refined by full-matrix least-squares procedures (XL).

Powder diffraction patterns were collected at room temperature on a Stoe STADI P powder X-ray diffractometer (Cu Ka1 radiation, λ = 1.540598 Å, focusing germanium monochromator) equipped with a Dectris Mythen 1 K silicon strip detector.

TGA/DSC measurements were performed on NETZSCH STA449F5 instrument connected to a EI-MS (AEOLOS III). About 5 mg of the samples was heated from 40°C to 600°C at a rate of 10 K min⁻¹ under argon flow. The line that transfers evolved gases from TGA to MS was maintained at 230°C. The TGA data obtained during the measurement was analyzed using Netzsch Proteus – Thermal Analysis Software.

Elemental analysis was performed by the ETH Zurich Microelemental Analysis service on a LECO TruSpec Micro apparatus.
Synthesis and Characterization

Preparation of Na(18-crown-6)[1] from Na[OCP](dioxane)$_{2.14}$:

A dry and argon-flushed Schlenk flask equipped with a magnetic stirrer was charged with Na[OCP](dioxane)$_{2.14}$ (18.2 g, 67.3 mmol) suspended in toluene/DME 1:1 (60 mL) and cooled to -20°C. Chlorotriphenylsilane (22.8 g, 77.3 mmol, 1.15 equivalents) and sodium hexamethyldisilazide (14.2 g, 77.3 mmol, 1.15 equivalents) dissolved together in toluene/DME 10:1 (330 mL) were added over 30 minutes dropwise via cannula. The mixture was allowed to warm up to room temperature overnight and stirred for two more days after which the solvent was evaporated. The residue was extracted with tetrahydrofuran (THF, 300 mL) and the suspension was filtered over celite. The solid was washed with THF (2 x 150 mL). The filtrate was evaporated and 18-crown-6 (17.8 g, 67.3 mmol, 1 equivalent) dissolved in DFB (140 mL) was added to the residue, resulting in precipitation of a colorless solid with a red supernatant after a few minutes of stirring. The supernatant was removed by decantation and the solid was washed with toluene (2 x 150 mL) and diethyl ether (100 mL). Drying in vacuo afforded Na(18-crown-6)[1] as a pale beige powder (29.9 g, 49.5 mmol, 64 % yield). Colorless crystals suitable for X-Ray Diffraction were obtained by layering a concentrated solution of Na(18-crown-6)[1] in DFB with n-hexane.

Notes on the synthesis: Full conversion of Na(OCP) into Ph$_3$SiPCO is difficult to achieve even when triphenylsilyl trifluoromethanesulfonate is used as a reagent[2], and the silyl phosphaketene is not stable for extended periods in solution, which is why NaN(SiMe$_3)_2$ was added in combination with Ph$_3$SiCl to intercept the transient silyl phosphaketene immediately after its formation. The slight excess of chlorosilane and hexamethyldisilazide ensures that all the 2-phosphaethynolate will be entirely consumed in the reaction even if some formation of Ph$_3$SiN(SiMe$_3)_2$ occurs. Note that the tris(silyl)amine side-product which is soluble in apolar solvents is much easier to separate from Na(18-crown-6)[1] than residual Na(OCP), therefore we aimed at the full conversion of Na(OCP) in this reaction for easier purification of the product. Completion of the reaction can be monitored by $^{31}$P-NMR of aliquots. The reaction was considered complete once no 2-phosphaethynolate and no heteroallene 4 were detected in solution. We were unable to determine with certainty what 4 is converting into in this synthesis, but we infer that it could react with NaN(SiMe$_3)_2$ to generate Ph$_3$SiN(SiMe$_3)_2$ and Na[1] or it may simply convert into insoluble oligomers that could not be detected by $^{31}$P-NMR.

Figure S1: Structure of Na(18-crown-6)[1] in the crystal (hydrogens omitted for clarity). Selected bond distances [Å] and angles [°]: P1-Si1 2.2059(4); P1-C1 1.7619(12); C1-N1 1.1607(15); Na1-N1 2.4370(11); C1-P1-Si1 95.50(4); N1-C1-P1 174.49(10).

Melting point: 171°C (decomp.)
**Generation of [2] from Na[OCP](dioxane)_{0.61}**

A dry and argon-flushed Schlenk flask equipped with a magnetic stirrer was charged with Na[OCP](dioxane)_{0.61} (134 mg, 1 mmol, 1 equivalent), sodium hexamethyldisilazide (183 mg, 1 mmol, 1 equivalent), and THF (5 mL). The solution was cooled at 0 °C. Under vigorous stirring, chlorotriphenylgermane (339 mg, 1 mmol, 1 equivalent) dissolved in THF (5 mL) was added dropwise over 5 minutes. The resulting suspension was analyzed via $^{31}$P-NMR of an aliquot which showed a single resonance at -278 ppm after 16 hours. Filtration afforded a solution from which a dark solid rapidly precipitated. Crystals of Na(18-crown-6)[2] suitable for X-Ray Diffraction were obtained from layering a solution of Na(18-crown-6)N(SiMe$_3$)$_2$ in toluene with an equimolar amount of Ph$_3$GePCO dissolved in toluene at -25 °C. Powder X-Ray diffraction was performed on the precipitate obtained from the same mixture left to decompose at room temperature for 48 hours. The diffraction pattern could not be matched to any known compound.

**Note on the crystal structure of Na(18-crown-6)[2]:** A slight difference in the configuration of the 18-crown-6 around sodium was observed in the crystal of Na(18-crown-6)[2] which was measured compared to Na(18-crown-6)[1] and Na(18-crown-6)[3]. This is due to the absence of coordination of the sodium to one oxygen atom of a neighboring ion pair.

$^{31}$P{$^{1}$H}-NMR (121.5 MHz, THF, ppm): -278 (s, [2])
**Figure S2:** Structure of Na(18-crown-6)[2] in the crystal (hydrogens omitted for clarity, ellipsoids at 50 % probability). Selected bond distances [Å] and angles [°]: P1-Ge1 2.2784(5); P1-C1 1.763(2); C1-N1 1.160(3); Na1-N1 2.388(2); C1-P1-Ge1 92.29(6); N1-C1-P1 176.87(18)

**Crystallization of Na(18-crown-6)[3]**

Crystals of Na(18-crown-6)[3] suitable for X-Ray Diffraction were obtained from layering a solution of Na(18-crown-6)N(SiMe₃)₂ in toluene with an equimolar amount of Ph₃SnPCO dissolved in toluene at -25 °C. Powder X-Ray diffraction was performed on the precipitate obtained from the same mixture left to decompose at room temperature for 48 hours, revealing the presence of microcrystalline NaCN.

**Figure S3:** Structure of Na(18-crown-6)[3] in the crystal (hydrogens omitted for clarity, ellipsoids at 50 % probability). Selected bond distances [Å] and angles [°]: Sn1-P1 2.4428(6); N1-C1 1.165(3); P1-C1 1.758(2); Na1-N1 2.423(2); C1-P1-Sn1 93.15(8); N1-C1-P1 175.3(2)
SUPPORTING INFORMATION

Reaction of Na(18-crown-6)[1] with chlorotriphenylsilane and generation of 4

A vial was charged with Na(18-crown-6)[1] (30.2 mg, 0.05 mmol, 1 equivalent). Chlorotriphenylsilane (14.7 mg, 0.05 mmol, 1 equivalent) dissolved in toluene, THF-d₆, DFB/C₆D₆ 9:1 or pure C₆D₆ (0.5 mL) was added and the tube was shaken vigorously. A colorless precipitate was formed. The product generated in C₆D₆, THF-d₆, and DFB/C₆D₆ 9:1 was characterized by ³¹P{¹H}-NMR and ²⁹Si{¹H}-NMR on a 500MHz spectrometer at various temperatures. Filtration and layering of a toluene solution with n-hexane (1 mL) at -25 °C afforded colorless crystals of 4-(18-crown-6) suitable for single-crystal XRD. Decantation and washing of the crystals with 1 mL hexane followed by drying afforded 4-(18-crown-6), 0.73 (ratio determined by NMR) as a yellowish powder (16.1 mg, 0.021 mmol, 42 % yield).

NMR Data for 4:

³¹P{¹H}-NMR (202.5 MHz, C₆D₆, ppm): -300 (s, ¹JP,PSi = 47 Hz)
²⁹Si{¹H}-NMR (99.4 MHz, C₆D₆, ppm): 1 (d, ¹JP,PSi = 48 Hz, PSi), -23 (s, NSi),
¹³C{¹H}-NMR (125.8 MHz, C₆D₆, ppm): 170.3 (d, ¹JP,PCN = 89.4 Hz, PCN), 136.5 (d, ²JP,PC = 10.1 Hz, PSiPh ipso), 136.2 (d, ³JP,PC = 2.3 Hz, PSiPh ortho), 135.6 (NSiPh ortho), 131.2 (s, NSiPh ipso), 131.0 (s, Ph para), 129.7 (s, Ph para), 128.5 (s, Ph meta), 128.3 (s, Ph meta)
¹H-NMR (500.1 MHz, C₆D₆, ppm): 7.77-7.71 (m, 6 H, PSiPh ortho), 7.32-7.27 (m, 6H, NSiPh ortho), 7.16-7.07 (m, 6 H, Ph para) 7.07-6.97 (m, 12 H, Ph meta)

Elemental Analysis for 4-(18-crown-6), 0.73 (ratio determined by NMR) (%):
Calc. C: 71.49 H 6.23 N 1.82
Found C: 71.17 H 5.78 N 2.18

Reaction of Na(18-crown-6)[1] with chlorotriphenylgermane and generation of 5

A vial was charged with Na(18-crown-6)[1] (30.2 mg, 0.05 mmol, 1 equivalent). Chlorotriphenylgermane (16.9 mg, 0.05 mmol, 1 equivalent) dissolved in THF-d₆, DFB/C₆D₆ 9:1 or pure C₆D₆ (0.5 mL) was added and the tube was shaken vigorously. A colorless precipitate was formed. The product generated in C₆D₆, THF-d₆, and DFB/C₆D₆ 9:1 was characterized by ³¹P{¹H}-NMR and ²⁹Si{¹H}-NMR on a 500MHz spectrometer at various temperatures. No crystals suitable for X-Ray diffraction could be grown from solutions of 5.

³¹P{¹H}-NMR (202.5 MHz, C₆D₆, ppm): -195 (s, [P(CN)₃]), -292 (s, 5), -295 (s, 5’’’)
²⁹Si{¹H}-NMR (99.4 MHz, C₆D₆, ppm): -23 (s, 5)
¹³C{¹H}-NMR (125.8 MHz, C₆D₆, ppm): 171.7 (d, ¹JP,PC = 89.4 Hz, PCN 5)

Reaction of Na(18-crown-6)[1] with triphenyltin chloride and generation of 6

A dry and argon-flushed NMR tube was charged with Na(18-crown-6)[1] (30.2 mg, 0.05 mmol, 1 equivalent). Triphenyltin chloride (19.3 mg) dissolved in THF (0.5 mL) was added and the tube was shaken vigorously. A colorless precipitate was formed. The product was characterized by its ¹¹⁹Sn{¹H}-NMR signal on a 300 MHz spectrometer. Attempts at isolating this product by filtration and layering with n-hexane were unsuccessful as a brown insoluble material precipitated at every attempt. Product 6 was also formed using THF/toluene 1:1 as solvent but also decomposed after filtration, reduction of the filtrate to half the volume, and layering with n-hexane.

¹¹⁹Sn{¹H}-NMR (186.5 MHz, C₆D₆, ppm): -42 (d, ¹JP,¹¹⁹Sn = 830 Hz)
³¹P{¹H}-NMR (202.5 MHz, C₆D₆, ppm): -328 (s, ¹JP,¹¹⁹Sn = 794 Hz and ¹JP,¹¹⁹Sn = 830 Hz)
Reaction of Na(18-crown-6)[1] with triphenylborane and generation of Na(18-crown-6)(DFB)[7]

In a glovebox, an 18 mL vial equipped with a magnetic stirrer was charged with Na(18-crown-6)[1] (60.4 mg, 0.1 mmol, 1 equivalent) and DFB (0.5 mL). Triphenylborane (24.2 mg, 0.1 mmol, 1 equivalent) dissolved in DFB (1 mL) was added dropwise while stirring vigorously. After 5 minutes the colorless solution was layered with n-hexane (4.5 mL) and light orange crystals suitable for X-Ray diffraction identified as adduct Na(18-crown-6)(DFB)[7] were formed overnight. The crystals were washed with n-hexane (2 mL), dried in vacuo and 15 mg of the resulting light orange solid was redissolved in THF-d8 for characterization on a 500MHz spectrometer. The 31P-NMR spectrum reveals the presence of Na(18-crown-6)(DFB)[7] (-300 ppm) as the major product along with a resonance which we believe corresponds to [1] (-283 ppm, broad) in equilibrium with Na(18-crown-6)(DFB)[7]. NMR data is only reported for Na(18-crown-6)(DFB)[7] for

**Preparation of Na(18-crown-6)[8]**

In a glovebox, an 18 mL vial equipped with a magnetic stirrer was charged with Na(18-crown-6)[1] (120.7 mg, 0.2 mmol, 1 equivalent) and DFB (1.5 mL). Mesityl isocyanate (32.2 mg, 0.2 mmol, 1 equivalent) dissolved in THF (1.5 mL) was added dropwise under vigorous stirring. The resulting colorless solution was layered with n-hexane (10 mL) and cooled to -30 °C, affording colorless crystals of Na(18-crown-6)[8] suitable for X-Ray diffraction overnight. The supernatant was removed by decantation, the solid was washed with n-hexane (2 x 2.5 mL) and dried in vacuo, affording Na(18-crown-6)[8] (133 mg, 0.16 mmol, 87 % yield) as a white powder.

**Melting point:** 140°C (decomp.)

**SUPPORTING INFORMATION**

| NMR | Frequency | Solvent | Remarks |
|-----|-----------|---------|---------|
| 28Si{1H}-NMR | 99.4 MHz | C6D6 | ppm: -28 (s) |
| 13C{1H}-NMR | 125.8 MHz | C6D6 | ppm: 169.4 (d, JPC = 101.4 Hz, PCN) |
| 31P{1H}-NMR | 202.5 MHz | THF-d8 | ppm: -300 (s, JPSi = 57 Hz, [7]), -283 (br, [1]) |
| 29Si{1H}-NMR | 99.4 MHz | THF-d8 | ppm: 0 (d, JPSi = 57 Hz, [7]) |
| 13C{1H}-NMR | 125.8 MHz | THF-d8 | ppm: 156.5 (m, BPH3 ipso) 140.7 (d, JPC = 10.0 Hz, SiPH3 ipso), 139.5 (d, JPC = 112.0 Hz, CN), 136.6 (d, JPC = 2.7 Hz, SiPH3 ortho), 134.3 (s, BPH3 ortho) 128.4 (s, SiPH3 para), 127.6 (s, SiPH3 meta), 126.3 (s, BPH3 meta), 123.5 (s, BPH3 para), 70.4 (s, 18-c-6) |
| 11B-NMR | 160.5 MHz | THF-d8 | ppm: -4 (br) |
| 1H-NMR | 500.1 MHz | THF-d8 | ppm: 7.54-7.50 (m, 6H), 7.14-7.08 (m, 3H), 7.07-7.03 (m, 6H), 7.02-6.99 (m, 6H), 6.80-6.77 (m, 6H), 6.76-6.71 (m, 3H), 3.42 (s, 24H, 18-c-6) |
| IR | ATR, 298 K, cm⁻¹ | | | |
| 28Si{1H}-NMR | 99.4 MHz | THF-d8 | ppm: -28 (s) |
| 13C{1H}-NMR | 125.8 MHz | THF-d8 | ppm: 193.2 (br, NCO), 142.7 (d, JPC = 8 Hz, SiPH3 ipso), 137.9 (s, Mes m), 137.8 (d, JPC = 105.2 Hz, PCN), 137.2 (s, SiPH3 ortho), 133.8 (br, Mes i) 132.5 (s, Mes p), 129.0 (s, SiPH3 para), 128.2 (s, Mes m), 127.3 (s, SiPH3 meta), 70.4 (s, 18-c-6), 20.2 (s, p-CH3), 19.4 (s, o-CH3) |
**Supporting Information**

**^1H-NMR** (500.1 MHz, THF-d$_8$, ppm): 7.70-7.66 (m, 6H, Ph ortho), 7.24-7.19 (m, 3H, Ph para), 7.18-7.13 (m, 6H, Ph meta), 6.47 (m, 2H, Mes m), 3.42 (s, 24H, 18-c-6), 2.08 (s, 3H, p-C$_3$H$_3$), 1.88 (s, 6H, o-C$_3$H$_3$)

**IR** (ATR, 298 K, cm$^{-1}$): 2899 (br), 2865 (br), 2100 (m, CN), 1526 (m), 1478 (w), 1427 (w), 1353 (w), 1296 (br), 1237 (br), 1169 (m), 1151 (m), 1099 (br s), 1029 (m), 970 (m), 949 (w), 929 (m), 856 (w), 830 (w), 743 (m), 725 (m), 702 (s), 674 (w), 640 (m), 568 (m), 521 (m), 503 (s), 487 (s), 434 (s)

**Elemental analysis** for C$_{41}$H$_{50}$O$_7$N$_2$NaPSi (%):
Calc. C 64.38 H 6.59 N 3.66
Found C 64.13 H 6.28 N 4.13

**Generation of [8] from 4**

A solution of 4 in THF was formed in a vial equipped with a magnetic stirrer as described above, and one equivalent of mesityl isocyanate was added to the stirred solution in one portion. $^{31}$P-NMR revealed the presence of [8] in solution with a broad resonance around -100 ppm

**Preparation of Na(18-crown-6)[9]**

In a glovebox, an 18 mL vial equipped with a magnetic stirrer was charged with Na(18-crown-6)[1] (120.7 mg, 0.2 mmol, 1 equivalent) and THF (1.5 mL). 1,3-di-p-tolylcarbodiimide (44.5 mg, 0.2 mmol, 1 equivalent) dissolved in THF (1.5 mL) was added dropwise under vigorous stirring. The resulting yellow solution was layered with n-hexane (10 mL), affording yellow crystals of Na(18-crown-6)[9](THF) suitable for X-ray diffraction overnight. The supernatant was removed by decantation, the solid was washed with n-hexane (2 x 2.5 mL) and dried in vacuo, affording Na(18-crown-6)[9] (139 mg, 0.17 mmol, 84 % yield) as a yellow powder.

**Melting point** (TGA): 78 °C (decomp.)

$^{31}$P{$^1$H}-NMR (202.5 MHz, THF-d$_8$, ppm): -120 (s)

$^{29}$Si{$^1$H}-NMR (99.4 MHz, THF-d$_8$, ppm): -38 (s)

$^{13}$C{$^1$H}-NMR (125.8 MHz, THF-d$_8$, ppm): 186.1 (d, $^1$J$_{PC}$ = 83.2 Hz, N-CN), 145.3 (d, $^3$J$_{PC}$ = 2.7 Hz, tolyl N-C), 142.2 (s, SiPh$_3$ ipso), 136.6 (s, SiPh$_3$ ortho), 134.4 (d, $^1$J$_{PC}$ = 105.2 Hz, P-CN), 130.4 (s, C(CH)$_3$) 128.0 (s, C(H)C(CH)$_3$), 127.4 (s, SiPh$_3$para), 127.3 (s, NCCH), 126.8 (s, SiPh$_3$ meta), 70.4 (s, 18-c-6), 21.0 (s, CH$_3$)

$^1$H-NMR (500.1 MHz, THF-d$_8$, ppm): 7.51-7.48 (m, 6H), 7.07-7.01 (m, 9H), 6.65-6.59 (m, 8H, tolyl), 3.42 (s, 24H, 18-c-6), 2.09 (s, CH$_3$)

**IR** (ATR, 298 K, cm$^{-1}$): 3065 (br), 2907 (br), 2086 (m, CN), 1606 (w), 1531 (m br), 1507 (m), 1454 (m), 1426 (m), 1352 (w), 1249 (w), 1216 (w), 1173 (w), 1147 (m), 1096 (s br), 1020 (w), 939 (m br), 866 (m), 818 (m), 742 (s), 696 (w), 581 (w), 534 (w), 490 (s), 466 (s br), 444 (w), 425 (w)

**Elemental analysis** for C$_{46}$H$_{53}$O$_6$N$_3$NaPSi (%):
Calc. C 66.89 H 6.47 N 5.09
Found C 66.85 H 6.27 N 5.21
Spectra

NMR Spectra

**Figure S4**: $^{31}$P{$^{1}$H}-NMR Spectrum of the reaction between chlorotriphenylsilane, Na[OCP](dioxane)$_{2.14}$ and sodium hexamethyldisilazide in a toluene/DME mixture: resonances of [1] (major) and 4 (minor)

**Figure S5**: $^{31}$P{$^{1}$H}-NMR Spectrum of Na(18-crown-6)[1] in THF-d$_{8}$
**Figure S6**: $^1$H-NMR spectrum of Na(18-crown-6)[1] in THF-d$_8$

**Figure S7**: $^{13}$C($^1$H)-NMR spectrum of Na(18-crown-6)[1] in THF-d$_8$
**Figure S8:** $^{29}$Si$^1$H$^1$-NMR Spectrum of Na(18-crown-6)$[1]$ in THF-$d_8$

**Figure S9:** $^{31}$P$^1$H$^1$-NMR Spectrum of 4 in $C_6D_6$
**Figure S10:** $^{29}$Si($^1$H)-NMR Spectrum of 4 in C$_6$D$_6$

**Figure S11:** $^{13}$C($^1$H)-NMR Spectrum of 4 in C$_6$D$_6$
**Figure S12:** $^1$H-NMR Spectrum of 4 in C$_6$D$_6$

**Figure S13:** $^{31}$P{$^1$H}-NMR Spectrum of Na(18-crown-6)[1] and Ph$_3$SiCl 1:1 mixture in DFB/C$_6$D$_6$ 9:1 mixture at 298 K; broad coalescence signal at -293 ppm from the exchange of 4 and [1] and two minor side products (marked with *)
**Figure S14**: $^{31}$P{$^1$H}-NMR Spectrum of Na(18-crown-6)[1] and Ph$_3$SiCl 1:1 mixture in DFB/C$_6$D$_6$ 9:1 mixture at 243 K: resolved signals of [1] (-281 ppm) and 2 (-300 ppm) and minor side-products (marked with *)

**Figure S15**: $^{31}$P{$^1$H}-NMR Spectrum of Na(18-crown-6)[1] and Ph$_3$SiCl 1:1 mixture in THF-d$_8$ at 170 K: poorly resolved signals of [1] (-284 ppm), 4 (-299 ppm) and two side-products (marked with *)
Figure S16: $^{31}$P{$^{1}$H}-NMR spectra of the reaction between chlorotriphenylgermane, Na[OCP](dioxane)$_{2.14}$ and sodium hexamethyldisilazide in THF at 0°C: after 30 min (red) and after 16 hours (blue). Resonances of $[2]^{-} (-278$ ppm) and $[P(CN)_{2}]^{-} (-195$ ppm).

Figure S17: $^{31}$P{$^{1}$H}-NMR Spectrum of Na(18-crown-6)[1] and Ph$_{3}$GeCl 1:1 mixture in THF-d$_{8}$ after 30 minutes at room temperature: broad resonance around -291 ppm; side products including $[P(CN)_{2}]^{-} (-195$ ppm, singlet) and other side-products (marked with *, -244 ppm to -255 ppm).
**Figure S18:** $^{31}$P($^1$H)-NMR Spectrum of Na(18-crown-6)[1] and Ph$_3$GeCl 1:1 mixture in DFB/C$_6$D$_6$ 1:1 after 30 minutes at room temperature (blue) and at 243 K after 30 minutes at room temperature: broad resonance (red), poorly resolved broad resonances

**Figure S19:** $^{29}$Si($^1$H)-NMR Spectrum of Na(18-crown-6)[1] and Ph$_3$GeCl 1:1 mixture in DFB/C$_6$D$_6$ 1:10 at 243 K after 30 minutes at room temperature: resonances of 5 (-23 ppm) and 5' (doublet, 1 ppm)
Figure S20: $^{31}$P{$^1$H}-NMR Spectrum of Na(18-crown-6)[1] and Ph$_3$GeCl 1:1 mixture in C$_6$D$_6$ after one hour at room temperature: well-resolved resonances of [P(CN)$_2$]$^-$ (-194 ppm), 5 (-292 ppm) and 5' (-295 ppm).

Figure S21: $^{31}$P{$^1$H}-NMR Spectrum of Na(18-crown-6)[1] and Ph$_3$GeCl 1:1 mixture in C$_6$D$_6$ after 16 hours at room temperature: major resonance of 5'.
Figure S22: $^{13}$C($^1$H)-NMR Spectrum of Na(18-crown-6)[1] and Ph$_3$GeCl 1:1 mixture in C$_6$D$_6$ after 16 hours at room temperature: doublet of the allenic carbon of 5 at 172 ppm.

Figure S23: $^1$H-NMR Spectrum of Na(18-crown-6)[1] and Ph$_3$GeCl 1:1 mixture in C$_6$D$_6$ after 16 hours at room temperature in the aromatic region.
**Figure S24:** $^{31}$P{$^1$H}-NMR Spectrum of 6 in THF-d$_8$

**Figure S25:** $^{29}$Si{$^1$H}-NMR Spectrum of 6 in THF-d$_8$
**Figure S26:** $^{119}\text{Sn}[^1\text{H}]-\text{NMR}$ Spectrum of 6 in THF-d$_8$

**Figure S27:** $^{13}\text{C}[^1\text{H}]-\text{NMR}$ Spectrum of the reaction of Na(18-crown-6)[1] and Ph$_3\text{SnCl}$ in THF-d$_8$: resonance of the allenic carbon of 6 at 170 ppm (doublet)
Figure S28: $^1$H-NMR spectrum of the reaction of Na(18-crown-6)[1] and Ph$_3$SnCl in THF-d$_8$ in the aromatic region.

Figure S29: $^{31}$P-$^1$H-NMR Spectrum of the reaction between Na(18-crown-6)[1] and triphenylborane in THF-d$_8$: Resonances of 7 (-289 ppm) and [1] (-283 ppm).
**Figure S30:** $^1$H-NMR of the reaction between Na(18-crown-6)[1] and triphenylborane in THF-d$_8$

**Figure S31:** $^{13}$C($^1$H)-NMR of the reaction between Na(18-crown-6)[1] and triphenylborane in THF-d$_8$
Figure S32: $^{29}$Si-$^1$H HMBC NMR Spectrum of the reaction between Na(18-crown-6)[1] and triphenylborane in THF-$d_8$

Figure S33: $^{11}$B-NMR of the reaction between Na(18-crown-6)[1] and triphenylborane in THF-$d_8$
Figure S34: In red: $^{31}$P{$^1$H}-NMR spectrum of Na(18-crown-6)[8] in THF-d8. In blue: $^{31}$P{$^1$H}-NMR of the reaction of 4 (generated in situ) with mesityl isocyanate, the signal of [8] around -100 ppm and side-products (*)

Figure S35: Variable temperature $^{31}$P{$^1$H}-NMR spectra of Na(18-crown-6)[8] in THF-d8: at 233 K (yellow), 213 K (purple), 193 K (green), 183 K (red), 175K (blue)
**Figure S36**: $^1$H-NMR Spectrum of Na(18-crown-6)[8] in THF-$d_8$

**Figure S37**: $^{13}$C($^1$H)-NMR Spectrum of Na(18-crown-6)[8] in THF-$d_8$
Figure S38: $^{29}$Si($^1$H)-NMR Spectrum of Na(18-crown-6)[8] in THF-$d_8$

Figure S39: $^{31}$P($^1$H)-NMR Spectrum of Na(18-crown-6)[9] in THF-$d_8$
Figure S40: $^1$H-NMR Spectrum of Na(18-crown-6)[9] in THF-$d_8$

Figure S41: $^{13}$C{$^1$H}-NMR Spectrum of Na(18-crown-6)[9] in THF-$d_8$
Figure S42: $^{29}$Si-$^1$H-NMR Spectrum of Na(18-crown-6)[9] in THF-$d_8$
IR Spectra (ATR)

Figure S43: IR Spectrum of Na(18-crown-6)[1]

Figure S44: IR Spectrum of Na(18-crown-6)[7]
Figure S45: IR spectrum of Na(18-crown-6)[8]

Figure S46: IR spectrum of Na(18-crown-6)[9]
### Crystallographic Details

**Table S1:** Crystal data and structure refinement for Na(18-crown-6)[1]

| Parameter                  | Value                     |
|----------------------------|---------------------------|
| Identification code        | GLC3SiPCN_0m              |
| Empirical formula          | C_{10.33}H_{13}N_{0.33}Na_{0.33}O_{2}P_{0.33}Si_{0.33} |
| Formula weight             | 201.23                    |
| Temperature/K              | 100.0                     |
| Crystal system             | monoclinic                |
| Space group                | P2$_1$/n                  |
| a/Å                        | 16.0511(4)                |
| b/Å                        | 12.9744(4)                |
| c/Å                        | 16.0927(5)                |
| α/°                        | 90                        |
| β/°                        | 113.4090(10)              |
| γ/°                        | 90                        |
| Volume/Å$^3$               | 3075.51(16)               |
| Z                          | 12                        |
| $\rho_{\text{calc}}$/cm$^3$| 1.304                     |
| $\mu$/mm$^{-1}$            | 0.186                     |
| F(000)                     | 1280.0                    |
| Crystal size/mm$^3$        | 0.33 × 0.15 × 0.07        |
| Radiation                  | MoKα (λ = 0.71073)        |
| 2Θ range for data collection/°| 5.516 to 54.966          |
| Index ranges               | -20 ≤ h ≤ 20, -16 ≤ k ≤ 16, -20 ≤ l ≤ 20 |
| Reflections collected      | 48177                     |
| Independent reflections    | 6983 [R$_{\text{int}} = 0.0222$, R$_{\sigma}$ = 0.0140] |
| Data/restraints/parameters | 6983/0/370                |
| Goodness-of-fit on F$^2$   | 1.042                     |
| Final R indexes [I>=2σ (I)] | $R_1 = 0.0280$, wR$_2 = 0.0704$ |
|                             | $R_1 = 0.0313$, wR$_2 = 0.0727$ |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.32/-0.22              |
Table S2: Crystal data and structure refinement for Na(18-crown-6)[2]

| Parameter                        | Value                                      |
|----------------------------------|--------------------------------------------|
| Identification code              | GePCN                                      |
| Empirical formula                | C_{10.33}H_{13}Ge_{0.33}N_{0.33}Na_{0.33}O_{2}P_{0.33} |
| Formula weight                   | 216.06                                     |
| Temperature/K                    | 100.0                                      |
| Crystal system                   | monoclinic                                 |
| Space group                      | P2\textsubscript{1}/c                     |
| a/Å                              | 15.5035(8)                                 |
| b/Å                              | 13.4951(7)                                 |
| c/Å                              | 16.9290(8)                                 |
| α/°                              | 90                                         |
| β/°                              | 116.994(2)                                 |
| γ/°                              | 90                                         |
| Volume/Å\textsuperscript{3}      | 3156.0(3)                                  |
| Z                                | 12                                         |
| \(\rho_{\text{calc}}\)/cm\textsuperscript{3}  | 1.364                                      |
| μ/mm\textsuperscript{-1}        | 1.077                                      |
| F(000)                           | 1352.0                                     |
| Crystal size/mm\textsuperscript{3} | 0.2 x 0.12 x 0.02                        |
| Radiation                        | MoKα (\(\lambda = 0.71073\))             |
| 2Θ range for data collection/°   | 4.838 to 53.5                              |
| Index ranges                     | -19 ≤ h ≤ 19, -17 ≤ k ≤ 17, -21 ≤ l ≤ 21  |
| Reflections collected            | 33566                                      |
| Independent reflections          | 6698 [\(R_{\text{int}} = 0.0417, R_{\text{sigma}} = 0.0319\)] |
| Data/restraints/parameters       | 6698/0/370                                 |
| Goodness-of-fit on F\textsuperscript{2} | 1.030                                      |
| Final R indexes [I>2σ (I)]       | R\textsubscript{1} = 0.0325, wR\textsubscript{2} = 0.0647 |
| Final R indexes [all data]       | R\textsubscript{1} = 0.0445, wR\textsubscript{2} = 0.0680 |
| Largest diff. peak/hole / e Å\textsuperscript{-3} | 0.40/-0.32                                |
### Table S3: Crystal data and structure refinement for Na(18-crown-6)[3]

| Parameter                                | Value                      |
|------------------------------------------|----------------------------|
| Identification code                      | GLC5SnPCN_0m               |
| Empirical formula                        | C_{10.33}H_{13}N_{0.33}Na_{0.33}O_{2}P_{0.33}Sn_{0.33} |
| Formula weight                           | 231.43                     |
| Temperature/K                            | 100.0                      |
| Crystal system                           | monoclinic                 |
| Space group                              | P2₁/n                      |
| a/Å                                      | 16.1638(8)                 |
| b/Å                                      | 13.0312(6)                 |
| c/Å                                      | 16.4164(8)                 |
| α/°                                      | 90                         |
| β/°                                      | 113.917(2)                 |
| γ/°                                      | 90                         |
| Volume/Å³                                | 3160.9(3)                  |
| Z                                        | 12                         |
| ρcalcg/cm³                               | 1.459                      |
| μ/mm⁻¹                                   | 0.915                      |
| F(000)                                   | 1424.0                     |
| Crystal size/mm³                         | 0.33 × 0.11 × 0.1          |
| 2Θ range for data collection/°           | 4.32 to 54.244             |
| Index ranges                             | -20 ≤ h ≤ 20, -16 ≤ k ≤ 16, -21 ≤ l ≤ 20 |
| Reflections collected                    | 48209                      |
| Independent reflections                  | 6957 [R_{int} = 0.0284, R_{sigma} = 0.0198] |
| Data/restraints/parameters               | 6957/0/370                 |
| Goodness-of-fit on F²                    | 1.051                      |
| Final R indexes [I>=2σ (I)]              | R₁ = 0.0252, wR₂ = 0.0673  |
| Final R indexes [all data]               | R₁ = 0.0311, wR₂ = 0.0718  |
| Largest diff. peak/hole / e Å⁻³          | 1.23/-0.38                 |
### Table S4: Crystal data and structure refinement for 4

| Property                  | Value                                      |
|---------------------------|--------------------------------------------|
| Identification code       | GLC5073_0m                                  |
| Empirical formula         | C_{43}H_{42}NO_{3}PSi_{2}                   |
| Formula weight            | 707.92                                     |
| Temperature/K             | 100.0                                      |
| Crystal system            | triclinic                                  |
| Space group               | P-1                                        |
| a/Å                       | 9.8622(4)                                  |
| b/Å                       | 12.8353(4)                                 |
| c/Å                       | 16.2011(6)                                 |
| α/°                       | 70.876(2)                                  |
| β/°                       | 74.838(2)                                  |
| γ/°                       | 84.820(2)                                  |
| Volume/Å³                 | 1870.15(12)                                |
| Z                         | 2                                          |
| ρ_{calc}/g/cm³            | 1.257                                      |
| μ/mm⁻¹                    | 0.178                                      |
| F(000)                    | 748.0                                      |
| Crystal size/mm³          | 0.7 × 0.35 × 0.07                          |
| Radiation                 | MoKα (λ = 0.71073)                         |
| 2Θ range for data collection/° | 4.478 to 53.492 |
| Index ranges              | -12 ≤ h ≤ 12, -16 ≤ k ≤ 16, -20 ≤ l ≤ 20 |
| Reflections collected     | 77326                                      |
| Independent reflections   | 7946 [R_{int} = 0.0283, R_{sigma} = 0.0138] |
| Data/restraints/parameters| 7946/0/469                                 |
| Goodness-of-fit on F²     | 1.046                                      |
| Final R indexes [I>2σ(I)] | R₁ = 0.0350, wR₂ = 0.0800                  |
| Final R indexes [all data]| R₁ = 0.0419, wR₂ = 0.0865                  |
| Largest diff. peak/hole / e Å⁻³ | 0.49/-0.58                           |
### Table S5: Crystal data and structure refinement for Na(18-crown-6)[7]

| Property                              | Value                  |
|---------------------------------------|------------------------|
| Identification code                   | PCNB                   |
| Empirical formula                     | C_{11.58}H_{12.21}B_{0.21}F_{0.42}N_{0.21}Na_{0.21}O_{1.26}P_{0.21}Si_{0.21} |
| Formula weight                        | 202.08                 |
| Temperature/K                         | 100.0                  |
| Crystal system                        | orthorhombic           |
| Space group                           | Pna2₁                  |
| a/Å                                   | 15.8564(5)             |
| b/Å                                   | 20.1226(6)             |
| c/Å                                   | 15.4947(5)             |
| α/°                                   | 90                     |
| β/°                                   | 90                     |
| γ/°                                   | 90                     |
| Volume/Å³                             | 4943.9(3)              |
| Z                                      | 19                     |
| ρ_{calc}/g/cm³                        | 1.290                  |
| μ/mm⁻¹                                | 0.148                  |
| F(000)                                | 2024.0                 |
| Crystal size/mm³                      | 0.25 × 0.22 × 0.2      |
| Radiation                             | MoKα (λ = 0.71073)     |
| 2Θ range for data collection/°        | 4.794 to 53.488        |
| Index ranges                          | -20 ≤ h ≤ 20, -25 ≤ k ≤ 25, -19 ≤ l ≤ 18 |
| Reflections collected                 | 72801                  |
| Independent reflections               | 10394 [R_{int} = 0.0374, R_{sigma} = 0.0207] |
| Data/restraints/parameters            | 10394/1/613            |
| Goodness-of-fit on F²                 | 1.057                  |
| Final R indexes [I>=2σ (I)]           | R₁ = 0.0279, wR₂ = 0.0653 |
| Final R indexes [all data]            | R₁ = 0.0345, wR₂ = 0.0703 |
| Largest diff. peak/hole / e Å⁻³       | 0.17/-0.24             |
| Flack parameter                       | 0.231(19)              |
**Table S6:** Crystal data and structure refinement for Na\((18\text{-crown-6})[8]\)

| Parameter                      | Value                        |
|--------------------------------|------------------------------|
| Identification code            | lac221020_1_1                |
| Empirical formula              | C\(_{41}\)H\(_{50}\)N\(_2\)NaO\(_7\)PSi |
| Formula weight                 | 764.88                       |
| Temperature/K                  | 99.99(10)                    |
| Crystal system                 | triclinic                    |
| Space group                    | P-1                          |
| a/Å                            | 9.43240(10)                  |
| b/Å                            | 11.13800(10)                 |
| c/Å                            | 20.3690(2)                   |
| \(\alpha^\circ\)              | 87.5770(10)                  |
| \(\beta^\circ\)               | 78.8370(10)                  |
| \(\gamma^\circ\)              | 73.0500(10)                  |
| Volume/Å\(^3\)                | 2008.01(4)                   |
| Z                              | 2                            |
| \(\rho_{\text{calc}}/\text{cm}^3\) | 1.265                        |
| \(\mu/\text{mm}^{-1}\)        | 1.413                        |
| \(F(000)\)                    | 812.0                        |
| Crystal size/mm\(^3\)         | 0.08 \times 0.06 \times 0.04 |
| Radiation                      | CuK\(\alpha\) (\(\lambda = 1.54184\)) |
| 2\(\Theta\) range for data collection/\(^\circ\) | 4.422 to 159.682 |
| Index ranges                   | -12 \leq h \leq 11, -14 \leq k \leq 14, -25 \leq l \leq 25 |
| Reflections collected          | 51181                        |
| Independent reflections        | 8469 [\(R_{\text{int}} = 0.0447, R_{\text{sigma}} = 0.0262\)] |
| Data/restraints/parameters     | 8469/0/481                   |
| Goodness-of-fit on F\(^2\)     | 1.083                        |
| Final R indexes [I>2\(\sigma\) (I)] | \(R_1 = 0.0352, wR_2 = 0.0944\) |
| Final R indexes [all data]     | \(R_1 = 0.0382, wR_2 = 0.0963\) |
| Largest diff. peak/hole / e Å\(^{-3}\) | 0.34/-0.33                   |
Table S7: Crystal data and structure refinement for Na(18-crown-6)[9]

| Property | Value |
|----------|-------|
| Identification code | glc3149 (1) |
| Empirical formula | C_{40}H_{48.8}N_{2.4}Na_{0.8}O_{5.6}P_{0.8}Si_{0.8} |
| Formula weight | 718.45 |
| Temperature/K | 100(1) |
| Crystal system | orthorhombic |
| Space group | P2_12_12 |
| a/Å | 14.5801(3) |
| b/Å | 18.0779(4) |
| c/Å | 18.5205(4) |
| α/° | 90 |
| β/° | 90 |
| γ/° | 90 |
| Volume/Å³ | 4881.59(18) |
| Z | 5 |
| \( \rho_{\text{calc}} \)/cm³ | 1.222 |
| \( \mu / \text{mm}^{-1} \) | 0.142 |
| F(000) | 1912.0 |
| Crystal size/mm³ | 1.6 × 1.2 × 1.2 |
| Radiation | MoKα (λ = 0.71073) |
| 2Θ range for data collection/° | 4.21 to 52.74 |
| Index ranges | -12 ≤ h ≤ 18, -21 ≤ k ≤ 22, -23 ≤ l ≤ 20 |
| Reflections collected | 18611 |
| Independent reflections | 9838 [R_int = 0.0215, R_{sigma} = 0.0367] |
| Data/restraints/parameters | 9838/81/637 |
| Goodness-of-fit on F² | 1.032 |
| Final R indexes [I>2σ(I)] | R₁ = 0.0346, wR₂ = 0.0778 |
| Final R indexes [all data] | R₁ = 0.0398, wR₂ = 0.0805 |
| Largest diff. peak/hole / e Å⁻³ | 0.27/-0.25 |
| Flack parameter | -0.04(3) |
Figure S47: Powder X-Ray diffractogram of the precipitate obtained from decomposition of Na(18-crown-6)[2] at room temperature.

Figure S48: Powder X-Ray diffractogram of the precipitate obtained from decomposition of Na(18-crown-6)[2] at room temperature, matched with NaCN.
Density functional calculations were performed using Gaussian09, revision D.01. Geometry optimizations were performed using the M06-2X-D3 functional in combination with the def2-SVP basis set. Solvent effects were considered implicitly using the SMD method with THF as solvent. The nature of each stationary point was confirmed by frequency calculations (no imaginary frequencies for minima and one for transition states). Intrinsic reaction coordinate (IRC) calculations were performed to obtain additional proof for the transition state geometries. Cartesian coordinates are given in angstroms (Å) and energies in Hartree. NMR calculations were performed using the Gauge-Including Atomic Orbital (GIAO) method with the 6-311+G(2d,2p) basis set. 

Table S8: GIAO NMR calculations results. Chemical shifts in ppm as calculated by M06-2X-D3/6-311+G(2d,p) basis set. THF as solvent was treated as a continuum using SMD. Values referenced to phosphoric acid for $^{31}$P and tetramethylsilane for $^{29}$Si.

| Compound | $^{31}$P $\delta_{\text{abs}}$ | $^{31}$P $\delta_{\text{GIAO}}$ | $^{29}$Si $\delta_{\text{abs}}$ | $^{29}$Si $\delta_{\text{GIAO}}$ |
|----------|-------------------------------|-------------------------------|-----------------------------|-------------------------------|
| H$_3$PO$_4$ | -299.1126 | 0.0 | - | - |
| TMS | - | - | -330.1348 | 0.0 |
| Na(18-c-6)[1] | -588.5178 | -289.4 | -322.2054 | 7.9 |
| Na(18-c-6)[1'] | -567.6241 | -268.5 | -350.2922 | -20.2 |
| Na(18-c-6)[2] | -592.9602 | -293.8 | - | - |
| Na(18-c-6)[2'] | -579.5281 | -280.4 | - | - |
| 4 (P-Si) | -622.4211 | -323.3 | -356.7833 | -26.6 |
| 4 (N-Si) | - | - | -318.6188 | 11.5 |
| 4' | -494.5423 | -195.4 | -334.0028 | -3.9 |
| 4'' | -421.2076 | -122.1 | -342.8999 | -12.8 |
| 5 | -625.5699 | -326.5 | -353.6457 | -23.5 |
| 5' | -513.5164 | -214.4 | -337.3741 | -7.2 |
| 5'' | -449.6807 | -150.6 | -343.4744 | -13.3 |
| 5''' | -602.2090 | -303.1 | -320.7463 | 9.4 |
| [8] | -358.0265 | -58.9 | -350.1998 | -20.1 |
| [8'] (O-silylated) | -405.2102 | -106.1 | -348.6196 | -18.5 |

Scheme S1: Isomerization of [1] into [1'] and transition state
Supporting Information

List of detailed parameters for the calculated molecular models

Na(18-c-6)[1]

\[ E(RM062X) = -2501.8387838 \]

- Thermochemistry -

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.

Zero-point correction= 0.662447 (Hartree/Particle)
Thermal correction to Energy= 0.703709
Thermal correction to Enthalpy= 0.704653
Thermal correction to Gibbs Free Energy= 0.584410
Sum of electronic and zero-point Energies= -2501.176336
Sum of electronic and thermal Energies= -2501.135075
Sum of electronic and thermal Enthalpies= -2501.134131
Sum of electronic and thermal Free Energies= -2501.254374

Charge = 0 Multiplicity = 1

P -0.912929000 0.556567000 -2.316918000
C 0.243253000 -0.708588000 -2.747399000
N 1.010860000 -1.536289000 -3.051210000
Si -0.436975000 0.307276000 -0.157174000
C 1.402045000 0.527755000 0.257174000
C 1.872707000 1.706790000 0.857819000
C 2.349090000 -0.453439000 -0.090445000
C 3.233449000 1.904149000 1.102094000
C 3.710217000 -0.257921000 0.145883000
C 4.156624000 0.921796000 0.744485000
H 1.164819000 2.490741000 1.141303000
H 2.026065000 -1.385674000 -0.562530000
H 3.573063000 2.829303000 1.572284000
H 4.420935000 -1.032348000 -0.147064000
H 5.221392000 1.074392000 0.931950000
C -1.407217000 1.642982000 0.775309000
C -1.679711000 2.889299000 0.187632000
C -1.843547000 1.427410000 2.092798000
C -2.360718000 3.885330000 0.889725000
C -2.523270000 2.420808000 2.800563000
C -2.783271000 3.652117000 2.198985000
H -1.353481000 3.088071000 -0.837675000
H -1.653391000 0.465198000 2.577477000
H -2.563070000 4.840645000 0.412046000
H -2.853479000 2.230337000 3.823870000
H -3.316942000 4.429422000 2.749509000
C -0.981791000 -1.378426000 0.533959000
C -2.184889000 -1.950872000 0.086658000
C -0.263789000 -2.057421000 1.531475000
C -2.662505000 -3.146418000 0.623779000
C -0.731115000 -3.261896000 2.066580000
C -1.934542000 -3.805190000 1.617161000
H -2.752229000 -1.450225000 -0.703555000
H 0.675874000 -1.640059000 1.904661000
H -3.604215000 -3.567389000 0.264060000
H -0.156108000 -3.772770000 2.842020000
H -2.303937000 -4.743187000 2.037081000
Na 2.153812000 -3.615073000 -3.236310000
O 1.091744000 -5.153891000 -1.556216000
O 4.351731000 -2.517940000 -2.211623000
O 3.528305000 -2.233413000 -4.775429000
O 3.864966000 -5.146860000 -1.482417000
O -0.224977000 -4.197133000 -3.639285000
O 1.489532000 -3.934665000 -5.732837000
O 4.536628000 -4.259436000 -0.620961000
H 5.255371000 -4.807224000 0.015616000
H -0.234670000 -4.716620000 -1.351046000
H -0.247065000 -3.662774000 -1.015620000
H -0.732557000 -5.330411000 -0.581158000
H -0.963683000 -4.874695000 -2.660310000
H -1.040205000 -5.948600000 -2.916127000
H -1.987210000 -4.465303000 -2.575150000
C -0.698283000 -4.372464000 -4.946491000
H -1.755085000 -4.060642000 -5.032176000
H -0.629325000 -5.436907000 -5.241648000
C 1.751093000 -5.567430000 -0.368189000
H 1.179253000 -6.364659000 0.123355000
H 1.849688000 -4.724972000 0.324109000
C 5.279952000 -3.262114000 -1.461639000
H 5.882866000 -2.602811000 -0.809351000
H 5.974644000 -3.792021000 -2.139175000
C 0.144799000 -3.522850000 -5.857846000
H -0.195510000 -3.647836000 -6.900104000
H 0.030090000 -2.461374000 -5.576469000
|   |  C     |  H     |  H     |
|---|--------|--------|--------|
| C | 4.983473000 | -1.578048000 | -3.050403000 |
| H | 5.841401000  | -2.055234000  | -3.558411000  |
| H | 5.363457000  | -0.720496000  | -2.465129000  |
| C | 3.097373000  | -6.112622000  | -0.803464000  |
| H | 3.639540000  | -6.498384000  | 0.077697000   |
| H | 2.938970000  | -6.945452000  | -1.503680000  |
| C | 3.999871000  | -1.100096000  | -4.082447000  |
| H | 3.159503000  | -0.564160000  | -3.609918000  |
| H | 4.515572000  | -0.408689000  | -4.773035000  |
| C | 2.814220000  | -1.919130000  | -5.945403000  |
| H | 3.457490000  | -1.368588000  | -6.656857000  |
| H | 1.947582000  | -1.276015000  | -5.704205000  |
| C | 2.373496000  | -3.221767000  | -6.571040000  |
| H | 1.910001000  | -3.031775000  | -7.554491000  |
| H | 3.256294000  | -3.859620000  | -6.724650000  |
| H | 3.829721000  | -3.730441000  | 0.044157000   |
E(RM062X) = -2501.76501880

- Thermochemistry -

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.

Zero-point correction= 0.662469 (Hartree/Particle)
Thermal correction to Energy= 0.703495
Thermal correction to Enthalpy= 0.704439
Thermal correction to Gibbs Free Energy= 0.585939

Sum of electronic and zero-point Energies= -2501.102550
Sum of electronic and thermal Energies= -2501.060580
Sum of electronic and thermal Enthalpies= -2501.061524
Sum of electronic and thermal Free Energies= -2501.179080

Charge = 0 Multiplicity = 1
|   |   |   |   |   |
|---|---|---|---|---|
| H | 5.750892000 | -2.127348000 | -4.212177000 |
| H | 5.508339000 | -1.015367000 | -2.828227000 |
| C | 3.731100000 | -6.692901000 | -1.667011000 |
| H | 4.439390000 | -7.170207000 | -0.967140000 |
| H | 3.534072000 | -7.393308000 | -2.491404000 |
| C | 3.826760000 | -1.172292000 | -4.165060000 |
| H | 3.135650000 | -0.691403000 | -3.450117000 |
| H | 4.181534000 | -0.401063000 | -4.870294000 |
| C | 2.421461000 | -1.800368000 | -5.967822000 |
| H | 3.054742000 | -1.234998000 | -6.675820000 |
| H | 1.599028000 | -1.134206000 | -5.648553000 |
| C | 1.912671000 | -3.049030000 | -6.652874000 |
| H | 1.324409000 | -2.772458000 | -7.546035000 |
| H | 2.772600000 | -3.652119000 | -6.978595000 |
| H | 4.302620000 | -4.322326000 | -0.552012000 |
E(RM062X) = -2501.83647328

- Thermochemistry -

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.

Zero-point correction= 0.663620 (Hartree/Particle)

Thermal correction to Energy= 0.705031

Thermal correction to Enthalpy= 0.705976

Thermal correction to Gibbs Free Energy= 0.586091

Sum of electronic and zero-point Energies= -2501.172853

Sum of electronic and thermal Energies= -2501.250382

Sum of electronic and thermal Enthalpies= -2501.250382

Sum of electronic and thermal Free Energies= -2501.30498

Charge = 0 Multiplicity = 1
### SUPPORTING INFORMATION

|   |   |   |   |
|---|---|---|---|
| H | -0.216618000 | -3.321259000 | -7.130571000 |
| H | -0.307778000 | -2.400156000 | -5.597722000 |
| C | 4.547848000 | -1.307878000 | -2.632523000 |
| H | 5.400245000 | -1.274297000 | -3.335539000 |
| H | 4.819274000 | -0.735977000 | -1.726399000 |
| C | 3.715089000 | -6.573921000 | -1.811955000 |
| H | 4.370146000 | -7.077786000 | -1.079920000 |
| H | 3.542606000 | -7.261675000 | -2.652418000 |
| C | 3.339340000 | -0.698642000 | -3.296486000 |
| H | 2.497685000 | -0.601438000 | -2.589167000 |
| H | 3.602170000 | 0.306700000 | -3.670121000 |
| C | 2.120229000 | -1.002964000 | -5.322739000 |
| H | 2.515929000 | -0.040959000 | -5.695811000 |
| H | 1.119148000 | -0.815918000 | -4.887308000 |
| C | 2.055356000 | -1.998263000 | -6.460460000 |
| H | 1.457776000 | -1.587934000 | -7.292476000 |
| H | 3.076856000 | -2.178926000 | -6.826156000 |
| H | 4.469457000 | -4.531060000 | -0.476026000 |
- Thermochemistry -

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.

Zero-point correction= 0.564378 (Hartree/Particle)
Thermal correction to Energy= 0.601356
Thermal correction to Entropy= 0.602300
Thermal correction to Gibbs Free Energy= 0.487603
Sum of electronic and zero-point Energies= -2400.609811
Sum of electronic and thermal Energies= -2401.174189
Sum of electronic and thermal Enthalpies= -2400.571889
Sum of electronic and thermal Free Energies= -2400.571889

Charge = 0 Multiplicity = 1
|    |       |       |        |
|----|-------|-------|--------|
| H  | -9.549631000 | -2.130287000 | -4.035808000 |
| H  | -9.393986000 | -2.411928000 | -6.504246000 |
Supporting Information

E(RM062X) = -4289.19064369

- Thermochemistry -

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.

Zero-point correction= 0.660845 (Hartree/Particle)
Thermal correction to Energy= 0.703552
Thermal correction to Enthalpy= 0.704496
Thermal correction to Gibbs Free Energy= 0.580511

Sum of electronic and zero-point Energies= -4288.529798
Sum of electronic and Thermal Energies= -4288.487092
Sum of electronic and thermal Enthalpies= -4288.486148
Sum of electronic and thermal Free Energies= -4288.610133

Charge = 0 Multiplicity = 1

| Atom | X       | Y       | Z       |
|------|---------|---------|---------|
| C    | 1.96   | 1.75    | 1.00    |
| C    | 2.28   | 2.08    | 1.37    |
| C    | 4.37   | 4.68    | 4.33    |
| H    | 5.13   | 4.08    | 2.42    |
| C    | -1.59  | -2.09   | 3.56    |
| C    | -2.58  | 2.41    | 2.78    |
| H    | -1.66  | 2.68    | -0.98   |

| Atom | X       | Y       | Z       |
|------|---------|---------|---------|
| Na   | -2.82  | -2.90   | -3.45   |
| C    | 0.10   | 0.58    | 4.74    |
| O    | 0.35   | 1.12    | 1.23    |
| C    | 0.26   | 0.12    | 0.16    |

H -1.729591000  0.457392000  2.715698000
H -2.826006000  4.563708000  0.134406000
H -2.900383000  2.336097000  3.822442000
H -3.454423000  4.396729000  2.538538000
C -1.091733000 4.261903000  0.909324000
C -2.348693000 2.265690000  0.681024000
C -0.221811100 -2.306885000  1.807627000
C -2.727544000 -3.435077000  1.340858000
C -0.589372000 -3.487924000  2.460730000
C -1.843431000 -4.053295000  2.229203000
H -3.040731000 -1.805770000 -0.031764000
H 0.763453000 -1.874239000  2.005379000
H -3.712114000 -3.870690000  1.158005000
H 0.105197000 -3.964153000  3.156287000
H -2.133728000 -4.972787000  2.741185000
Na 2.275108000 -3.456584000 -3.332935000
O 1.048840000 -4.695879000 -1.545356000
O 4.505469000 -2.620612000 -2.361127000
O 3.742165000 -2.322252000 -4.937739000
O 3.768617000 -5.121139000 -1.411046000
O -0.125737000 -3.842556000 -3.743158000
O 1.561408000 -3.850337000 -5.859121000
C 4.475670000 -4.209227000 -0.608333000
C 4.115106000 -4.743355000  0.118484000
C -0.200549000 -4.048506000 -1.412793000
H -0.054487000 -2.969583000 -1.234354000
H -0.772940000 -4.462799000 -0.564743000
C -0.960508000 -4.260687000 -2.696837000
H -1.216645000 -5.330889000 -2.814608000
H -1.897361000 -3.673664000 -2.676821000
C -0.648582000 -4.035285000 -5.028161000
H -1.666289000 -3.612418000 -5.110298000
H -0.703619000 -5.114606000 -5.266552000
C 1.597095000 -5.166557000 -0.340309000
C 0.895944000 -5.853933000  0.167798000
C 1.795072000 -4.328116000  0.353619000
C 5.336570000 -3.365115000 -1.503733000
C 5.965486000 -2.694998000 -0.883232000
H 6.009458000 -4.012965000 -2.095219000
C 0.258219000 -3.326307000 -5.997977000
H -0.109486000 -3.478677000 -7.028648000
H 0.245624000 -2.243988000 -5.779345000
C 5.248333000 -1.782805000 -3.217099000
H 6.050564000 -2.367145000 -3.695573000
C 5.712343000 -0.956062000 -2.648186000
C 2.860189000 -5.920263000 -0.690775000
H 3.327518000 -6.320251000  0.227257000
H 2.600813000 -6.766530000 -1.342711000
C 4.336436000 -1.228072000 -4.276900000
H 3.558930000 -0.583935000 -3.833246000
|   |   |   |   |
|---|---|---|---|
|   | 4.936741000 | -0.626376000 | -4.982854000 |
| C | 3.063720000 | -1.968902000 | -6.118491000 |
| H | 3.759749000 | -1.503163000 | -6.840817000 |
| H | 2.264297000 | -1.238333000 | -5.895358000 |
| C | 2.502120000 | -3.238903000 | -6.714359000 |
| H | 2.053737000 | -3.027159000 | -7.700380000 |
| H | 3.323238000 | -3.956673000 | -6.857699000 |
| H | 3.789910000 | -3.555823000 | -0.038373000 |
SUPPORTING INFORMATION

Na\(18\)-\(c\)-\(6\)[\(2^+\)]

| Atom | x   | y   | z   |
|------|-----|-----|-----|
| C    | 4.492460000 | 0.543289000 | 0.743485000 |
| C    | 3.487660000 | 1.176445000 | 0.315978000 |
| C    | 2.657182000 | 0.895186000 | 1.027332000 |
| N    | 0.651779000 | 0.314954000 | 0.946575000 |

Sum of electronic and thermal Free Energies =
Sum of electronic and thermal Energies =

Zero Temperature 298.150 Kelvin. Pressure 1.00000 Atm.

Charge = 0 Multiplicity = 1

E(RM062X) = \(-4289.17402891\)

- Thermochemistry -

| Atom | x   | y   | z   |
|------|-----|-----|-----|
| C    | 4.802163000 | -1.822625000 | 1.123677000 |
| C    | 5.306247000 | -0.519662000 | 1.137018000 |
| H    | 2.548611000 | 1.145874000 | 0.039084000 |
| H    | 3.097782000 | -3.078711000 | 0.728032000 |
| H    | 4.879944000 | 1.563788000 | 0.757857000 |
| H    | 5.433242000 | -2.656438000 | 1.439550000 |
| H    | 6.332313000 | -0.333307000 | 1.460863000 |
| C    | -0.145591000 | 0.398709000 | -0.168323000 |
| C    | -0.252588000 | 1.176445000 | -1.331106000 |
| C    | -0.674656000 | 0.905186000 | 1.027332000 |
| C    | -0.867928000 | 2.428994000 | -1.298435000 |
| C    | -1.290747000 | 2.157722000 | 1.064635000 |
| C    | -1.386730000 | 2.921091000 | -0.099526000 |
| H    | 0.140137000 | 0.7962460000 | -2.278521000 |
| H    | -0.610749000 | 0.314954000 | 1.946575000 |
| H    | -0.994332000 | 3.020265000 | -2.212620000 |
| H    | -1.698441000 | 2.537454000 | 2.003541000 |
| H    | -1.870562000 | 3.899464000 | -0.074056000 |
| C    | -0.018275000 | -2.547997000 | 1.122886000 |
| C    | -1.174467000 | -3.267272000 | 0.776879000 |
| C    | 0.506197000 | -2.706647000 | 2.414120000 |
| C    | -1.781502000 | -4.127374000 | 1.693055000 |
| C    | -0.100717000 | -5.565503000 | 3.334096000 |
| C    | -1.243765000 | -4.278878000 | 2.972913000 |
| H    | -1.611528000 | -3.151687000 | -0.219899000 |
| H    | 1.402150000 | -2.154732000 | 2.712261000 |
| H    | -2.679681000 | -4.679075000 | 1.408746000 |
| H    | 0.320953000 | -3.677186000 | 4.334969000 |
| Na   | 2.151465000 | -3.564648000 | -3.285340000 |
| O    | 1.489802000 | -5.688033000 | -2.242930000 |
| O    | 4.242319000 | -2.721516000 | -2.262274000 |
| O    | 3.022703000 | -1.569374000 | -4.351552000 |
| O    | 4.243992000 | -5.508187000 | -2.243757000 |
| O    | 0.131431000 | -4.508903000 | -4.170172000 |
| O    | 1.544294000 | -3.165036000 | -6.098393000 |
| C    | 4.961967000 | -4.767838000 | -1.288721000 |
| H    | 5.859464000 | -5.323737000 | -0.959679000 |
| C    | 0.108255000 | -5.502019000 | -2.025978000 |
| H    | -0.071218000 | -4.564208000 | -1.472946000 |
| H    | -0.315478000 | -6.339453000 | -1.444968000 |
| C    | -0.545155000 | -5.457346000 | -3.383624000 |
| H    | -0.480163000 | -6.452717000 | -3.862200000 |
| H    | -1.610432000 | -5.183977000 | -3.277346000 |
| C    | -0.358734000 | -4.447938000 | -5.486075000 |
| H    | -1.463758000 | -4.429354000 | -5.486013000 |
| H    | -0.029524000 | -5.339067000 | -6.053320000 |
| C    | 2.208436000 | -6.228528000 | -1.162882000 |
| H    | 1.700611000 | -7.126755000 | -0.767809000 |
| H    | 2.285692000 | -5.495195000 | -0.336978000 |
|   |   |   |   |
|---|---|---|---|
| C | 5.384493000 | -3.464043000 | -1.903004000 |
| H | 5.994163000 | -2.903021000 | -1.172550000 |
| H | 6.008473000 | -3.649976000 | -2.796926000 |
| C | 0.135635000 | -3.186188000 | -6.136971000 |
| H | -0.222659000 | -3.149918000 | -7.182493000 |
| H | -0.285844000 | -2.322263000 | -5.595054000 |
| C | 4.576072000 | -1.394757000 | -2.605313000 |
| H | 5.429990000 | -1.400812000 | -3.307400000 |
| H | 4.869121000 | -0.825754000 | -1.704290000 |
| C | 3.569131000 | -6.617497000 | -1.697563000 |
| H | 4.169329000 | -7.097436000 | -0.905065000 |
| H | 3.430479000 | -7.343262000 | -2.512098000 |
| C | 3.396410000 | -0.740785000 | -3.275805000 |
| H | 2.550885000 | -0.618826000 | -2.576936000 |
| H | 3.699278000 | 0.258469000 | -3.636135000 |
| C | 2.162822000 | -0.972056000 | -5.293046000 |
| H | 2.571044000 | -0.001422000 | -5.628567000 |
| H | 1.165710000 | -0.788005000 | -4.847248000 |
| C | 2.079638000 | -1.916120000 | -6.471699000 |
| H | 1.487389000 | -1.458313000 | -7.282768000 |
| H | 3.097195000 | -2.097351000 | -6.848047000 |
| H | 4.343136000 | -4.566757000 | -0.396741000 |
**E(RM062X) = -2401.16852121**

- **Thermochemistry** -

| Temperature 298.150 Kelvin | Pressure 1.00000 Atm. |
|-----------------------------|------------------------|
| Zero-point correction       | 0.564193 (Hartree/Particle) |
| Thermal correction to Energy| 0.601363 |
| Thermal correction to Enthalpy| 0.602307 |
| Thermal correction to Gibbs Energy| 0.490111 |
| Sum of electronic and zero-point Energies| -2400.604328 |
| Sum of electronic and thermal Energies| -2400.567158 |
| Sum of electronic and thermal Enthalpies| -2400.566214 |
| Sum of electronic and thermal Free Energies| -2400.678410 |

Charge = 0 Multiplicity = 1
| Symbol | X-Coordinate | Y-Coordinate | Z-Coordinate |
|--------|--------------|--------------|--------------|
| H      | 1.357396000  | 4.733411000  | -6.182917000 |
| H      | -0.845426000 | 4.204531000  | -7.216953000 |
E(RM062X) = -2401.17668473

- Thermochemistry -

Temperature 298.150 Kelvin.  Pressure 1.00000 Atm.

Zero-point correction= 0.566184 (Hartree/Particle)
Thermal correction to Energy= 0.602292
Thermal correction to Enthalpy= 0.603236
Thermal correction to Gibbs Free Energy= 0.494925

Sum of electronic and zero-point Energies= -2400.610501
Sum of electronic and thermal Energies= -2401.113092
Sum of electronic and thermal Enthalpies= -2401.176685
Sum of electronic and thermal Free Energies= -2401.176180

Charge = 0 Multiplicity = 1
|   |        |        |        |
|---|--------|--------|--------|
| C | -0.81700100 | 3.393930000 | -5.39980100 |
| C | 0.357135000 | 1.926505000 | -6.914005000 |
| C | -0.521073000 | 2.987489000 | -6.702767000 |
| H | -0.490079000 | 3.069993000 | -3.306028000 |
| H | 1.614842000 | 0.434663000 | -6.011924000 |
| H | -1.511529000 | 4.218121000 | -5.227654000 |
| H | 0.586856000 | 1.599266000 | -7.929682000 |
| H | -0.981166000 | 3.495824000 | -7.552238000 |
SUPPORTING INFORMATION

E(RM062X) = -4188.52864413

| 6 | 0.498414000 | 5.698948000 | 0.141072000 |
| 6 | 0.419710000 | 0.144093000 | 3.122991000 |
| 6 | 1.163623000 | 0.980767000 | 2.281248000 |
| 1 | 1.904807000 | 4.105663000 | -0.204565000 |
| 6 | 2.345976000 | 0.980767000 | 2.281248000 |
| 1 | 1.904807000 | 4.105663000 | -0.204565000 |

- Thermochemistry -

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.

Zero-point correction= 0.562847 (Hartree/Particle)
Thermal correction to Energy= 0.600369
Thermal correction to Enthalpy= 0.601313
Thermal correction to Gibbs Free Energy= 0.487125
Sum of electronic and zero-point Energies= -4187.965797
Sum of electronic and thermal Energies= -4187.928275
Sum of electronic and thermal Enthalpies= -4187.927331
Sum of electronic and thermal Free Energies= -4188.041519

Charge = 0 Multiplicity = 1

5

| 1 | 1.208751000 | 6.478610000 | -0.140827000 |
| 6 | 0.840105000 | -0.111170000 | 4.430568000 |
| 1 | 0.245965000 | -0.761476000 | 5.075737000 |
| 6 | -0.376172000 | -1.091599000 | -0.382259000 |
| 6 | 2.097626000 | -3.202862000 | -2.550310000 |
| 6 | 2.128610000 | -1.969095000 | -3.219648000 |
| 1 | 1.783948000 | -1.060478000 | -2.714510000 |
| 4 | 0.455510000 | 0.912958000 | -2.715579000 |
| 6 | 1.163623000 | 0.980767000 | -3.452853000 |
| 6 | 0.703277000 | -4.935401000 | -0.393499000 |
| 6 | 2.507086000 | -2.461149000 | 1.751293000 |
| 1 | 1.457410000 | -2.467603000 | 2.061058000 |
| 6 | -0.538261000 | -7.396746000 | 0.139224000 |
| 6 | -0.1022358000 | -8.353040000 | 0.364319000 |
| 6 | -0.1028639000 | -6.573296000 | -0.877207000 |
| 6 | -0.1894646000 | -6.884690000 | -1.464038000 |
| 6 | 0.567988000 | -6.997818000 | 0.888172000 |
| 6 | 0.952595000 | -7.640777000 | 1.681850000 |
| 6 | 3.038137000 | -3.033915000 | -5.189466000 |
| 6 | 1.3800182000 | -2.986541000 | -6.073140000 |
| 6 | 2.013732000 | 0.469108000 | 4.912535000 |
| 6 | 2.341075000 | 0.273350000 | 5.936508000 |
| 6 | 4.822072000 | -2.012785000 | 2.273842000 |
| 1 | 5.583690000 | -1.678795000 | 2.981106000 |
| 6 | 2.545161000 | -4.350196000 | -3.224591000 |
| 6 | 2.522396000 | -5.323414000 | -2.725778000 |
| 6 | 1.881653000 | 1.769566000 | -2.098468000 |
| 6 | 0.979887000 | 2.328959000 | -2.365885000 |
| 6 | 1.701218000 | 5.039746000 | 0.889083000 |
| 6 | -2.716031000 | 5.302486000 | 1.193822000 |
| 6 | 4.213675000 | -2.823005000 | 0.079041000 |
| 6 | 4.510108000 | -3.109900000 | -0.933957000 |
| 6 | 4.816721000 | 0.346235000 | -1.448644000 |
| 1 | 5.087126000 | -0.216155000 | -1.190700000 |
| 6 | 3.168699000 | 0.495005000 | -0.502718000 |
| 6 | 3.291754000 | 0.044591000 | 0.487745000 |
| 6 | 1.184255000 | -5.773102000 | 0.623450000 |
| 6 | 2.049350000 | -5.469312000 | 1.219083000 |
| 6 | 2.594189000 | -1.885502000 | -4.531813000 |
| 1 | 2.608823000 | -0.920224000 | -5.041997000 |
| 6 | -0.796597000 | 6.040673000 | 0.531610000 |
| 6 | -1.102300000 | 7.088353000 | 0.555050000 |
| 6 | 2.897541000 | 1.621350000 | -3.042584000 |
| 6 | 2.787357000 | 2.065033000 | -4.034945000 |
| 6 | 3.015493000 | -4.266618000 | -4.535507000 |
| 6 | 3.359631000 | -5.165719000 | -5.048270000 |
| 6 | 5.189791000 | -2.407929000 | 0.987098000 |
| 6 | 6.239039000 | -2.384544000 | 0.686477000 |
| 6 | 3.479558000 | -2.045948000 | 2.659517000 |
| 6 | -1.384470000 | -1.739135000 | 3.665861000 |
|   | 1.525043000 | -3.301803000 | -0.775751000 |
|---|-------------|--------------|--------------|
| 14|             |              |              |
E(RM062X) = -4188.52074725

- Thermochemistry -

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.

Zero-point correction= 0.562376 (Hartree/Particle)
Thermal correction to Energy= 0.600281
Thermal correction to Enthalpy= 0.601226
Thermal correction to Gibbs Free Energy= 0.487077

Sum of electronic and zero-point Energies= -4187.958371
Sum of electronic and thermal Energies= -4187.920466
Sum of electronic and thermal Enthalpies= -4187.919522
Sum of electronic and thermal Free Energies= -4188.033670

Charge = 0 Multiplicity = 1
|   |   |   |   |
|---|---|---|---|
| H | -3.994601000 | -3.411435000 | 1.611218000 |
| C | -10.310158000 | -0.629864000 | 0.328722000 |
| H | -10.840034000 | -1.188186000 | 1.102657000 |
| C | -10.332302000 | 0.635726000 | -1.729986000 |
| H | -10.879390000 | 1.073796000 | -2.566817000 |
| Si | -6.369246000 | 0.495583000 | -0.443675000 |
- Thermochemistry -

Temperature 298.15 Kelvin. Pressure 1.00000 Atm.

Zero-point correction = 0.563685 (Hartree/Particle)
Thermal correction to Energy = 0.600817
Thermal correction to Enthalpy = 0.601762
Thermal correction to Gibbs Free Energy = 0.488787
Sum of electronic and zero-point Energies = -4187.955797
Sum of electronic and thermal Energies = -4187.918664
Sum of electronic and thermal Enthalpies = -4187.917720
Sum of electronic and thermal Free Energies = -4188.030695

Charge = 0 Multiplicity = 1

\[ E(RM062X) = -4188.51948155 \]
| Element | X-Coordinate  | Y-Coordinate  | Z-Coordinate |
|---------|--------------|--------------|--------------|
| C       | -6.413210000| -0.054337000| 2.932642000  |
| H       | -6.785818000| -0.822144000| 3.613186000  |
| C       | -10.474602000| -0.658306000| -1.287364000|
| H       | -11.230234000| -1.026753000| -0.590793000|
| C       | -9.815753000| -0.027958000| -3.523007000|
| H       | -10.050792000| 0.090511000  | -4.582478000|
| Si      | -6.496658000| 0.713389000  | -1.181064000|
SUPPORTING INFORMATION

E(RM062X) = -4188.51557921

- Thermochemistry -

Temperature 298.150 Kelvin, Pressure 1.00000 Atm.

Zero-point correction= 0.563158 (Hartree/Particle)
Thermal correction to Energy= 0.600504
Thermal correction to Enthalpy= 0.601448
Thermal correction to Gibbs Free Energy= 0.488464
Sum of electronic and zero-point Energies= -4187.952421
Sum of electronic and thermal Energies= -4187.915075
Sum of electronic and thermal Enthalpies= -4187.914131
Sum of electronic and thermal Free Energies= -4188.027115

Charge = 0 Multiplicity = 1
### SUPPORTING INFORMATION

|   |   |   |   |
|---|---|---|---|
| C | 1.913495000 | -2.459400000 | 3.878143000 |
| H | 1.354404000 | -1.903862000 | 4.633411000 |
| Ge | 1.535577000 | -3.276391000 | -0.260280000 |
SUPPORTING INFORMATION

- Thermochemistry -

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.

Zero-point correction = 0.853674 (Hartree/Particle)
Thermal correction to Energy = 0.907708
Thermal correction to Enthalpy = 0.908652
Thermal correction to Free Energy = 0.761119

Sum of electronic and zero-point Energies = -3018.118558
Sum of electronic and thermal Energies = -3018.064524
Sum of electronic and thermal Enthalpies = -3018.211113
Sum of electronic and thermal Free Energies = -3018.211113

Charge = 0 Multiplicity = 1
| Atom | X Coordinates | Y Coordinates | Z Coordinates |
|------|---------------|---------------|---------------|
| H    | 5.867673000   | 5.031945000   | 1.083339000   |
| C    | 4.888765000   | 0.861969000   | 4.735675000   |
| H    | 4.347870000   | 0.505915000   | 5.630218000   |
| H    | 5.468241000   | 1.761300000   | 5.017084000   |
| C    | -2.595364000  | 2.976187000   | 6.555860000   |
| H    | -3.285393000  | 3.214282000   | 7.360960000   |
| C    | -5.596706000  | 2.263580000   | -2.382374000  |
| H    | -5.835580000  | 1.454325000   | -3.082196000  |
| H    | -5.214446000  | 3.120952000   | -2.958474000  |
| H    | -6.538200000  | 2.588040000   | -1.908739000  |
| C    | -0.510878000  | 3.354905000   | 5.398884000   |
| H    | 0.435343000   | 3.892823000   | 5.303521000   |
| C    | 2.420988000   | 2.627072000   | 2.717849000   |
| H    | 1.799399000   | 1.826189000   | 2.294240000   |
| H    | 1.782501000   | 3.509206000   | 2.912987000   |
| C    | 6.655845000   | -0.709624000  | -0.804780000  |
| H    | 7.677840000   | -0.908439000  | -0.429151000  |
| H    | 6.678473000   | -0.829764000  | -1.902942000  |
| C    | 5.661391000   | -1.681179000  | -0.207067000  |
| H    | 4.662609000   | -1.488097000  | -0.621338000  |
| H    | 5.955840000   | -2.714916000  | -0.460312000  |
| C    | 3.039094000   | 2.147068000   | 4.018114000   |
| H    | 3.522150000   | 2.975602000   | 4.568727000   |
| H    | 2.251053000   | 1.729820000   | 4.670755000   |
| C    | 6.526177000   | 2.928072000   | -0.581664000  |
| H    | 7.269041000   | 3.736186000   | -0.708845000  |
| H    | 5.760766000   | 3.036543000   | -1.371525000  |
| C    | 7.206869000   | 1.590013000   | -0.716210000  |
| H    | 7.608774000   | 1.491954000   | -1.740039000  |
| H    | 8.052112000   | 1.507405000   | -0.006789000  |
| C    | -1.386399000  | 3.664461000   | 6.441472000   |
| H    | -1.128746000  | 4.443486000   | 7.161664000   |
SUPPORTING INFORMATION

C
C
N
O
O
Na
-

E(RM062X) = -3018.97076627

Thermochemistry

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.

Zero-point correction= 0.853683 (Hartree/Particle)
Thermal correction to Energy= 0.907593
Thermal correction to Enthalpy= 0.908537
Thermal correction to Gibbs Free Energy= 0.761929

Sum of electronic and zero-point Energies= -3018.117084
Sum of electronic and thermal Energies= -3018.063174
Sum of electronic and thermal Enthalpies= -3018.062229
Sum of electronic and thermal Free Energies= -3018.208838

Charge = 0 Multiplicity = 1

Si
P
Na
O
O
O
O
N
N
C
C
C
C
C
C
C

H

-2.501625000 0.530506000 2.249758000
1.220073000 0.145879000 0.010974000
2.562729000 -2.247903000 4.411481000
2.600088000 -4.654942000 3.447391000
2.477241000 -3.978947000 6.127051000
-1.003147000 0.058628000 1.599078000
4.388513000 -0.890622000 5.376869000
0.571080000 -2.103391000 5.778662000
1.891298000 0.079338000 4.866285000
4.734485000 -2.896790000 3.628926000
-1.178741000 1.514257000 -0.107137000
1.746274000 -1.703194000 2.233809000
-0.467588000 0.641555000 0.504369000
-0.735093000 2.092342000 -1.305683000
-0.997775000 1.445129000 -2.529130000
-3.961393000 0.433929000 1.071794000
-2.285391000 2.249524000 2.963665000
1.484912000 -0.965931000 1.369777000
-2.731976000 -0.776884000 3.580669000

C
H
H
C
C
C
C
C
C
C
C
C
C
C

-1.690404000 0.109040000 -2.532470000
-1.058526000 -0.662995000 -2.064023000
-1.921596000 -0.211620000 -3.557136000
-2.626462000 0.147733000 -1.952791000
-2.017812000 -1.985224000 3.529249000
-1.266600000 -2.135436000 2.750353000
-4.697863000 -0.754585000 0.954362000
-4.432423000 -1.624010000 1.562316000
-0.608347000 2.068124000 -3.719681000
-0.813011000 1.563121000 -4.668173000
-3.669141000 -0.597477000 4.611511000
-4.236383000 0.336059000 4.679782000
-4.340387000 1.533494000 0.282170000
-3.769761000 2.463296000 0.345540000
-2.224693000 -2.988219000 4.474249000
-1.677817000 -3.902999000 4.418018000
0.029130000 3.311190000 -3.730407000
-3.379207000 3.046739000 3.335600000
-4.399757000 2.683920000 3.180515000
-5.769975000 -0.850807000 0.063767000
-6.324501000 -1.787152000 -0.022134000
-3.892716000 -1.595659000 5.560223000
-6.426683000 -1.439937000 6.355066000
-0.990765000 2.758505000 3.157739000
-0.121621000 2.163212000 2.859756000
-0.102518000 3.352558000 -1.290532000
2.797805000 -5.671330000 4.405822000
3.536301000 -6.415887000 4.062637000
1.843478000 -6.205324000 4.532930000
-3.181223000 -2.796027000 5.488717000
-3.359542000 -3.580783000 6.227046000
-6.131113000 0.250133000 -0.711070000
-6.969935000 0.178493000 -1.406307000
0.270920000 3.939644000 -2.501354000
0.764385000 4.913538000 -2.485476000
3.261299000 -5.082301000 5.730896000
3.251355000 -5.868852000 6.507907000
4.288470000 -4.700844000 5.644902000
-5.417686000 1.446431000 -0.596933000
-5.697501000 2.310188000 -1.202940000
0.143694000 4.032059000 0.027474000
-0.801190000 4.178003000 0.574657000
0.624965000 5.009349000 -0.113211000
0.790609000 3.414754000 0.671663000
2.590906000 0.499069000 6.011661000
2.389474000 -0.165109000 6.872315000
2.306820000 1.528487000 6.296646000
1.134224000 -4.289582000 6.427696000
1.077555000 -5.030095000 7.245611000
0.620280000 -4.707590000 5.544872000
| Element | X         | Y         | Z         |
|---------|-----------|-----------|-----------|
| C       | 4.058878  | 0.046179  | 5.679601  |
| H       | 4.261859  | 1.091822  | 4.806599  |
| H       | 4.656316  | 0.816191  | 6.531921  |
| C       | -0.442427 | -3.015910 | 6.837101  |
| H       | -0.620767 | -3.225333 | 7.054808  |
| H       | 0.906624  | -0.202052 | 7.752083  |
| C       | -3.186807 | 4.312250  | 3.893231  |
| H       | -4.048433 | 4.920902  | 4.173909  |
| C       | 0.436880  | 3.976662  | -5.020145 |
| H       | 0.242802  | 3.324599  | -5.883014 |
| H       | 1.505269  | 4.231427  | -5.017710 |
| C       | -0.120281 | 4.914979  | -5.175692 |
| C       | -0.794561 | 4.023049  | 3.713415  |
| H       | 0.218759  | 4.406614  | 3.849149  |
| C       | 0.484819  | 0.108742  | 4.965631  |
| H       | 0.113027  | -0.184379 | 3.971947  |
| H       | 0.122717  | 1.127452  | 5.194558  |
| C       | 4.919488  | -4.123297 | 2.963902  |
| H       | 5.342100  | -4.874544 | 3.857908  |
| H       | 5.630706  | -4.013235 | 2.125372  |
| C       | 3.575847  | -4.572276 | 2.431583  |
| H       | 3.199335  | -3.833961 | 1.710810  |
| H       | 3.690698  | -5.541419 | 1.914755  |
| C       | -0.027578 | -0.852172 | 6.018155  |
| H       | 0.231643  | -0.503793 | 7.035031  |
| H       | -1.129055 | -0.915551 | 5.960692  |
| C       | 5.636791  | -1.024489 | 4.741605  |
| H       | 6.457300  | -0.683566 | 5.398588  |
| H       | 5.656102  | -0.411946 | 3.821854  |
| C       | 5.842437  | -2.474603 | 4.387423  |
| H       | 6.778103  | -2.573461 | 3.809808  |
| H       | 5.937727  | -3.092173 | 5.300956  |
| C       | -1.893520 | 4.800624  | 4.083202  |
| H       | -1.741840 | 5.792038  | 4.514521  |
$E(RM062X) = -643.695985167$

**Thermochemistry**

Temperature 298.150 Kelvin, Pressure 1.00000 Atm.

Zero-point correction = 0.048416 (Hartree/Particle)

Thermal correction to Energy = 0.054670

Thermal correction to Enthalpy = 0.055615

Thermal correction to Gibbs Free Energy = 0.018948

Sum of electronic and zero-point Energies = -643.647596

Sum of electronic and thermal Energies = -643.641342

Sum of electronic and thermal Enthalpies = -643.640398

Sum of electronic and thermal Free Energies = -643.677065

Charge = 0 Multiplicity = 1

P  -6.462984000  12.994111000  -2.390329000

O  -7.753337000  13.241515000  -1.464317000

O  -6.398098000  14.362124000  -3.216899000

O  -5.192803000  13.153788000  -1.440214000

O  -6.473181000  11.726294000  -3.132667000

H  -5.158786000  13.994944000  -0.957175000

H  -8.166206000  12.407211000  -1.189551000

H  -7.119319000  14.458140000  -3.859669000
E(RM062X) = -448.860823383

- Thermochemistry -

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Temperature 298.150 Kelvin. Pressure 1.00000 Atm.

Zero-point correction = 0.146701 (Hartree/Particle)
Thermal correction to Energy = 0.155998
Thermal correction to Enthalpy = 0.156942
Thermal correction to Gibbs Free Energy = 0.114327
Sum of electronic and zero-point Energies = -448.714123
Sum of electronic and thermal Energies = -448.704826
Sum of electronic and thermal Enthalpies = -448.703881
Sum of electronic and thermal Free Energies = -448.746496

Charge = 0 Multiplicity = 1

Si  -1.725415000  -0.002968000  -0.088405000
C   -3.025025000  0.143389000   1.266723000
H   -3.785958000  -0.648696000  1.179087000
H   -2.568884000  0.060542000  2.266252000
H   -3.544014000   1.113920000  1.212752000
C   -2.547394000   0.177865000  -1.772654000
H   -1.806168000   0.104242000  -2.584674000
H   -3.303868000  -0.606232000  -1.936362000
H   -3.050186000   1.153914000  -1.865828000
C   -0.881373000  -1.682246000   0.026450000
H   -0.414519000  -1.823767000  1.014517000
H   -1.601731000  -2.502250000  -0.124695000
H   -0.091589000  -1.784402000  -0.734905000
C   -0.442567000   1.358907000   0.130263000
H   0.064985000   1.272924000  1.104544000
H   0.328970000   1.308107000  -0.654752000
H   -0.906808000   2.356755000   0.079169000
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Author Contributions

G. Le Corre performed the synthesis and characterization of materials and wrote the original manuscript (lead contribution)

J.J. Gamboa Carballo performed the theoretical calculations and corrected the manuscript (supporting contribution)

Z. Li co-initiated the project and corrected the manuscript (supporting contribution)

H. Grützmacher provided the funding, administered the project, and corrected the manuscript (lead contribution)