The Reactivity of Isomeric Nitrenium Lewis Acids with Phosphines, Carbenes, and Phosphide

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1. General Remarks

All reactions and work-up procedures were performed under an inert atmosphere of dry, oxygen-free N\textsubscript{2} by means of standard Schlenk techniques or glovebox techniques (MBraun glovebox equipped with a -35 °C freezer) unless otherwise specified. All glassware was oven-dried and cooled under vacuum before use. Dichloromethane (CH\textsubscript{2}Cl\textsubscript{2}), 1,2-difluorobenzene (ODFB), and toluene were distilled over CaH\textsubscript{2} and tetrahydrofuran (THF) was distilled over Na/benzophenone. Pentane and hexane were collected from a Grubbs-type column system manufactured by Innovative Technology and degassed. Solvents were stored over activated 4 Å molecular sieves. Molecular sieves, type 4 Å (pellets, 3.2 mm diameter) purchased from Sigma Aldrich were activated prior to usage by iteratively heating under vacuum for 24 hours. CDCl\textsubscript{3} purchased from Cambridge Isotope Laboratories was vacuum distilled over CaH\textsubscript{2}. Unless otherwise mentioned, chemicals were purchased from Sigma Aldrich or TCI. Spiro[fluorene-9,3′-indazole],\textsuperscript{S1} 1,3-Bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene (SIMes),\textsuperscript{S2} and bis(diisopropylamino)cyclopropenylidene (BAC)\textsuperscript{S3} were prepared according to previously reported synthetic procedures. Tert-butyl chloride was degassed and stored over activated 4 Å molecular sieves in a Schlenk flask prior to use. NMR spectra were recorded at room temperature (298K) unless otherwise mentioned on a Bruker Avance III 400 MHz, an Agilent DD2 500, and an Agilent DD2 600 Spectrometers. Spectra were referenced to the residual solvent signals (CDCl\textsubscript{3}: \textsuperscript{1}H= 7.26 ppm and \textsuperscript{13}C = 77.2 ppm). Chemical shifts (\(\delta\)) are reported in ppm and coupling constants (\(J\)) are listed as absolute values in Hz. Multiplicities are reported as singlet (s), doublet (d), triplet (t), quartet (q), multiplet (m), overlapping (ov), and broad (br). Electron paramagnetic resonance (EPR) measurements were performed at 298 K using a Bruker ECS-EMX X-band EPR spectrometer equipped with an EP4119HS cavity. Simulations were performed using PEST WinSIM software. High resolution mass spectrometry was performed in house employing electrospray ionisation techniques in positive ion mode on an AB/Sciex QStarXL mass spectrometer (ESI).

S1. G. Baum and H. Shechter, J. Org. Chem. 1976, 12, 2120.
S2. X. Bantreil and S. P. Nolan, Nature Protocols 2011, 6, 69.
S3. V. Lavallo, Y. Canac, B. Donnadieu, W. W. Schoeller, and G. Bertrand, Science 2006, 5774, 722.

2. Synthesis and Characterisations

2.1 Compound 1 and 2

Tert-butyl chloride (165 µL, 1.50 mmol) was added dropwise to a dichloromethane solution of spiro[fluorene-9,3′-indazole] (335.4 mg, 1.25 mmol) and AgBF\textsubscript{4} (243.3 mg, 1.25 mmol). Upon addition, the solution turned to dark red with white precipitates and was allowed to stir at room temperature for 10 min. The suspension was filtered and the volatiles were removed under vacuum. The orange solid was washed with dichloromethane and toluene (v/v=1/4), dried under vacuum. The crude mixture was again dissolved in dichloromethane (2 mL), layer with pentane (0.8 mL), and stored at -35°C overnight. Compound 1 was decanted, dried under vacuum, and obtained as bright orange crystals. To the remaining aliquot, 1 mL of pentane was added and the solution was stored at -35°C overnight again. Compound 2 was decanted, dried under vacuum, and obtained as a dusty orange powder. If
1 and 2 still have a trace amount of impurities, further recrystallization from saturated CH₂Cl₂ solution layering with pentane would yield pristine products.

![Figure S1: ¹H (CDCl₃) NMR spectrum of the crude mixture.](image)

1: 

Yield: 122.6 mg (24% isolated yield). ¹H NMR (400 MHz, CDCl₃): δ 8.91 (d, J_H-H = 8.6 Hz, Ar, 1H), 8.07 (t, J_H-H = 8.1 Hz, Ar, 1H), 7.96 (d, J_H-H = 7.8 Hz, Ar, 2H), 7.83 (t, J_H-H = 7.6 Hz, Ar, 1H), 7.64 (t, J_H-H = 7.6 Hz, Ar, 2H), 7.35 (ov, Ar, 3H), 6.76 (d, J_H-H = 7.8 Hz, Ar, 2H), 2.16 (s, tBu, 9H). ¹¹B{¹H} NMR (128 MHz, CDCl₃): δ -0.9 (s). ¹⁹F{¹H} NMR (377 MHz, CDCl₃): δ -152.8 (s). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 145.6, 144.7, 144.1, 136.0, 132.9, 132.3, 132.1, 130.0, 125.0, 124.6, 122.4, 122.4, 97.1 (fluorene-C), 79.5, 29.3. ESI MS: m/z: 325.1699 (calcd for M+: 325.1699).
Figure S2: $^1H$ (CDCl$_3$) NMR spectrum of 1.

Figure S3: $^{11}B(1H)$ (CDCl$_3$) NMR spectrum of 1.
Figure S4: $^{19}$F$^{1}$H (CDCl$_3$) NMR spectrum of 1.

Figure S5: $^{13}$C$^{1}$H (CDCl$_3$) NMR spectrum of 1.

2:

Yield: 336.1 mg (65% isolated yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.83 (d, $^3$J$_{H-H}$ = 8.1 Hz, Ar, 1H), 8.00 - 7.82 (ov, Ar, 4H), 7.64 (td, $^3$J$_{H-H}$ = 7.6 Hz, $^4$J$_{H-H}$ = 1.0 Hz, Ar, 2H), 7.39 (td, $^3$J$_{H-H}$ = 7.6 Hz, $^4$J$_{H-H}$ = 1.0 Hz, Ar, 2H), 7.05 (dd, $^3$J$_{H-H}$ = 7.6 Hz, $^4$J$_{H-H}$ = 0.9 Hz, Ar, 2H), 7.01 (d, $^3$J$_{H-H}$ = 6.6 Hz, Ar, 1H), 1.54 (s, tBu, 9H). $^{11}$B$^{1}$H NMR (128 MHz, CDCl$_3$): $\delta$ -1.0 (s). $^{19}$F$^{1}$H NMR (377 MHz, CDCl$_3$): $\delta$ -152.5 (s). $^{13}$C$^{1}$H NMR (126 MHz, CDCl$_3$): $\delta$ 151.1, 143.1, 142.5, 140.2, 133.0, 132.6, 132.5, 130.4, 129.9, 125.1, 122.1, 99.6 (fluorene-C), 79.7, 30.1. ESI MS: m/z: 325.1693 (calcd for M+: 325.1699).
Figure S5: $^1$H (CDCl$_3$) NMR spectrum of 2.

Figure S6: $^{11}$B$^{{}^1}$H} (CDCl$_3$) NMR spectrum of 2.

Figure S7: $^{19}$F$^{{}^1}$H} (CDCl$_3$) NMR spectrum of 2 (Asterisk denoted ODFB impurity in CDCl$_3$).
Figure S8: $^{13}$C($^1$H) (CDCl$_3$) NMR spectrum of 2.

2.2 Compound 3

To a solution of 1 (41.2 mg, 0.10 mmol) in dichloromethane (3 mL), a THF solution of PMe$_3$ (1.0 M, 0.12 mL, 0.12 mmol) was added dropwise. The solution was allowed to stir at ambient temperature for 10 mins. All volatiles were removed in vacuo and the residue was washed with hexane (2 x 1 mL) and dried under vacuum. Compound 3 was obtained as a white powder. Single crystals suitable for X-ray diffraction were grown from liquid diffusion of pentane into a saturated dichloromethane solution at -35 °C. Yield: 46.3 mg (95% isolated yield).

$^1$H NMR (400 MHz, CDCl$_3$): δ 7.76 (t, $^3$J$_{H-H}$ = 8.1 Hz, Ar, 2H), 7.59 – 7.46 (m, Ar, 3H), 7.42 – 7.22 (m, Ar, 4H), 7.11 (td, $^3$J$_{H-H}$ = 7.5 Hz, $^2$J$_{H-H}$ = 1.1 Hz, Ar, 1H), 6.80 (d, $^3$J$_{H-H}$ = 7.7 Hz, Ar, 1H), 6.63 (d, $^3$J$_{H-H}$ = 7.7 Hz, Ar, 1H), 1.74 (d, $^3$J$_{P-H}$ = 12.8 Hz, PMe$_3$, 9H), 1.40 (s, tBu, 9H).

$^{11}$B($^1$H) NMR (128 MHz, CDCl$_3$): δ -1.1 (s).

$^{31}$P($^1$H) NMR (162 MHz, CDCl$_3$): δ 62.8 (s).

$^{13}$C($^1$H) NMR (126 MHz, CDCl$_3$): δ 150.1 (d, $^3$J$_{C-P}$ = 2.2 Hz), 146.9 (d, $^2$J$_{C-P}$ = 7.0 Hz), 145.3 (d, $^2$J$_{C-P}$ = 6.8 Hz), 142.2, 138.7, 135.9, 132.1, 130.4, 128.9, 128.7, 128.3, 126.8, 126.4, 125.5, 123.7, 121.1 (d, $^2$J$_{C-P}$ = 11.6 Hz), 116.8, 81.3 (d, $^2$J$_{C-P}$ = 3.2 Hz), 64.2 (d, $^2$J$_{C-P}$ = 5.8 Hz), 30.2, 13.2 (d, $^2$J$_{C-P}$ = 64.1 Hz). ESI MS: m/z: 401.2141 (calcd for M+: 401.2141).
Figure S9: $^1$H (CDCl$_3$) NMR spectrum of 3 (Asterisk denoted hexane).

Figure S10: $^{11}$B($^1$H) (CDCl$_3$) NMR spectrum of 3.
Figure S11: $^{19}$F{$^{[1]H}$} (CDCl$_3$) NMR spectrum of 3. (Asterisk denoted ODFB residue in CDCl$_3$)

Figure S12: $^{31}$P{$^{[1]H}$} (CDCl$_3$) NMR spectrum of 3.

Figure S13: $^{11}$C{$^{[1]H}$} (CDCl$_3$) NMR spectrum of 3.
2.3 Compound 4

To a solution of 2 (41.2 mg 0.1 mmol) in dichloromethane (3 mL), a THF solution of PMe3 (1.0 M, 0.12 mL, 0.12 mmol) was added dropwise. The solution was allowed to stir at room temperature for 10 min. All volatiles were removed \textit{in vacuo} and the residue was washed with hexane (2 X 1 mL) and dried under vacuum. Compound 4 was obtained as an orange powder. Crystals were grown from liquid diffusion of pentane into a saturated dichloromethane solution at room temperature. Yield: 44.1 mg (92% isolated yield). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.87 – 7.78 (ov, 4H), 7.68 (m, 1H), 7.44 (t, $^3$J$_{H-H}$ = 7.5 Hz, 2H), 7.33 – 7.16 (m, ov with CDCl$_3$ signal, proposed 3H), 6.78 (d, $^2$J$_{H-P}$ = 13.5 Hz, 1H), 6.28 (s, CH, 1H), 2.00 (d, $^2$J$_{H-P}$ = 14.2 Hz, PMe$_3$, 9H), 1.46 (s, tBu, 9H). $^{11}$B($^1$H) NMR (128 MHz, CDCl$_3$): $\delta$ -1.0 (s). $^{31}$P($^1$H) NMR (126 MHz, CDCl$_3$): $\delta$ 22.0 (s). $^{19}$F($^1$H) NMR (377 MHz, CDCl$_3$): $\delta$ -149.6. $^{13}$C($^1$H) NMR (126 MHz, CDCl$_3$): $\delta$ 154.2, 146.6, 141.8 (d, $J_{C-P}$ = 12.9 Hz), 141.4, 130.5 (d, $J_{C-P}$ = 11.3 Hz), 129.7 (d, $J_{C-P}$ = 11.3 Hz), 128.0 (d, $J_{C-P}$ = 31.9 Hz), 125.3, 123.5, 122.8, 120.5, 118.9 (d, $J_{C-P}$ = 13.4 Hz), 70.4, 47.2 (fluorene-C), 27.1, 9.3 (d, $J_{C-P}$ = 56.8 Hz). ESI MS: m/z: 401.2145 (calcd for M+: 401.2141).

Figure S14: $^1$H (CDCl$_3$) NMR spectrum of 4.
Figure S15: $^{11}$B-$^1$H (CDCl$_3$) NMR spectrum of 4.

Figure S16: $^{31}$P-$^1$H (CDCl$_3$) NMR spectrum of 4.
Figure S17: $^{19}$F{H} (CDCl$_3$) NMR spectrum of 4.

Figure S18: $^{13}$C{H} (CDCl$_3$) NMR spectrum of 4.
2.4 Compound 5

To a solution of 2 (41.2 mg 0.1 mmol) in dichloromethane (3 mL), nBu3P (22.7 mg, 0.11 mmol) was added dropwise. The solution was allowed to stir at room temperature for 10 min. All volatiles were removed in vacuo and the residue was washed with hexane (2 X 1 mL) and dried under vacuum. Compound 5 was obtained as an orange powder. Single crystals suitable for X-ray diffraction were grown from liquid diffusion of pentane into a saturated dichloromethane solution at -35 °C. Yield: 241.3 mg (95% isolated yield). 1H NMR (500 MHz, CDCl3): δ 7.86 (d, JH-H = 7.7 Hz, Ar, 2H), 7.76 – 7.68 (ov, Ar, 2H), 7.44 (t, JH-H = 7.4 Hz, Ar, 2H), 7.31 – 7.21 (ov, Ar, 4H), 6.65 (d, JH-P = 12.3 Hz, Ar, 1H), 6.28 (s, CH, 1H), 2.27 (td, JH-P = 12.2 Hz, JH-H = 7.0 Hz, PnBu3, 6H), 1.48 (s, tBu, 9H), 1.25 (dt, JH-P = 32.0 Hz, JH-H = 8.3 Hz, PnBu3, 12H), 0.77 (t, JH-H = 7.2 Hz, , PnBu3, 9H). 11B{1H} NMR (128 MHz, CDCl3): δ -1.0 (s). 31P{1H} NMR (162 MHz, CDCl3): δ 29.9 (s). 19F{1H} NMR (377 MHz, CDCl3): δ -151.4. 13C{1H} NMR (126 MHz, CDCl3): δ 153.8, 146.9, 141.9 (d, JC-P = 11.4 Hz), 141.2, 132.4, 131.4 (d, JC-P = 9.3 Hz), 130.9 (d, JC-P = 9.1 Hz), 127.8 (d, JC-P = 39.5 Hz), 125.1, 120.4, 118.9 (d, JC-P = 12.3 Hz), 70.3, 46.9 (fluorene-C), 27.0, 23.6 (overlapped with the doublet of 23.5 ppm), 23.5, 19.40(d, JC-P = 48.4 Hz), 13.2. ESI MS: m/z: 527.3544 (calcd for M+: 527.3550).
Figure S20: $^1$H (CDCl₃) NMR spectrum of 5 (Asterisk denoted ODFB residue in CDCl₃).

Figure S21: $^{11}$B($^1$H) (CDCl₃) NMR spectrum of 5.
Figure S22: $^{31}\text{P}^1\text{H}$ (CDCl$_3$) NMR spectrum of 5.

Figure S23: $^{19}\text{F}^1\text{H}$ (CDCl$_3$) NMR spectrum of 5. (Asterisk denoted ODFB residue in CDCl$_3$).
To a solution of 1 (41.2 mg, 0.1 mmol) in ODFB (2 mL), a solution of SIMes (30.8 mg, 0.1 mmol) in ODFB was added dropwise. The solution was allowed to stir at ambient temperature for 10 min. All volatiles were removed in vacuo and the residue was washed with hexane (2 X 1 mL) and dried under vacuum. Compound 6 was obtained as a purple powder. Yield: 48.3 mg (67% isolated yield). Compound 6 decomposes readily in halogenated solvents. Attempts to observe the product by high-resolution mass spectrometry failed due to the instability of the compound under mass spectrometry conditions, by either ESI or DART methods. In positive mode ESI, [M-1]+ and [M-2]+ were observed.

Figure S25: Experimental and simulated EPR spectra of 6.
Table S1. Experimental and simulated EPR data of 6.

| MF (Par file) | HCF (sim) | G shift | g-factor | Hyperfine couplings (sim) |
|---------------|-----------|---------|----------|---------------------------|
| 9.35385       | 3335.4    | -2.097  | 2.004933387 | (14N) 11.50 G, (14N) 4.18 G, (1H) 0.59 G, (1H) 0.41 G, (1H) 0.21 G, (14N) 0.98G, (14N) 0.33 G |

Scheme S1. proposed redox scheme of 6.

2.6 Compound 7

To a solution of 2 (41.2 mg, 0.1 mmol) in ODFB (2 mL), a solution of SIMes (30.8 mg, 0.1 mmol) in ODFB was added dropwise. The solution was allowed to stir at ambient temperature for 10 min. All volatiles were removed in vacuo and the residue was washed with hexane (2 X 1 mL) and dried under vacuum. Compound 7 was obtained as a red powder. Single crystals suitable for X-ray diffraction were grown from liquid diffusion of pentane into a saturated THF solution at -35 °C. Yield: 57.6 mg (80% isolated yield). Compound 7 decomposes readily in halogenated solvents. Attempts to observe the product by high-resolution mass spectrometry failed due to the instability of the compound under mass spectrometry conditions, by either ESI or DART methods. In positive mode ESI, [M-1]+ and [M-2]+ were observed.
Figure S26: Experimental and simulated EPR spectra of 7.

Table S2.  Experimental and simulated EPR data of 7.

| MF (Par file) | HCF (sim) | G shift | g-factor | Hyperfine couplings (sim) |
|--------------|-----------|---------|----------|--------------------------|
| 9.346389     | 3332      | -0.195  | 2.004234885 | (14N) 6.67 G, (14N) 9.386 G, (1H) 0.597 G, (1H) 2.666 G, (1H) 0.532 G, (14N) 0.481 G, (14N) 0.391 G |

Scheme S2. Proposed redox scheme of 7.

2.7 Compound 8

To a solution of 2 (41.2 mg, 0.1 mmol) in ODFB (2 mL), a solution of BAC (24.0 mg, 0.1 mmol) in ODFB was added dropwise. The solution was allowed to stir at ambient temperature for 10 min. All volatiles were removed in vacuo and the residue was washed with hexane (2 X 1 mL) and dried under vacuum. Compound 8 was isolated as a black powder. Single crystals suitable for X-ray diffraction were grown from liquid diffusion of pentane into a saturated THF solution at -35 °C. Yield: 49.8 mg (78% isolated yield). 1H NMR (500 MHz, CDCl3): δ 7.79 – 7.70 (m, Ar, 2H), 7.42-7.39 (ov, Ar, 4H), 7.31 – 7.20 (ov, Ar, 3H), 6.92 (d, JH-H = 8.2 Hz, Ar,
1H), 6.78 (t, \text{J}_{	ext{H-H}} = 7.5 \text{ Hz}, \text{Ar}, 1\text{H}), 6.14 (d, \text{J}_{	ext{H-H}} = 7.6 \text{ Hz}, \text{Ar}, 1\text{H}), 4.19 (\text{hept}, \text{J}_{	ext{H-H}} = 6.8 \text{ Hz}, \text{iPr}, 4\text{H}), 1.52 – 1.45 (m, \text{iPr}, 25\text{H}), 1.02 (s, \text{tBu}, 9\text{H}). \text{\textsuperscript{11}B{\textsuperscript{1}H} NMR (128 MHz, CDCl\textsubscript{3})}: \delta -1.0 (s). \text{\textsuperscript{19}F{\textsuperscript{1}H} NMR (377 MHz, CDCl\textsubscript{3})}: \delta -153.0 (br). \text{\textsuperscript{13}C{\textsuperscript{1}H} NMR (126 MHz, CDCl\textsubscript{3})}: \delta 145.24, 134.70, 130.92, 129.33, 129.05, 127.80, 124.79, 121.52, 120.37, 115.29, 112.94, 79.81 (fluorene-C), 68.14, 62.10, 29.76, 25.77. Attempts to observe the product by high-resolution mass spectrometry failed due to the instability of the compound under mass spectrometry conditions, by either ESI or DART methods. In positive mode ESI, [\text{C}_{23}\text{H}_{21}\text{N}_{2}]^+ was observed.

Figure S27: \textsuperscript{1}H (CDCl\textsubscript{3}) NMR spectrum of 8.

Figure S28: \textsuperscript{11}B{\textsuperscript{1}H} (CDCl\textsubscript{3}) NMR spectrum of 8.
Figure S29: $^{19}$F{^1}H (CDCl$_3$) NMR spectrum of 8 (Asterisk denoted ODFB impurity in CDCl$_3$).

Figure S30: $^{13}$C{^1}H (CDCl$_3$) NMR spectrum of 8.

### 3. Crystallographic data

**X-ray Diffraction Studies**

Single crystals were coated with paratone oil, mounted on a cryoloop and frozen under a stream of cold nitrogen. Data were collected on a Bruker Apex2 X-ray diffractometer at 150(2) K for compound 1-3 and 5-7 crystals using graphite monochromated Mo-Kα radiation (0.71073 Å). Data were collected using Bruker APEX-2 software and processed using SHELX and an absorption correction applied using multi-scan within the APEX-2 program. Compound 4 was collected with a Cu microsource and Bruker CMOS PHOTON II detector gave very weak data. However the structure obtained is of sufficient precision to allow us to identify and confirm the compound synthesised. All structures were solved and refined by
intrinsic phasing within the SHELXTL package. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre.

S4. (a) G. M. Sheldrick, SADABS, An Empirical Absorption Correction Program for Area Detector Data; University of Göttingen, Göttingen, Germany, 1996; (b) G. M. Sheldrick, SHELXS-97 and SHELXL-97, University of Göttingen, Göttingen, Germany, 1997 and 2008; (c) G. M. Sheldrick, SHELXL-2014, University of Göttingen, Göttingen, Germany, 2014; (d) O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, OLEX2: a complete structure solution, refinement and analysis program, J. Appl. Cryst., 2009, 42, 339-341; (e) SMART Version 5.628, Bruker AXS Inc., Madison, WI, 2002; (f) SAINT+ Version 6.22a, Bruker AXS Inc., Madison, WI, 2002; (g) SAINT+ Version v7.68A, Bruker AXS Inc., Madison, WI, 2009; (h) SHELXLT NT/2000, Version 6.1, Bruker AXS Inc., Madison, WI, 2002.

Table S3. Crystallographic data and refinement parameters for 1-5, 7, and 8.

|          | 1                | 2                | 3                |
|----------|------------------|------------------|------------------|
| Empirical formula | C_{25}H_{25}BCl_{4}F_{4}N_{2} | C_{23}H_{22}BF_{4}N_{2} | C_{26}H_{30}BF_{4}N_{2}P |
| Formula weight | 582.08           | 412.23           | 488.30           |
| Colour     | Red              | Orange           | Colourless       |
| Crystal system | monoclinic       | monoclinic       | orthorhombic     |
| Space group | C2/c             | P2_1/n           | P2_1212_1        |
| a/Å        | 22.3554(13)      | 11.099(7)        | 10.895(2)        |
| b/Å        | 11.5871(6)       | 16.092(12)       | 14.037(3)        |
| c/Å        | 22.7385(19)      | 11.325(5)        | 15.791(3)        |
| α/°        | 90               | 90               | 90               |
| β/°        | 113.902(3)       | 94.27(2)         | 90               |
| γ/°        | 90               | 90               | 90               |
| Volume/Å³  | 5384.9(6)        | 2017(2)          | 2414.9(7)        |
| Z          | 8                | 4                | 4                |
| \(\rho_{calc}/\text{cm}^3\) | 1.436            | 1.357            | 1.343            |
| F(000)     | 2384.0           | 856.0            | 1024.0           |
| T(K)       | 150(2)           | 150(2)           | 150(2)           |
| 2θ range for data collection/° | 3.918 to 52.04 | 4.406 to 52.896 | 4.542 to 54.37 |
| Reflections collected | 34565           | 30168            | 44163            |
| Independent reflections | 5323 \(R_{int} = 0.0488, \sigma = 0.0471\) | 4151 \(R_{int} = 0.1154, \sigma = 0.1233\) | 5341 \(R_{int} = 0.0884\) |
| Data/restraints/parameters | 5323/30/338 | 4151/0/274 | 5341/0/313 |
| Goodness-of-fit on \(F^2\) | 1.050            | 1.011            | 1.032            |
| Final R indexes \( [I > 2\sigma(I)] \) | R_1 = 0.0730, wR_2 = 0.1618 | R_1 = 0.0597, wR_2 = 0.1102 | R_1 = 0.0513, wR_2 = 0.0878 |
| Largest diff. peak/hole / e Å⁻³ | 0.92/-0.90 | 0.48/-0.47 | 0.25/-0.36 |

|          | 4                |
|----------|------------------|
| Empirical formula | C_{29.50}H_{34}BF_{4}N_{2}P |
| Formula weight   | 534.36            |
| Wavelength (Å)   | 1.54178           |
| Colour           | Orange            |
| Crystal system   | Monoclinic        |
| Space group      | P2_1/c            |
| 5 | 7 | 8 |
|---|---|---|
| Empirical formula | C_{76}H_{100}B_{2}ClF_{8}N_{4}P_{2} | C_{52}H_{63}F_{4}N_{4}BO_{2} | C_{42}H_{57}BF_{4}N_{4}O |
| Formula weight | 1340.60 | 862.87 | 720.72 |
| Colour | Orange | Red | Black |
| Crystal system | triclinic | triclinic | orthorhombic |
| Space group | P-1 | P-1 | Pna2_{1} |
| a/Å | 13.9515(18) | 13.236(3) | 15.1948(7) |
| b/Å | 16.383(2) | 13.457(3) | 13.4053(7) |
| c/Å | 18.022(2) | 15.124(3) | 19.3295(8) |
| α/° | 85.244(3) | 91.958(5) | 90 |
| β/° | 79.244(3) | 111.437(6) | 90 |
| γ/° | 67.835(3) | 110.427(5) | 90 |
| Volume/Å³ | 3747.4(8) | 2308.9(7) | 3937.2(3) |
| Z | 2 | 2 | 4 |
| ρ_{calc}g/cm³ | 1.188 | 1.241 | 1.216 |
| F(000) | 1426.0 | 920.0 | 1544.0 |
| T(K) | 150(2) | 150(2) | 150(2) |
| θ range for data collection/° | 2.684 to 50.914 | 3.61 to 52.852 | 3.698 to 51.39 |
| Reflections collected | 77967 | 41640 | 59201 |
| Independent reflections | 13742 [R_{int} = 0.1466, R_{sigma} = 0.2244] | 9480 [R_{int} = 0.0559, R_{sigma} = 0.0768] | 7477 [R_{int} = 0.1051, R_{sigma} = 0.0821] |
| Data/restraints/parameters | 13742/151/819 | 9480/365/691 | 7477/31/492 |
| Goodness-of-fit on F² | 0.1051 | 0.0768 | 0.0821 |
| Final R indexes [I>=2σ (I)] | R_{1} = 0.0988, wR_{2} = 0.2321 | R_{1} = 0.0680, wR_{2} = 0.1802 | R_{1} = 0.0607, wR_{2} = 0.1308 |
| Largest diff. peak/hole / e Å⁻³ | 0.586 and -0.322 e.Å⁻³ |
4. Kinetic data

Compound 1 dissolves in chloroform, CH₂Cl₂, THF, and ODFB. In order to be able to monitor the reactions by ¹H NMR spectroscopy, we chose affordable CDCl₃ as solvent.

Compound 1 was dissolved in CDCl₃ in a sealed NMR tube. The concentrations of 1 and 2 were monitored by ¹H NMR spectroscopy at 50 °C (323 K) over 175 mins. 1,2-Dichloroethane was used as the internal standard.

![Figure S31: Concentrations of compound 1 and 2 at 323 K over 175 mins.](image)

![Figure S32: Kinetic data of compound 1 at two concentrations over 100 mins at 323 K.](image)

The initial experiment run to full consumption showed the kinetic profile of the formation of 2 to be linear until ca. 33 minutes (Figure S31). As such, only aliquots taken in the first 33 minutes (n = 5) were analyzed for all parallel experiments from 303 to 323 K. 1 (ca. 4.4 mg) was dissolved in 0.6 mL of CDCl₃ in a sealed NMR tube. The concentration of 2 was
monitored by $^1$H NMR spectroscopy. 1,2-Dichloroethane (0.0399 M) was used as the internal standard.

Figure S33: Concentrations of compound 2 under various temperatures.

Table S4. Rate constants derived from kinetic experiments (Figure S33).

| T (K) | 1/T (1/K) | k(Ms$^{-1}$) | ln(k/T) |
|------|-----------|-------------|---------|
| 323  | 0.00309   | 2.44E-06    | -18.70  |
| 318  | 0.00314   | 1.49E-06    | -19.17  |
| 313  | 0.00319   | 6.84E-07    | -19.94  |
| 308  | 0.00324   | 2.37E-07    | -20.98  |
| 303  | 0.00330   | 7.42E-08    | -22.12  |

Figure S34: Eyring plot of data from table S4.
Standard errors were calculated using regression analysis in the Microsoft Excel program. The activation parameters for the reaction were found to be (at 95% confident level): $\Delta H^\ddagger = 34 \pm 3 \text{ kcal/mol}$, $\Delta S^\ddagger = 21 \pm 9 \text{ cal/(mol\cdot K)}$ and an associated $\Delta G^\ddagger_{298 \text{ K}} = 28 \pm 5 \text{ kcal/mol}$.

5. Observation of the radical 9

A THF solution of KPPh$_2$ (0.1 mL, 0.5 M) was slowly added to a solution of 1 (21.8 mg, 0.053 mmol) while stirring. The solution immediately turned dark green and was stirred for an additional 15 minutes until submitted to EPR analysis. Formation of spiro[fluorene-9,3'-indazole] was confirmed by X-ray crystallography.

Figure S35: $^{31}\text{P}^{(1}\text{H})$ NMR spectrum of reaction mixture in THF.

Figure S36: Experimental and simulated EPR spectra of 9 in THF.
Table S5. Experimental and simulated EPR data of radical 9.

| MF (Par file) | HCF (sim) | G shift | g-factor | Hyperfine couplings (sim) |
|---------------|-----------|---------|----------|---------------------------|
| 9.348171      | 3334.19   | -1.032  | 2.003803 | (14N) 11.603 G, (14N) 6.534 G, (1H) 1.673, (1H) 1.753 G, (1H) 0.489 G, (1H) 0.307 G, |

6. Observation of the radical 10

A THF solution of KPPPh₂ (0.1 mL, 0.5 M) was slowly added to a solution of 2 (21.8 mg, 0.053 mmol) while stirring. The solution immediately turned dark green and was stirred for an additional 15 minutes until submitted to EPR analysis. Formation of spiro[fluorene-9,3'-indazole] was confirmed by X-ray crystallography.

Figure S37: $^{31}$P{1H} NMR spectrum of reaction mixture in THF.

Figure S38: Experimental and simulated EPR spectra of 10 in THF.
Table S6. Experimental and simulated EPR data of radical 10.

| MF (Par file) | HCF (sim) | G shift | g-factor | Hyperfine couplings (sim) |
|---------------|-----------|---------|----------|---------------------------|
| 9.345129      | 3334.6    | -2.285  | 2.00365799 | (14N) 8.481 G, (14N) 8.486 G, (1H) 3.115, (1H) 3.482 G, (1H) 0.276 G, (1H) 0.2 G, |

7. Observation of H2 in reaction of 2 and SIMes

2 (10.0 mg, 0.024 mmol) was carefully transferred to a J-Young tube. A solution of SIMes (12.8 mg, 0.024 mmol) in C6D6 (0.5 mL) was added. Due to the poor solubility of compound 2 in C6D6, the reaction preceded very slowly and the reaction was monitored at room temperature by 1H NMR spectroscopy.

Figure S39: 1H NMR spectra of reaction of 2 and SIMes at room temperature over time. Blue dot indicates the formation of H2 and red dots indicate unknown organic species.

8. Electrochemistry

Cyclic voltammetry experiments performed using BASi-Epsilon RDE-2 model. A standard three-electrode cell configuration was employed using a glassy graphite working electrode, a platinum wire counter electrode, and a silver wire serving as a reference electrode. Formal redox potentials were referenced to the ferrocenium/ferrocene redox couple. [nBu4N][BF4] (0.085 M) was used as supporting electrolyte. CVs of compound 1 and 2 are measured with 2 mM analytes while CVs of compound 6 and 7 are measured with 1 mM analytes. All measurements were performed at room temperature.
Figure S40: Cyclic voltammogram of 1 in ODFB (scan rate: 200mV/s).

Figure S41: Cyclic voltammogram of 2 in ODFB (scan rate: 200mV/s).

Figure S42. Cyclic voltammograms of (a) 6 and (b) 7 (scan rate: 100 mV/s)
9. Computational details

The quantum chemical DFT calculations have been performed with the TURBOMOLE 7.3 suite of programs\(^1\) The structures are fully optimized at the TPSS-D3/def2-TZVP + COSMO(CHCl\(_3\)) level of theory, which combines the TPSS meta-GGA density functional\(^2\) with the BJ-damped DFT-D3 dispersion correction\(^3, 4\) and the def2-TZVP basis set\(^5, 6\) using the Conductor-like Screening Model (COSMO) continuum solvation model\(^7\) for CHCl\(_3\) solvent (dielectric constant \(\varepsilon \approx 4.8\) and solvent diameter \(R_{\text{solv}} = 3.17 \text{ Å}\)). The density-fitting RI-J approach\(^5, 8, 9\) is used to accelerate the geometry optimization and numerical harmonic frequency calculations\(^10\) in solution. The optimized structures are characterized by frequency analysis to identify the nature of located stationary points (no imaginary frequency for true minima and only one imaginary frequency for transition state) and to provide thermal corrections (at 298.15 K and 1 atm) according to the modified ideal gas–rigid rotor–harmonic oscillator model\(^11\). This choice of dispersion-corrected meta-GGA functional makes the efficient exploration of all potential reaction paths possible.

The final solvation free energies in CHCl\(_3\) are computed with the COSMO-RS solvation model\(^12\) (parameter file: BP_TZVP_C30_1601.ctd) using the COSMOtherm program package\(^13\) on the above TPSS-D3 optimized structures, and corrected by +1.89 kcal·mol\(^{-1}\) to account for higher reference solute concentration of 1 mol·L\(^{-1}\) usually used in solution. To check the effects of the chosen DFT functional on the reaction energies and barriers, single-point calculations at the meta-GGA TPSS-D3\(^2\) and hybrid-meta-GGA PW6B95-D3\(^14\) levels are performed using a larger def2-QZVP basis set.\(^5, 15\) The final reaction Gibbs free energies (\(\Delta G\)) are determined from the electronic single-point energies plus TPSS-D3 thermal corrections and COSMO-RS solvation free energies. The computed reaction free energies from both DFT functionals are in good mutual agreement of \(-0.9 \pm 1.9\) for reaction free energies (average and standard deviations, see Table S1 below) despite 3.5 \(\pm 2.2\) kcal/mol higher barriers at PW6B95-D3 level as expected. In our discussion, higher-level PW6B95-D3 Gibbs free energies (in kcal/mol, at 298.15 K and 1 mol/L concentration) will be used in our discussion unless specified otherwise.
### Table S7.

TPSS-D3/def2-TZVP + COSMO computed imaginary frequency (ImF), zero-point energies (ZPE), gas-phase enthalpic (Hc) and Gibbs free-energy (Gc) corrections; the COSMO-RS computed solvation enthalpic (Hsol) and Gibbs free-energy (Gsol) corrections in CHCl₃ solution; TPSS-D3/def2-QZVP and PW6B95-D3/def2-QZVP single-point energies (TPSS-D3 and PW6B95-D3); the total PW6B95-D3 free energies Gᵢ; the relative electronic energies (∆Eᵢ and ∆Eᵢ) and Gibbs free-energies (∆Gᵢ and ∆Gᵢ) at the TPSS-D3 and PW6B95-D3 levels.

| Reactions | ImF | ZPE | Hc | Gc | Hsol | Gsol | TPSS-D3 | PW6B95-D3 | Gᵢ | ∆Eᵢ | ∆Eᵢ | ∆Gᵢ | ∆Gᵢ |
|-----------|-----|-----|----|----|------|------|---------|------------|-----|------|------|------|------|
|           | cm⁻¹ | kcal/mol | kcal/mol | kcal/mol | kcal/mol | kcal/mol | Eh | Eh | Eh | kcal/mol | kcal/mol | kcal/mol | kcal/mol |
| Separated ion pairs of cations 1⁺, 2⁺ and PMe₃⁺ and anion BF₄⁻ in CHCl₃ solution |     |     |     |     |     |     |     |     |     |     |     |     |     |
| 1⁺ + BF₄⁻ | 0 | 246.10 | 262.31 | 202.45 | -127.69 | -104.12 | -1423.81046 | -1425.32366 | -1425.16094 | 0.00 | 0.00 | 0.00 | 0.00 |
| 1⁺ | 0 | 247.08 | 263.82 | 214.95 | -59.97 | -43.58 | -1423.91236 | -1425.42660 | -1425.15049 | -63.94 | -64.60 | 6.55 | 7.21 |
| 2⁺ + BF₄⁻ | 0 | 245.30 | 261.80 | 201.42 | -126.64 | -103.35 | -1423.81730 | -1425.33086 | -1425.16857 | 0.00 | 0.00 | 0.00 | 0.00 |
| 2⁺ | 0 | 246.03 | 263.09 | 213.84 | -50.18 | -35.08 | -1423.93269 | -1425.44792 | -1425.16004 | -72.41 | -73.46 | 5.35 | 6.40 |
| PMe₃⁺ + BF₄⁻ | 0 | 87.68 | 95.37 | 54.63 | -128.81 | -108.16 | -886.38863 | -887.20525 | -887.28452 | 0.00 | 0.00 | 0.00 | 0.00 |
| PMe₃⁺BF₄⁻ | 0 | 87.87 | 95.87 | 64.82 | -35.57 | -24.54 | -886.53170 | -887.34933 | -887.28213 | -89.78 | -90.41 | 1.50 | 2.13 |
| Facile N...P addition reaction of 1⁺ and phosphine PMe₃ |     |     |     |     |     |     |     |     |     |     |     |     |     |
| 1⁺ + PMe₃ | 0 | 307.79 | 325.11 | 262.71 | -62.56 | -50.71 | -1460.27076 | -1461.74167 | -1461.39780 | 0.00 | 0.00 | 0.00 | 0.00 |
| T51⁺ | 110i | 306.06 | 324.17 | 273.23 | -53.10 | -45.95 | -1460.27907 | -1461.74306 | -1461.37785 | -5.22 | -0.87 | 12.52 | 8.17 |
| 3⁺ | 0 | 308.04 | 325.55 | 276.27 | -54.87 | -47.69 | -1460.30758 | -1461.78212 | -1461.41484 | -23.11 | -25.38 | -10.70 | -8.42 |
| T51a⁺ | 204i | 305.29 | 323.77 | 271.71 | -56.49 | -48.23 | -1460.26672 | -1461.72911 | -1461.36997 | 2.53 | 7.88 | 17.46 | 12.11 |
| 3α⁺ | 0 | 308.67 | 326.09 | 276.80 | -60.35 | -51.29 | -1460.27086 | -1461.73841 | -1461.37602 | -0.07 | 2.05 | 13.67 | 11.56 |
| 3b⁺ | 0 | 309.71 | 326.99 | 277.96 | -58.82 | -50.64 | -1460.31162 | -1461.78881 | -1461.42354 | -21.35 | -25.06 | -11.37 | -7.66 |
| ...tBu⁺ transfer to PMe₃ is prevented by a high barrier |     |     |     |     |     |     |     |     |     |     |     |     |     |
| T51m⁺ | 263i | 303.75 | 323.01 | 268.87 | -54.72 | -46.72 | -1460.24217 | -1461.70359 | -1461.34656 | 17.94 | 23.89 | 32.15 | 26.20 |
| 1m⁺ + tBuPMe₃⁺ | 0 | 307.34 | 324.60 | 261.42 | -75.08 | -62.78 | -1460.28661 | -1461.76112 | -1461.43855 | -9.95 | -12.20 | -25.57 | -23.31 |
| ...PMe₃ aided H⁺ shift within 3α⁺ is exergonic but prevented by a high barrier via TS3p⁺ |     |     |     |     |     |     |     |     |     |     |     |     |     |
| 1⁺ + 2PMe₃ | 0 | 378.10 | 399.92 | 315.70 | -72.79 | -55.80 | -1921.50530 | -1923.36507 | -1922.94185 | 0.00 | 0.00 | 0.00 | 0.00 |
| 3α⁺ + PMe₃ | 0 | 378.97 | 400.90 | 329.79 | -70.58 | -56.37 | -1921.50541 | -1923.36181 | -1922.92007 | -0.07 | 2.05 | 13.67 | 11.56 |
| TS3p⁺ | 972i | 372.97 | 396.57 | 334.61 | -65.55 | -54.31 | -1921.48736 | -1923.33619 | -1922.88650 | 11.26 | 18.12 | 34.73 | 27.86 |
| 3p + PMe₃H⁺ | 0 | 380.14 | 401.56 | 331.43 | -96.52 | -79.53 | -1921.44698 | -1923.30247 | -1922.89502 | 36.60 | 39.28 | 29.39 | 26.70 |
| TS3b⁺ | 0 | 374.33 | 398.33 | 335.41 | -57.65 | -48.58 | -1921.52115 | -1923.37588 | -1922.91577 | -9.95 | -6.78 | 16.36 | 13.20 |
| 3b⁺ + PMe₃ | 0 | 380.01 | 401.79 | 330.95 | -69.05 | -55.72 | -1921.54617 | -1923.41221 | -1922.96759 | -25.64 | -29.58 | -16.15 | -12.22 |

*Isomerization from cation 1⁺ to 2⁺ via 1,2-tBu shift*
\begin{table}[h]
\centering
\begin{tabular}{cccccccccccc}
\hline
\textbf{1} & & \textbf{2} & \textbf{3} & \textbf{4} & \textbf{5} & \textbf{6} & \textbf{7} & \textbf{8} & \textbf{9} & \textbf{10} & \textbf{11} \\
\hline
\textbf{1} & 0.237 & 0.253 & 0.209 & -0.52 & -0.45 & -0.99 & -0.10 & -0.9 & -0.9 & -0.8 & -0.8 & -0.8 \\
\textbf{11} & 0.231 & 0.245 & 0.251 & -0.60 & -0.50 & -0.99 & -0.10 & -0.9 & -0.9 & -0.8 & -0.8 & -0.8 \\
\textbf{2} & 0.236 & 0.249 & 0.208 & -0.51 & -0.44 & -0.99 & -0.10 & -0.9 & -0.9 & -0.8 & -0.8 & -0.8 \\
\textbf{1m + tBu} & 0.231 & 0.245 & 0.251 & -0.79 & -0.67 & -0.99 & -0.10 & -0.9 & -0.9 & -0.8 & -0.8 & -0.8 \\
\textbf{Single electron transfer (SET) reduction of cations 1 and 2} \\
\textbf{1} & 0.237 & 0.253 & 0.209 & -0.52 & -0.45 & -0.99 & -0.10 & -0.9 & -0.9 & -0.8 & -0.8 & -0.8 \\
\textbf{1r (or 9)} & 0.238 & 0.251 & 0.211 & -0.26 & -0.18 & -0.99 & -0.10 & -0.9 & -0.9 & -0.8 & -0.8 & -0.8 \\
\textbf{2} & 0.236 & 0.249 & 0.208 & -0.51 & -0.44 & -0.99 & -0.10 & -0.9 & -0.9 & -0.8 & -0.8 & -0.8 \\
\textbf{2r (or 10)} & 0.236 & 0.249 & 0.208 & -0.24 & -0.17 & -0.99 & -0.10 & -0.9 & -0.9 & -0.8 & -0.8 & -0.8 \\
\textbf{2} & 0.233 & 0.246 & 0.205 & -0.78 & -0.60 & -0.99 & -0.10 & -0.9 & -0.9 & -0.8 & -0.8 & -0.8 \\
\textbf{Using dimeric (KPPPh\textsubscript{2}) as SET reductant: only first reduction to radicals 1r and 2r is efficient.} \\
\textbf{(KPPPh\textsubscript{2})\textsubscript{2}} & 0.225 & 0.243 & 0.190 & -0.56 & -0.37 & -0.28 & -0.10 & -0.9 & -0.9 & -0.8 & -0.8 & -0.8 \\
\textbf{(KPPPh\textsubscript{2})\textsuperscript{+}} & 0.227 & 0.244 & 0.193 & -0.74 & -0.63 & -0.28 & -0.10 & -0.9 & -0.9 & -0.8 & -0.8 & -0.8 \\
\textbf{2KPPPh} & 0.224 & 0.242 & 0.175 & -0.90 & -0.61 & -0.28 & -0.10 & -0.9 & -0.9 & -0.8 & -0.8 & -0.8 \\
\textbf{(PPh\textsubscript{3})\textsubscript{2} formation...} \\
\textbf{(KPPPh\textsubscript{2})\textsubscript{2} + 1} & 0.462 & 0.493 & 0.400 & -0.10 & -0.3 & -0.38 & -0.10 & -0.9 & -0.9 & -0.8 & -0.8 & -0.8 \\
\textbf{(KPPPh\textsubscript{2})\textsubscript{2} + 1r} & 0.462 & 0.496 & 0.405 & -0.10 & -0.3 & -0.38 & -0.10 & -0.9 & -0.9 & -0.8 & -0.8 & -0.8 \\
\textbf{(KPPPh\textsubscript{2})\textsubscript{2} + BF\textsubscript{3} \textsuperscript{-}} & 0.236 & 0.256 & 0.186 & -0.14 & -0.12 & -0.32 & -0.10 & -0.9 & -0.9 & -0.8 & -0.8 & -0.8 \\
\textbf{KBf + (KPPPh\textsubscript{2})\textsubscript{2}} & 0.236 & 0.257 & 0.185 & -0.80 & -0.58 & -0.32 & -0.10 & -0.9 & -0.9 & -0.8 & -0.8 & -0.8 \\
\textbf{K(PPh\textsubscript{3})\textsubscript{3} + 1} & 0.465 & 0.493 & 0.405 & -0.10 & -0.3 & -0.38 & -0.10 & -0.9 & -0.9 & -0.8 & -0.8 & -0.8 \\
\textbf{K(PPh\textsubscript{3})\textsubscript{3} + 1r} & 0.465 & 0.494 & 0.405 & -0.93 & -0.76 & -0.32 & -0.10 & -0.9 & -0.9 & -0.8 & -0.8 & -0.8 \\
\textbf{K(PPh\textsubscript{3})\textsubscript{3} + BF\textsubscript{3} \textsuperscript{-}} & 0.235 & 0.255 & 0.187 & -0.14 & -0.11 & -0.26 & -0.10 & -0.9 & -0.9 & -0.8 & -0.8 & -0.8 \\
\textbf{KBf + (PPh\textsubscript{3})\textsubscript{2}} & 0.235 & 0.255 & 0.185 & -0.59 & -0.42 & -0.26 & -0.10 & -0.9 & -0.9 & -0.8 & -0.8 & -0.8 \\
\textbf{(KPPPh\textsubscript{2})\textsubscript{2} + 2} & 0.462 & 0.493 & 0.394 & -0.10 & -0.8 & -0.38 & -0.10 & -0.9 & -0.9 & -0.8 & -0.8 & -0.8 \\
\textbf{(KPPPh\textsubscript{2})\textsubscript{2} + 2r} & 0.463 & 0.494 & 0.402 & -0.98 & -0.80 & -0.38 & -0.10 & -0.9 & -0.9 & -0.8 & -0.8 & -0.8 \\
\textbf{Phosphine PMe\textsubscript{3} is not reductive enough for SET reaction} \\
\textbf{PMe\textsubscript{3} + 1} & 0.307 & 0.325 & 0.262 & -0.62 & -0.50 & -1.46 & -0.10 & -0.9 & -0.9 & -0.8 & -0.8 & -0.8 \\
\textbf{PMe\textsubscript{3} + 1r} & 0.311 & 0.327 & 0.267 & -0.80 & -0.68 & -1.46 & -0.10 & -0.9 & -0.9 & -0.8 & -0.8 & -0.8 \\
\textbf{2r addition with phosphine PMe\textsubscript{3}: thermodynamic control for selective para-C site} \\
\textbf{Reversible P...para-C and P...N additions} \\
\textbf{S31}
\end{tabular}
\end{table}
| Reaction | ΔH (kcal/mol) | TS2* | TS2m* | 1m + tBuPMe3* | 2* + PMe3 | 4b + PMe3 | 2* + PMe | PMe + H* | 4p + HPMe5* | 4p | 4b + PMe3 | 4c + PMe3 | 4c* + PMe3 | 4c* | TS4d* | TS4e* | 4* |
|----------|---------------|------|--------|----------------|-----------|-----------|-----------|---------|-------------|----|-----------|-----------|-------------|----|--------|--------|---|
| 2* + PMe3 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| TS2* | 182i TS4d | 305.23 | 323.75 | 271.65 | -54.07 | -46.67 | -1460.28335 | -1461.74713 | -1461.38559 | -3.61 | 1.09 | 12.45 | 7.74 | 1.98 | 2.51 |
| 2p* | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| TS4a* | 159i TS4p | 305.47 | 323.77 | 272.36 | -54.25 | -47.06 | -1460.27711 | -1461.74453 | -1461.38248 | 0.31 | 2.72 | 14.40 | 11.98 | 1.98 | 2.51 |
| 4a* | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 4b* | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |

**..tBu* transfer from cation 2* to PMe3 is prevented by a high barrier**

**..Facile PMe3-aided H-shift within 2p* as rate-limiting step via TS4p***

**..further C-N ring-opening (TS4d*) followed by NH..C proton transfer (TS4e*) and aryl rotation (TS4*)**

**S32**
Table S8. The TPSS-D3/def2-TZVP + COSMO optimized atomic Cartesian coordinates (in Å) in CHCl₃ solution. Each structure is labeled by the specific name (See also Table S7), followed by the number of atoms, the total energy (in hartrees), and the detailed atomic coordinates (in double-column text list).

1m  tBu⁺ removed from cation 1⁺  51
33
Energy = -841.2474913933
C 2.6415312 -0.6081287 3.1341054
C 1.3922718 -0.0773088 3.4755209
C 2.9018461 -1.0537436 1.8354006
H 3.4187128 -0.6756161 3.8900611
C 0.3744209 0.0199100 2.5193826
H 1.2106705 0.2620305 4.4910325
C 1.8896822 -0.9596017 0.8784139
H 3.8744945 -1.4652266 1.5805004
C 0.6348333 -0.4246223 1.2310558
H -0.5948717 0.4326269 2.7852334
C 1.8550977 -1.3454266 -0.5364139
C -0.2904465 -0.4174363 0.0233845
C 0.5787166 -1.0486798 -1.0540048
C 2.8237646 -1.9246649 -1.3581493
C -1.6601065 -0.9873770 0.2131614
N -0.6004785 1.0392881 -0.3671461
C 0.2540399 -1.3173561 -2.3759191
C 2.4986967 -2.1976666 -2.6895779
H -0.7316935 -1.0854651 -2.7697723
C -2.5603696 0.0501835 -0.0488516
C -2.1278729 -2.2441247 0.5684558
N -1.8429314 1.2363244 -0.3909308
C 1.2283277 -1.8991809 -3.1955465
H -0.7316935 -1.0854651 -2.7697723
C 3.2414745 -2.6490148 -3.3412001
C -3.9398862 -0.1121553 0.0291840
C -3.5146218 -2.4267811 0.6521978
H -1.4482640 -3.0651044 0.7763780
H 0.9960657 -2.1211860 -4.2329385
C -4.0705670 -1.3788908 0.3872608
H -4.6163739 0.7105315 -0.1794338
H -3.9072934 -3.4011084 0.9281532
H -5.4760425 -1.5567330 0.4620442

1 ion pair of cation 1⁺ and BF₄⁻
H 1.0545173  2.8171119  -1.7212129  C -2.9694157  -0.0003165  1.7189360
H 1.8479707  1.2559238  -1.4036345  C -1.3711900  -0.0007431  3.5613086
H 0.2848154  1.3004479  -2.2482914  H 0.7372542  -0.0002761  3.0594376
H -1.7559768  2.4659072  0.7001771  C -2.9498381  0.0005985 -1.5433910
H -1.0475704  3.4515644  -0.8875195  H 1.8115863  -4.5235323 -0.1297282
H -1.8292276  1.9059809  -0.9884901  C -2.6904439  -0.0006747  3.0842262
H 1.2596148  3.4007269  0.6709415  H -3.9920459  -0.0002241  1.3676566
H 0.5503984  2.3994803  1.9468394  H -1.1955496  -0.0010471  4.6320953
H 1.9825698  1.8232745  1.0599944  C -2.3891865  0.0011173 -2.9635085
B 0.6444712  5.7441795  -0.9333857  C -3.7590778  -1.2801081 -1.2842243
F 1.8995100  5.0825346  -0.9138263  H -1.8674340  0.8644392  0.8875195
F -0.1666563  5.1622712  -1.9416169  C 3.6879712  1.6546086  -0.3078530
F 0.0124602  5.5696976   0.324996  H 1.8450697  4.5244843  -0.2127469
F 0.8276595  7.1135100  -1.1943454  C 2.6398328  0.7346019 -0.2310896

1+ Energy = -999.0255927172
C 3.3186116  3.0182236  -0.4561981  H -3.1348056  -2.1659997 -1.4307754
C 2.0185876  3.4614032  -0.1872285  H -4.5748219  1.3113770  -2.0097176
C 3.6177972  1.6539422   -0.5295819  H -4.1934565  1.3116236  -0.2831252
H 4.1089445  3.7471318  -0.6074838  H -3.1345758  2.1671125 -1.4290754
C 0.9815241  2.5432641  0.0116260  C -2.9691861  -0.0002761  1.7189360
H 1.8124405  4.5253423  -0.1284545  C 3.3852516  3.0191308   -0.3002655
C 2.5900941  0.7324503  -0.3313886  C 3.3852516  3.0191308  -0.3002655
H 4.6311299  1.3250745  -0.7366602  C 2.0591332  3.4594251  -0.2142565
C 1.2881331  1.1930966  -0.0582339  C 3.6879712  1.6546086  -0.3078530
H -0.0262154  2.8876439  0.2257027  H 1.8450697  4.5244843  -0.2127469
C 2.5899900 -0.7323585  -0.3314542  C 2.6398328  0.7346019 -0.2310896
C 0.3422752  0.0001117  0.1243638  H 4.7206001  1.3222065  -0.3727507
C 1.2879120 -1.1930320  -0.0585926  H 4.1886793  3.7478896  -0.3625428
C 3.6175416 -1.6565356  -0.5296251  C 1.0081829  2.5382238  -0.1295371
C -0.5487459 -0.0000775  1.3260180  C 1.0081829  2.5382238  -0.1295371
N -0.5962321  0.0003412  -1.0181775  C 1.3096890  1.1844383  -0.1391032
C 0.9810279  -2.5431508  0.0108740  H -0.0212234  2.8789084  -0.0566816
C 3.3181376 -3.0184285  -0.4565272  C 2.6397010 -0.7348351  -0.2328917
H 4.6309193 -1.3255021  -0.7369048  C 3.3428781  -0.0001431  -0.0526346
C -1.8674340 -0.0000797  0.8644392  C 1.3095536 -1.1846675  -0.1415592
C -0.2811175 -0.0003733  2.6859603  C 3.6879542  -1.6547911  -0.3084701
N -1.7810095  0.0002020  -0.5683528  C -0.5217178  -0.0014649  1.1906278
C 2.0179587  -3.4614297  -0.1880241  N -0.6197811  0.0010911  -1.1793540
H -0.0267853 -2.8874065   0.2247810  C 1.0080658  -2.5384181  -0.1318704
H 4.1084127  -3.7474505  -0.6075650  C 3.3854653  -3.0193350  -0.2978298

1r radical from SET reduction of 1+
H  4.7204303  -1.3223555  -0.3756075  C  0.2233230  -0.0606591  -0.0253134
C  -1.8599876  -0.0016314  0.7669840  C  -0.6897234  0.2786361  1.1582307
C  -0.1933752  -0.0007383  2.5345849  C  -2.8658965  -0.3191127  2.0588020
N  -1.8612291  -0.0001831  -0.6285386  C  1.5181254  -0.7041786  0.4214486
C  2.0592719  -3.4596129  -0.2128889  N  0.7815645  1.0993363  -0.7903343
H  -0.0215884  -2.8790881  -0.0625065  C  -0.4257038  1.0971398  2.2464664
H  4.1891569  -3.7481350  -0.3561346  H  -2.6104605  0.5228722  3.1447098
C  -2.9049088  -0.0011332  1.7023209  C  -3.018722  0.004741  -1.5239224
C  -1.2288722  0.0004363  3.4805322  H  -0.5177355  1.6294647  2.3280708
H  0.8466303  -0.009569  2.8495479  H  -3.3560420  0.6307397  3.9274174
C  -3.874147   -0.0024639  1.4090090  C  3.903119  -0.2152024  0.2722678
C  -0.9969083  0.0010200  4.5410973  C  3.0864750  -2.2030020  1.4276086
H  -3.9471417  -0.0024639  -0.4974426  H  0.9380600  -2.4941699  1.4739084
C  -3.8748627  1.2732652  -1.2560458  C  0.0399209  2.2635483  -1.3457167
H  -3.3589550  0.0027122  3.7965969  H  -1.2206579  1.8677408  4.0963049
H  -1.9817492  0.8868368  -3.2012340  H  4.1419040  -1.3818949  0.9960470
H  -1.9809918  -0.8820424  -3.2037649  H  4.7240346  0.4167885  -0.0634453
H  -3.4694480  0.0032849  -3.6218179  H  3.3017575  -3.1072028  1.9888531
H  -4.2334667  -1.3279062  -2.2966611  C  -1.4376886  1.9180845  -1.5516431
H  -4.7422430  -1.2879403  -1.9254251  C  0.1734408  3.4571536  -0.3809639
H  -3.2652881  -2.1607343  -1.4619024  C  0.6742066  2.6119075  -2.7027050
H  -4.7435244  1.2883579  -1.9217615  H  5.1644026  -1.6648135  1.2313241
H  -4.2346835  1.3241019  -0.2259209  H  -1.5642222  1.0970286  -2.2613126
H  -3.2673892  2.1612925  -1.4558952  H  -1.9289466  1.6557873  -0.6114203

2r    radical from SET reduction of 2+
     Energy = -999.1974617671
C  -2.5615070  -2.6661238  -1.9797613
C  -1.3475609  -2.4288938  -2.6360045
C  -2.8396535  -2.0677592  -0.7478732
H  -3.2963943  -3.3240577  -2.4350152
C  -0.3844997  -1.5873257  -2.0677511
H  -1.1519390  -2.9036960  -3.5931612
C  -1.8830395  -1.2220340  -0.1825415
H  -3.7849683  -2.2575763  -0.2467426
C  -0.6665290  -0.9833389  -0.8489007
H  0.5585019  -1.4003414  -2.5741261
C  -1.8970742  -0.4396366  1.0604826

2p+    P..C adduct of 2+ and PMe3
     Energy = -1460.263142509
C  1.0885290  3.4246226  -2.1548549
C  0.4168677  2.3695228  -2.7837978
C  1.6710363  3.2573956  -0.8954803
H  1.1663833  4.3839316  -2.6580139

S35
| Atom | X-coordinate | Y-coordinate | Z-coordinate |
|------|--------------|--------------|--------------|
| C    | 0.3059835    | 1.1236708    | -2.1550592   |
| H    | -0.0139563   | 2.5173659    | -3.7696138   |
| C    | 1.5674469    | 2.0141990    | -0.2677656   |
| H    | 2.2000582    | 4.0801094    | -0.4228499   |
| C    | 0.8794932    | 0.9642145    | 1.0129031    |
| C    | 0.8582075    | -0.2662456   | -0.0025455   |
| C    | 1.7319649    | 0.1730769    | 1.1693113    |
| C    | 2.8512776    | 2.1637212    | 1.9977768    |
| C    | -0.5563817   | -0.6141421   | 0.4388440    |
| N    | 1.2284907    | -1.5418742   | -0.6974936   |
| C    | 2.0917830    | -0.5452307   | 2.301472     |
| C    | 3.2338929    | 1.4352643    | 3.127250     |
| H    | -0.7822093   | -1.9720962   | 0.0044642    |
| C    | -1.4670887   | 0.1023554    | 1.194830     |
| N    | 0.2718753    | -2.4739851   | -0.6123915   |
| C    | 2.5866213    | 0.0956463    | 3.2800518    |
| H    | 1.7918370    | -1.5814942   | 2.4259109    |
| H    | 3.8279109    | 1.9155856    | 3.8991999    |
| C    | -1.9952999   | -2.6410193   | 0.3656737    |
| C    | -2.8469855   | -0.4768292   | 1.3216830    |
| H    | -1.2584163   | 1.0974281    | 1.5013658    |
| C    | 2.5646778    | -1.9584282   | -1.2137961   |
| C    | 3.1631712    | -0.4507908   | 4.1675863    |
| C    | -2.9589300   | -1.9560619   | 1.0251676    |
| H    | -2.1088679   | -3.7012359   | 0.1587458    |
| C    | -3.2362210   | -0.2465023   | 2.3237388    |
| C    | 3.4471681    | -0.7271783   | -1.4376920   |
| C    | 3.2264449    | -2.9099271   | -0.2010831   |
| C    | 2.3418719    | -2.6792679   | -2.554026    |
| H    | -3.8592320   | -2.4597182   | 1.3624616    |
| H    | 3.0156661    | -0.0526031   | 2.1810387    |
| H    | 3.6187480    | -0.1753438   | -0.509880    |
| H    | 4.4175291    | -1.0705064   | 1.8074143    |
| H    | 2.5660959    | -3.7568197   | 0.0069321    |
| H    | 4.1667070    | -3.2912946   | -0.6117266   |
| H    | 3.4450679    | -2.3892294   | 0.7355248    |
| H    | 3.3083811    | -2.9948162   | 2.9569877    |
| H    | 1.7108665    | -3.5603382   | -2.4174704   |
| H    | 1.8628265    | -2.0076015   | -3.2719573   |
| P    | -4.0038304   | 0.4340734    | 0.1764100    |

2⁻ two-electron reduction of cation 2⁺

Energy = -999.2705453770
| Atom | X     | Y     | Z     | Atom | X     | Y     | Z     |
|------|-------|-------|-------|------|-------|-------|-------|
| H    | 0.9415641 | -2.5686094 | 1.2204887 | C    | -1.4725691 | -2.7554000 | 1.6039766 |
| C    | 0.0355556 | 2.1945379 | -1.4081235 | N    | 0.0688179 | 0.0263157 | -0.0692631 |
| H    | -0.9536339 | 1.8439616 | 4.0673040 | C    | -1.6068282 | -4.1757485 | -3.1007220 |
| C    | 4.1026408 | -1.2691284 | 1.1874017 | H    | -1.9710732 | -2.2544637 | -2.1602145 |
| H    | 4.7128773 | 0.5996471 | 0.2943575 | H    | -1.0102886 | -6.0989911 | -3.8615445 |
| H    | 3.2730497 | -3.1112767 | 1.9928358 | C    | -1.5498396 | 0.1011925 | 1.8100517 |
| C    | -1.4046053 | 1.8303781 | -1.7853220 | C    | -2.7909966 | -2.0998240 | 2.5460862 |
| C    | 0.0264998 | 3.2661487 | -0.2962302 | C    | 0.7333355 | 2.7803178 | -2.6503448 |
| H    | -0.9536339 | 1.8439616 | 4.0673040 | H    | 5.1122377 | -1.4958348 | 1.5304431 |
| H    | 4.7128773 | 0.5996471 | 0.2943575 | H    | -1.4228045 | 1.0700783 | -2.5720990 |
| H    | 3.2730497 | -3.1112767 | 1.9928358 | C    | -1.4599379 | -3.8382715 | 1.5378604 |
| C    | 5.1122377 | -1.4958348 | 1.5304431 | C    | -2.3168564 | -0.6995262 | 2.6503516 |
| H    | -1.9143393 | 2.7288796 | -2.1526997 | H    | -2.9881467 | -2.6936823 | 3.2114818 |
| H    | 1.0458644 | 3.3899116 | 0.0810261 | C    | 2.7038800 | -1.3809419 | 2.0475209 |
| H    | -0.3309555 | 4.2236702 | -0.6952202 | H    | 0.6168409 | -0.5797952 | 3.2226515 |
| H    | -0.6247870 | 2.9755523 | 0.5317812 | C    | 1.8995552 | 0.9928197 | -1.7343828 |
| H    | 0.2128046 | 3.6853609 | -2.9872925 | H    | -2.9637887 | -0.2394001 | 3.3895206 |
| H    | 1.7707781 | 3.0244820 | -2.4110657 | H    | 3.2910191 | -1.0426213 | -2.9056424 |
| H    | 0.7273973 | 2.0417938 | -3.4595000 | H    | 3.3292331 | -1.3243862 | -1.1536402 |
| 2   | ion pair of cation 2+ and BF4- | 51 |
| Energy | -1423.883648735 |
| C    | 3.6046810 | -4.6700731 | 0.9382483 | H    | -0.3213847 | -0.0363122 | -3.0985603 |
| C    | 3.4253761 | -3.4472189 | 1.5939601 | H    | 1.1856573 | -0.1286180 | -4.0411108 |
| C    | 2.7329729 | -5.0802466 | -0.0745418 | H    | 0.4152021 | -1.6220998 | -3.4737840 |
| H    | 4.4319416 | -5.3127242 | 1.2242994 | H    | 1.0339127 | 1.6563439 | -1.7475610 |
| C    | 2.3642491 | -2.6032259 | 1.2459625 | H    | 2.4338921 | 1.1145820 | -0.7876226 |
| C    | 4.1112676 | -3.1505149 | 2.3811942 | H    | 2.5708681 | 1.2642587 | 2.5536309 |
| H    | 1.6770467 | -4.2409879 | -0.4316281 | H    | -2.7258249 | 1.2176425 | -1.7243419 |
| H    | 2.8782977 | -6.0347309 | -0.5718473 | H    | -2.5042542 | -0.1864064 | -1.6150425 |
| C    | 1.5139252 | -3.0118658 | 0.2315281 | H    | -1.5924701 | 1.8148674 | -2.3281985 |
| H    | 2.2221567 | -1.6555512 | 1.7579329 | F    | -3.8672417 | 1.4473893 | -2.5153184 |
| C    | 0.6181116 | -4.3853923 | -1.4363342 | F    | -2.9149401 | 1.7587497 | -0.4337595 |
| C    | 0.2720813 | -2.2964411 | -0.3151973 | 2+   | Energy | -999.0312778363 |
| C    | -0.2115968 | -3.2474783 | -1.4010885 | C    | -2.5235776 | -2.5679501 | -2.0708447 |
| C    | 0.3361793 | -5.4214535 | -2.3274330 | H    | -1.2776911 | -2.3560682 | -2.6709883 |
| C    | -0.7107391 | -1.9634211 | 0.7663565 | C    | -2.8391912 | -1.9917033 | -0.8371479 |
| N    | 0.6176254 | -0.8728270 | -0.7725870 | H    | -3.2568845 | -3.1925310 | -2.5715605 |
| C    | -1.334519 | -3.1326659 | -2.2086036 | C    | -0.3131373 | 1.5578646 | -2.0450255 |
| C    | -0.7783659 | -5.3018925 | -3.1613581 | H    | -1.0537650 | -2.8173435 | -3.6274447 |
| H    | 0.9638256 | -6.3069090 | -2.3696082 | C    | -1.8875949 | -1.8719588 | -0.2105994 |
| C    | -0.7533101 | -0.5659515 | 0.8781247 | H    | -3.8089781 | -2.1660473 | -0.3811400 |
\[
\begin{align*}
\text{3a}^+ \quad \text{P..C adduct of } 1^+ \text{ and PMe}_3 \\
\text{Energy} = -1460.24317198
\end{align*}
\]
| Atom | X      | Y      | Z      |
|------|--------|--------|--------|
| H    | -2.4407248 | 3.2909240 | 1.2252525 |
| H    | -1.3584093 | 2.9547333 | 2.5945265 |
| P    | -3.2357591 | -1.8803179 | -0.3800877 |
| C    | -5.0037133 | -1.8705890 | -0.7401422 |
| H    | -5.3857845 | -0.8505776 | -0.6490866 |
| H    | -5.1699636 | -2.2346669 | -1.7576409 |
| H    | -5.5272951 | -2.5177736 | -0.0313196 |
| C    | -2.9576014 | -1.2685130 | 1.2895201 |
| H    | -1.8887337 | -1.3264771 | 1.5110137 |
| H    | -3.2916221 | -0.2297537 | 1.3512975 |
| H    | -3.5166184 | -1.8794725 | 2.0026405 |
| C    | -2.6056725 | -3.5666726 | -0.4991379 |
| H    | -2.7551836 | -3.9432884 | -1.5145834 |
| H    | -1.5385103 | -3.5704817 | -0.2615967 |
| H    | -3.1367508 | -4.2083013 | 0.2089605 |

**3b**+ PMe3 aided H+-shift from para-C to N

| X      | Y      | Z      |
|--------|--------|--------|
| H      | -0.5216887 | 4.6929754 | -1.0677715 |

Energy = -1460.282017725

| Atom | X      | Y      | Z      |
|------|--------|--------|--------|
| C    | 2.4351286 | -2.8501255 | 3.0201832 |
| C    | 1.9237657 | -1.6289777 | 3.4750163 |
| C    | 2.5621143 | -3.1115645 | 1.6529810 |
| H    | 2.7419168 | -3.6030689 | 3.7405685 |
| H    | 1.5215567 | -0.6438680 | 2.5650462 |
| C    | 1.8412462 | -1.4447948 | 4.5421997 |
| C    | 2.1671978 | -2.1274886 | 0.7443196 |
| H    | 2.9651860 | -4.0608021 | 1.3111744 |
| C    | 1.6470405 | -0.9053202 | 1.2088345 |
| H    | 1.1280823 | 0.3071298 | 2.9131580 |
| C    | 2.1969809 | -2.0934939 | -0.7260337 |
| C    | 1.2548651 | -0.0145595 | 0.0384702 |
| C    | 1.6834803 | -0.8622838 | -1.1626606 |
| C    | 2.6375320 | -3.0415571 | -1.6560772 |
| C    | -0.211582 | 0.3477496 | -0.0219150 |
| N    | 1.8818797 | 1.3420834 | 0.1128094 |
| C    | 1.6045380 | -0.5514208 | -2.5135606 |
| C    | 2.5637589 | -2.7277561 | -3.0164949 |
| H    | 3.0354278 | -4.0044484 | -1.3536236 |
| C    | -0.3284751 | 1.7214223 | -0.3330425 |
| C    | -1.3082867 | -0.4613061 | 0.1442503 |
| N    | 0.9141513 | 2.2870392 | -0.4697453 |
| C    | 2.0568124 | -1.4955205 | -3.4438809 |
| H    | 1.2032737 | 0.4024224 | -2.8464525 |

**3p** deprotonation of 3a**+

Energy = -1459.77247700

| Atom | X      | Y      | Z      |
|------|--------|--------|--------|
| C    | -1.9357747 | -2.9340853 | -2.6057220 |
| C    | -1.5801004 | -1.7203535 | -3.2080612 |
| C    | -1.9822898 | -3.0532065 | -1.2134927 |
| H    | -2.1857186 | -3.7895324 | -3.2280076 |
| Atom | x          | y          | z          |
|------|------------|------------|------------|
| C    | -1.2561264 | -0.6061976 | -2.4246042 |
| H    | -1.5593158 | -1.6455677 | -4.2924177 |
| C    | -1.6639794 | -1.9381829 | -0.4333204 |
| H    | -2.2675233 | -3.996777  | -0.7540998 |
| C    | -1.2948318 | -0.7240354 | -1.0428086 |
| H    | -0.9866906 | 0.3408114  | -2.8853098 |
| C    | -1.6555427 | -1.7475548 | 1.0255482  |
| C    | -0.9591808 | 0.3453104  | 0.0051727  |
| C    | -1.2803953 | -0.4183719 | 1.2980549  |
| C    | -1.9643589 | -2.6237015 | 2.069507   |
| C    | 0.5100884  | 0.7606907  | -0.0548303 |
| N    | -1.7046206 | 1.6023459  | -0.1541670 |
| C    | -1.2263783 | 0.0510132  | 2.6025504  |
| C    | -1.9017900 | -2.1506763 | 3.388929   |
| N    | -0.7396136 | 0.3453104  | 0.0051727  |
| C    | -1.5404036 | -0.4183719 | 1.2980549  |
| H    | -2.254470  | -3.6528908 | 1.8716449  |
| C    | 0.5390098  | 2.1899099  | -0.2143898 |
| C    | 1.6383779  | 0.0051819  | 2.6025504  |
| N    | -0.7396136 | 0.3453104  | 0.0051727  |
| C    | -1.5404036 | -0.4183719 | 1.2980549  |
| H    | -0.9525858 | 1.0840032  | 2.8016868  |
| H    | -2.1433402 | -2.816828  | 4.2080783  |
| C    | 1.8204576  | 2.8276594  | -0.288677 |
| C    | 2.9301797  | 0.6382518  | -0.054208 |
| H    | -1.5548195 | -1.0742159 | 0.1412353  |
| C    | -1.3296215 | 3.9618244  | -0.4156156 |
| H    | -1.5075049 | -0.4723959 | 4.6780765  |
| C    | 2.9614579  | 2.0599131  | -0.208573 |
| H    | 1.9279016  | 3.8961518  | -0.4070804 |
| C    | -2.1972603 | 3.9507262  | -1.6869503 |
| C    | -2.2005708 | 4.2331369  | 0.8242085  |
| C    | -0.2706200 | 5.0589131  | -0.5376183 |
| N    | 3.9195381  | 2.5697183  | -0.279429 |
| H    | -1.5721104 | 3.7784658  | -2.570990 |
| H    | -2.9353694 | 3.1503600  | -1.6202088 |
| H    | -2.7013026 | 4.9169463  | -1.790892 |
| C    | -1.5775095 | 4.2639364  | 1.7249472  |
| H    | -2.7066324 | 5.1983162  | 0.7146365  |
| C    | -2.9371803 | 3.4362538  | 0.9360905  |
| H    | -0.7940952 | 6.0141871  | -0.6447522 |
| H    | 0.3585600  | 5.1195178  | 0.3548002  |
| H    | 0.3597817  | 4.9210702  | -1.4205144 |
| P    | 4.3591278  | -0.3257247 | 0.0544216  |
| C    | 5.8494924  | 0.6865033  | -0.094571  |

Energy = -1460.275411407

3+ direct N..P adduct of 1+ and PMe3

59
| Atom | x         | y         | z         |
|------|-----------|-----------|-----------|
| C    | 2.9201587 | 0.7154316 | -0.7363288|
| H    | -0.6969898| 4.8418820 | -1.0147951|
| C    | 2.3371282 | -0.228954 | 3.5856109 |
| H    | 3.6718534 | -0.8614748| 2.0056160 |
| H    | 0.8177796 | 0.4479686 | 4.9564711 |
| C    | 2.3764520 | 1.2942903 | -2.0429381|
| C    | 3.2071001 | 1.8672506 | 0.2434730 |
| H    | 3.0644744 | 4.3710756 | 1.1937366 |
| H    | 2.2418505 | 0.5310875 | -0.806628 |
| H    | 1.4263262 | 1.8110351 | -1.8976733|
| H    | 3.1096387 | 2.0133052 | -1.946670 |
| H    | 3.7894342 | 1.5340765 | 1.1051746 |
| H    | 3.7882805 | 2.6298149 | -0.2827011|
| H    | 2.9327117 | 2.3310709 | 0.6205987 |
| H    | 4.9881469 | 0.6417419 | -1.3638518|
| H    | 4.5993390 | -0.5030845| -0.0696996|
| C    | 4.0888508 | -0.8406943| -1.7334924|
| P    | 0.3363136 | -1.7726708| -1.4590809|
| C    | -1.3126002| -1.8558991| -2.1821211|
| C    | -0.2062873| -2.1687266| -1.4518275|
| H    | -1.5742691| -0.8939107| -2.6073948|
| C    | -1.264375 | -2.6062580| -2.0867317|
| C    | 0.6919851 | -3.2382456| -0.4636616|
| H    | 1.5958371 | -3.0477075| 0.1207100 |
| H    | -0.1402967| -3.4780112| 0.1961243 |
| C    | 0.8718572 | -4.0776176| -1.1415396|
| C    | 1.4590423 | -1.8692415| -2.8609362|
| H    | 1.2220205 | -1.0945998| -3.5919809|
| C    | 2.4958637 | -1.7861348| -2.5354378|
| H    | 1.3054755 | -2.8525399| -3.3171054|

**4a** direct P..N adduct of 2+ and PMe3

Energy = -1460.26435473
C  -3.5374751  0.0133293  -1.6245094  H  -1.7701810  3.8918054  -0.2351429
H  -4.0640329  0.9386951  -1.3851357  H  0.9303432  3.4499127  -0.8053764
H  -2.7809544  0.2115837  -2.3827023  C  3.9402363  0.6217132  -0.6344554
H  -4.2600776  -0.7128415  -2.0096377  C  3.4906972  3.0061382  -1.2259394
C  -4.2066892  -0.7284557   1.0310081  C  3.3419585  2.2727266  1.1692338
H  -4.2600776  -0.7128415  -2.0096377  H  -3.8464102  2.5760840  -0.1267172
H  -4.4518126   0.2947276  1.3288871  H  3.7090587  -0.2212081  0.0221908
H  -5.0650732  -1.1664837   0.5110338  H  3.7885813  0.3153840  -1.6723105

4b+  C-to-N H-shift of adduct 2p+
59  Energy = -1460.278176286
C  1.7582739  -1.8855972   3.4900075  H  2.9822971  3.9404201  -0.9610189
C  1.3798865  -0.5443909   3.6235224  H  4.5659006  3.1902192  -1.1412254
C  1.8796632  -2.4711288   2.2278736  H  3.2552846  2.7539536  -2.2643255
H  1.9478003  -2.4802363   4.3970635  C  4.3506378  2.6908141  1.2513887
C  1.1296905   0.2396687   2.492777  C  2.6257033  3.0402050  1.4776734
H  1.2775041  -0.1099690   4.6137020  H  3.2569127  1.4251554  1.8524517
C  1.6368341  -1.6871936   1.0972769  P  -4.3435067  -0.3188526  -0.0177669
H  2.1492277  -3.5194157   2.1327839  C  -5.7979258   0.7427478  -0.0428064
C  1.2905404  -0.3285997   1.2348174  H  -5.7871271  1.4128875   0.8201412
H  0.8262282   1.2767254   2.6019083  C  5.8198756  1.3255433  -0.9668079
C  1.6419767  -2.0371494  -0.3296433  C  6.6881758   0.1096820  0.0050427
C  0.9950303   0.2776397  -0.1516398  C  4.3704423  -1.3093963  1.4965512
C  1.2910189  -0.8976323  -1.0736525  H  -4.3719184  -0.6342930   2.3601215
C  1.9332481  -3.2374513   0.9816766  C  -5.2628319  -1.9357340  1.5145792
C  -0.4594783   0.7202709  -0.1791656  C  -4.4289886  -1.4565340  -1.4183676
N  1.6648681   1.5349386  -0.6170366  H  -4.4692916  -0.8811266  -2.3464729
C  1.2246419  -0.9310143  -2.4580696  H  -3.5393034  -2.0918976  -1.4257727
C  1.8687517  -3.2736346  -2.3771647  N  -5.3196740  -2.0849239  -1.3316765
H  2.2109229  -4.1264207  -0.4221260  4c+  C-to-N-tBu H-shift of adduct 2p+
C  -0.5035136  2.1244683  -0.2085651  59  Energy = -1460.266347096
C  -1.6126641 -0.0262338  -0.1199047  C  1.8845526  -1.8656998  3.4338251
N  0.7718539   2.6310802  -0.2233740  C  1.3295556  -0.5877204  3.5676079
C  1.5191238  -2.1333673  -3.1109435  C  2.0967781  -2.4284240  2.1724439
H  0.9662025  -0.0371905  -3.0186185  C  2.1373356  -2.4346646  4.3236548
H  2.0969422  -4.1976653  -2.9008040  C  0.9916899   0.1626997  2.4366170
C  -1.7269676  2.8082911  -0.1965545  H  1.1545064  -0.1777980  4.5575722
C  -2.8566851  0.6467913  -0.0972957  C  1.7672583  -1.6793672  1.0420523
H  -1.5552481  -1.123402  -0.1013601  H  2.4963025  -3.4341179  2.0796511
C  3.0914634   1.8495863  -0.2897028  C  1.2483689  -0.3766106  1.1832181
H  1.4799725  -2.1834444  -4.1952830  H  0.5478091   1.1482847  2.5394354
C  -2.8942461  2.0558989  -0.1360082  C  1.8131900  -2.0188370  -0.3867849
S44

Energy = -1460.276610510

4e+ N..H..C proton transfer of 4d+

59

H 0.0391949 -0.2526530 -0.3901805
C 3.0184413 -2.0104094 -0.1548408
N 1.5349074 1.1358397 2.0848592
C 0.8595578 3.0098348 3.4799105
H -0.4311063 4.4846580 2.5731665
H -1.3783928 -0.4685510
C -1.3323638 -0.4636280 -0.2609186
H 2.2730727 -1.1368834 -0.6459200
C 1.5632185 1.8117314 3.3101808
H 2.0768149 0.2019325 1.9629557
H 0.8939424 3.5200304 4.4382022
C -1.8637830 -1.7597830 -0.2350725
H -1.9814752 0.4060320 -0.1928488
C 4.4705055 -1.7909390 -0.3941083
H 2.1364330 1.4033139 4.1374016
C -1.0152900 -2.8745242 -0.3384158
C 1.0344040 -3.5164584 -0.5402846
H 1.5780450 1.1174182 -0.8960076
C 4.9422734 -3.0664634 -1.1181224
C 5.0935882 -1.7247829 1.0127514
C -1.4133331 -3.8836906 -0.3360304
H 4.6706659 -3.9577508 -0.5450098
H 4.4911517 -3.1346225 -2.1131963
H 6.0304856 -3.0363201 -1.2291424
H 4.4407816 0.3640324 -0.6922527
H 5.8751558 -0.4634867 -1.3372010
H 4.3193394 -0.5719925 -2.1909629
H 6.1837012 -1.6903831 0.9256418
C 4.7587367 -0.8259689 1.5408838
C 4.8126487 -2.6040445 1.5993710
P -3.6388567 -1.9381902 -0.0809444
H -4.1775180 -1.2372200 1.4913257
H -3.7111049 -1.7898399 2.3106343
H -3.8760203 -0.1876081 1.5436848
H -5.2659647 -1.3057828 1.5698736
H -4.1088960 -3.6731418 -0.1507569
H -3.8024131 -4.1046306 -1.1067961
H -3.6420845 -4.2197453 0.6723028
H -5.1961879 -3.7406276 -0.0562744
C -4.4511152 -1.0441455 -1.4209469
H -4.1555290 0.0077725 -1.3905782
4p.HPMe₃⁺  loose complex of 4p and PMe₃H⁺

Energy = -1921.487607046

4p...H deprotonation of 2p⁺

Energy = -1459.800921332
S46

4+ final product cation of $2^+$ and PMe₃

Energy = -1460.277726580
BF$_4^-$ counter anion in 1 and 2

Energy = -424.819590236

B -0.4675061 -0.28262278 -0.0000240
F -1.8832201 -0.2863414 0.0000007
F 0.0042110 -1.6210343 0.0000033
F 0.0043688 0.3811564 1.1558280
F 0.0043602 0.3811489 -1.1558080

KBF$_4$ : contact ion pair of K$^+$ and BF$_4^-$

Energy = -1024.72687638

B -0.4958967 -0.2643462 0.0000486
F -1.8770131 -0.3314507 0.0002907
F 0.0968145 -1.5624534 -0.0000213
F 0.0000686 0.4235241 1.1476965
F -0.0003116 0.4235136 -1.1477087
K 2.4385521 -0.1200854 -0.0003058

(KPPh$_2$)$_2$ : KPPh$_2$ dimer in solution

Energy = -2809.95658411

P -2.2908930 1.1989926 1.6232406
C -2.9368483 0.0362232 0.3655787
C -2.6715937 -1.3449684 0.5215279
C -3.1569043 -2.2937874 -0.3785383
C -3.9170993 -1.8931699 1.4800266
C -4.2040029 -0.5347744 -1.6505194
C -3.7361150 0.4105501 -0.7387186
H -4.0065232 1.4545343 -0.8709222
K 0.0549235 -0.0000047 3.759127
C 2.2420661 -0.7565605 1.9977524
C 1.5084072 -2.2591053 1.2788099
C 1.500041 -2.6650637 -0.0798458
C 0.7741933 -3.7758778 0.5139888
C 0.0360986 -4.5466804 0.3838443
C 0.0409858 -4.1861925 1.7392568
C 0.7658206 -3.0815406 2.1726134
C 0.7698206 -3.0815406 2.1726134
C 0.0360986 -4.5466804 0.3838443
C 0.0409858 -4.1861925 1.7392568
C 0.7658206 -3.0815406 2.1726134
C 0.7698206 -3.0815406 2.1726134
C 0.0360986 -4.5466804 0.3838443
C 0.0409858 -4.1861925 1.7392568
C 0.7658206 -3.0815406 2.1726134
C 0.7698206 -3.0815406 2.1726134
C 0.0360986 -4.5466804 0.3838443
C 0.0409858 -4.1861925 1.7392568
C 0.7658206 -3.0815406 2.1726134
C 0.7698206 -3.0815406 2.1726134
C 0.0360986 -4.5466804 0.3838443
C 0.0409858 -4.1861925 1.7392568
C 0.7658206 -3.0815406 2.1726134
C 0.7698206 -3.0815406 2.1726134
C 0.0360986 -4.5466804 0.3838443
C 0.0409858 -4.1861925 1.7392568
C 0.7658206 -3.0815406 2.1726134
C 0.7698206 -3.0815406 2.1726134
C 0.0360986 -4.5466804 0.3838443
C 0.0409858 -4.1861925 1.7392568
C 0.7658206 -3.0815406 2.1726134
C 0.7698206 -3.0815406 2.1726134
C 0.0360986 -4.5466804 0.3838443
C 0.0409858 -4.1861925 1.7392568
C 0.7658206 -3.0815406 2.1726134
C 0.7698206 -3.0815406 2.1726134
C 0.0360986 -4.5466804 0.3838443
C 0.0409858 -4.1861925 1.7392568
C 0.7658206 -3.0815406 2.1726134
C 0.7698206 -3.0815406 2.1726134
C 0.0360986 -4.5466804 0.3838443
C 0.0409858 -4.1861925 1.7392568
C 0.7658206 -3.0815406 2.1726134
C 0.7698206 -3.0815406 2.1726134
C 0.0360986 -4.5466804 0.3838443
C 0.0409858 -4.1861925 1.7392568
C 0.7658206 -3.0815406 2.1726134
C 0.7698206 -3.0815406 2.1726134
(KPPH₂)⁺²⁺ : radical cation

(KPPH₂)⁺²⁺ : radical

E = -2809.81819229

E = -2209.945128981
K(PPh₂)₂⁺ : K⁺ cation complex

Energy = -2209.849351977

K 0.4796410  -0.5184321  -0.5476853
C -0.6691168  -1.9364215  -0.6592335
C -0.4785998  -3.1271485  0.0560597
C -1.4306839  -4.1431091  -0.0119069
C  2.5797406  -3.9785350  -0.7895463

C  2.0605159  4.2322642  0.8128069
C  2.6904662  2.9816530  0.8442540
C  1.9469230  1.8178147  1.0434877
H  2.4531519  0.8563918  1.0618978
H  3.7670308  2.9109135  0.7077914
H  2.6375515  5.1383804  0.6530562
H  0.1703705  5.2608118  1.0192593
H -1.1403378  3.2166736  1.3983988
C -2.0389596  0.5676978  1.1403502
C -2.9744212  -0.2594154  1.8005080
C -4.3260296  -0.2397019  1.4707431
C -4.7957110  0.6107846  0.4637809
C -3.8894806  1.4397141  -0.2039201
H -1.8544555  2.0615579  -0.4192663
H -4.2379234  2.1004049  -0.9943938
H -5.8501347  0.6275615  0.2033108
H -5.0167468  -0.8944539  1.9957954
H -2.6191088  -0.9374844  2.5732439
H -4.0650588  -2.8613642  -1.0206710
H -3.2538176  -5.1822861  -0.5972462
H -0.8102879  -5.5896384  -0.3251199
H  0.7883134  -3.7243910  -0.465077
C  2.0251743  -1.3144094  -0.4493756
C  3.1428005  -0.9006472  -1.2040088
C  4.4437829  -1.1503865  -0.7720697
C  2.6932921  -1.9960808  0.762195
C  2.7282150  -2.2937043  1.3809220
C  3.7326344  -2.7868811  2.1238499
H  5.6780675  -2.0406158  0.7631636
H  5.2859816  -0.8199517  -2.1499875
C  2.1091066  -1.4515278  1.9346910
C  4.1882908  -2.1129329  -1.704869
C  2.5767512  -1.6374321  1.0620984
P  0.4796410  -0.5184321  -0.5476853
C -0.6691168  -1.9364215  -0.6592335
C -0.4785998  -3.1271485  0.0560597
C -1.4306839  -4.1431091  -0.0119069
C  2.5797406  -3.9785350  -0.7895463

Energy = -2209.849351977

K(PPh₂)₂⁺ : K⁺ cation complex

Energy = -2209.849351977
KPPh$_2$ monomer

Energy = -1404.962675497

P  0.6713600  1.9977525  -1.2339979
K  0.6713660  1.9977525  -1.2339979
C  -1.6468932  0.0151796  0.6225224
C  -2.6981259  0.9242339  0.3562418
C  -1.8810932  -1.3392145  0.2901002
C  -3.9033010  0.5099350  -0.2116136
H  -2.5594997  1.9744517  0.6105553
C  -3.0794766  -1.7519949  -0.6032392
C  -1.3387655  -1.1016491  0.4409558
H  -2.3687355  -0.7645035  0.3005712
H  -1.2604508  -2.1557743  0.1627303
H  -0.5030040  -0.9782605  1.4889182
C  -0.3988874  1.6182545  -0.1945254
H  0.2453577  2.1894289  -0.8655560
H  -1.4394656  1.9239743  -0.3301654
H  -0.1020753  1.7752458  0.8459356
C  1.4521803  -0.6931632  -0.4064087
H  1.5082968  -1.7493616  -0.696000
H  2.0954157  -0.1045541  -1.0580479

(PPh$_2$)$_2$

Energy = -1609.982298811

P  0.6713061  0.4711531  0.8568655
C  1.3254875  -1.2371153  0.6982949
C  2.2178853  -1.6243263  -0.3126147
C  2.6142837  -2.9555870  -0.4277805
C  0.1418558  -1.9107567  2.3691904
C  0.8433113  -4.2722213  2.1603539
C  2.4013484  2.1550052  0.5312841
C  0.3079860  3.2446870  -1.1283553
C  1.9509110  2.4311647  -0.7705940
H  0.7069764  2.5386797  -1.292356

PMe$_3$H$^+$$\text{BF}_4^-$: contact ion pair

Energy = -886.5172918428

P  0.6713061  0.4711531  0.8568655
H  0.6404476  -0.3054379  -1.9298785
B  0.8360896  0.4607116  -3.8973046
F  1.2873076  1.3089479  -2.8387073
F  1.4165745  0.8538668  -5.1054053
F  1.1918909  -0.8724406  -3.5770796
F  -0.5778521  0.5530327  -3.9654294
F  -0.6404476  -0.3054379  -1.9298785
B  0.8360896  0.4607116  -3.8973046
F  1.2873076  1.3089479  -2.8387073
F  1.4165745  0.8538668  -5.1054053
F  1.1918909  -0.8724406  -3.5770796
F  -0.5778521  0.5530327  -3.9654294

(PPh$_2$)$_2$
|   |     |     |     |   |     |     |     |   |     |     |     |   |     |     |   |     |     |     |     |   |     |     |     |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| H | -3.2817180 | -4.4326115 | 0.5610969 | H | -0.4774736 | -0.4371096 | -2.2859654 |
| H | -1.6293583 | -4.4168022 | -1.296922 | H | 1.0510662 | -0.8221574 | -1.4491043 |
| H | -0.5335355 | -2.951316 | -1.9620375 | C | 0.3947269 | -0.7546589 | 1.4083012 |
| C | -1.8364863 | 1.7296107 | -0.5988835 | H | 0.2482239 | -0.2306795 | 2.3582984 |
| C | -1.5263375 | 2.8306700 | 0.2115423 | H | 0.1112232 | -1.8023702 | 1.5514328 |
| C | -2.4413159 | 3.8721696 | 0.3788192 | H | 1.4550619 | -0.7053833 | 1.1322541 |
| C | -3.6816350 | 3.8258769 | -0.2578650 | C | -3.0018145 | 2.7325257 | -1.0682316 |
| C | -1.8364863 | 1.7296107 | -0.5988835 | C | -1.5263375 | 2.8306700 | 0.2115423 |
| C | -2.4413159 | 3.8721696 | 0.3788192 | H | 0.2482239 | -0.2306795 | 2.3582984 |
| H | -3.2817180 | -4.4326115 | 0.5610969 | C | -1.8364863 | 1.7296107 | -0.5988835 |
| H | -1.6293583 | -4.4168022 | -1.296922 | H | 0.2482239 | -0.2306795 | 2.3582984 |
| C | -0.5335355 | -2.951316 | -1.9620375 | C | -1.8364863 | 1.7296107 | -0.5988835 |
| H | -0.4774736 | -0.4371096 | -2.2859654 | C | -1.8364863 | 1.7296107 | -0.5988835 |
| P | 0.0001093 | -0.0001007 | -0.3209478 | P | 0.7572796 | -0.0000407 | -0.0001330 |
| C | -1.3032927 | -1.0747205 | 0.2314788 | C | -1.3032927 | -1.0747205 | 0.2314788 |
| H | -0.2484001 | -2.0862277 | -0.1458201 | H | -0.2484001 | -2.0862277 | -0.1458201 |
| C | -1.3032927 | -1.0747205 | 0.2314788 | C | -1.3032927 | -1.0747205 | 0.2314788 |
| H | -0.2484001 | -2.0862277 | -0.1458201 | H | -0.2484001 | -2.0862277 | -0.1458201 |
| C | -1.3032927 | -1.0747205 | 0.2314788 | C | -1.3032927 | -1.0747205 | 0.2314788 |
| H | -0.2484001 | -2.0862277 | -0.1458201 | H | -0.2484001 | -2.0862277 | -0.1458201 |
| H | -0.2484001 | -2.0862277 | -0.1458201 | H | -0.2484001 | -2.0862277 | -0.1458201 |
| H | -0.2484001 | -2.0862277 | -0.1458201 | H | -0.2484001 | -2.0862277 | -0.1458201 |
| H | -0.2484001 | -2.0862277 | -0.1458201 | H | -0.2484001 | -2.0862277 | -0.1458201 |
| P | 0.0001093 | -0.0001007 | -0.3209478 | P | 0.7572796 | -0.0000407 | -0.0001330 |
| C | -1.3032927 | -1.0747205 | 0.2314788 | C | -1.3032927 | -1.0747205 | 0.2314788 |
| H | -0.2484001 | -2.0862277 | -0.1458201 | H | -0.2484001 | -2.0862277 | -0.1458201 |
| C | -1.3032927 | -1.0747205 | 0.2314788 | C | -1.3032927 | -1.0747205 | 0.2314788 |
| H | -0.2484001 | -2.0862277 | -0.1458201 | H | -0.2484001 | -2.0862277 | -0.1458201 |
| H | -0.2484001 | -2.0862277 | -0.1458201 | H | -0.2484001 | -2.0862277 | -0.1458201 |
| H | -0.2484001 | -2.0862277 | -0.1458201 | H | -0.2484001 | -2.0862277 | -0.1458201 |
| H | -0.2484001 | -2.0862277 | -0.1458201 | H | -0.2484001 | -2.0862277 | -0.1458201 |
| H | -0.2484001 | -2.0862277 | -0.1458201 | H | -0.2484001 | -2.0862277 | -0.1458201 |
| H | -0.2484001 | -2.0862277 | -0.1458201 | H | -0.2484001 | -2.0862277 | -0.1458201 |
| H | -0.2484001 | -2.0862277 | -0.1458201 | H | -0.2484001 | -2.0862277 | -0.1458201 |
| H | -0.2484001 | -2.0862277 | -0.1458201 | H | -0.2484001 | -2.0862277 | -0.1458201 |

PMe₃H⁺  phosphonium  

Energy = -461.6566914888

PMe₃  

Energy = -461.215948590

tBu⁺  cation C(CH₃)₃⁺  

Energy = -157.7131521247
C 0.5163396 1.3646906 -0.0001379  H 4.4247299 0.0368695 3.3739359
H 0.6768038 -1.7738971 0.8609465  C -2.4285795 -1.4142185 1.8152501
H 0.6861806 -1.763185 -0.8694053  H -1.8866937 -3.2690478 0.9298241
H 1.9762524 -0.8515892 0.0073751  H -2.5837926 0.4772599 2.8588562
H -1.8750991 0.3005206 -0.8604430  C 1.7505145 -3.6941780 -1.8713974
H -1.7254698 -1.2858384 -0.8694053  H -0.0065351 1.6904393 -2.9993630 -2.7119205
H -1.8701201 0.2873023 0.8699311  H 2.6800429 -3.5059366 -1.3311606
H 1.1906667 1.4753916 0.8647851  H 1.7640604 -4.7175653 -2.2573703

TS1a+  TS for P...C addition of 1+ and PMe3
Energy = -1460.234620468
C 1.0493335 3.3234615 -2.7175002  H -0.1839379 -4.4884795 0.9117383
H 0.1510369 2.2856818 -2.9898199  H 0.7632169 -5.5440412 -0.1461710
C 1.9423296 3.2393836 -1.6458462  C -1.5973840 -4.2910870 0.8085553
H 1.0562955 4.2043970 -3.3525244  H -0.7042516 -4.8113441 -2.1915077
H -0.5265163 2.3667630 -3.8343939  H -1.6508762 -3.7527047 -1.1368130
C 1.9217537 2.0980934 -0.8415403  H -0.3831399 -3.0843144 -2.5705860
H 1.0562955 4.2043970 -3.3525244  P -3.6361059 1.0329622 0.5297272
C 0.1231393 1.1419901 -2.1830067  C -5.3900722 1.3861671 0.9000520
H -0.5265163 2.3667630 -3.8343939  C -5.8866583 0.4620629 1.2084577
C 1.9217537 2.0980934 -0.8415403  H -5.4476114 2.1105016 1.7167327
H -0.5689253 0.3335499 -2.4012664  H -5.8950060 1.7916418 0.0162397
C 2.7276861 1.7178017 0.3249660  C -3.6287791 -0.0668119 -0.9180378
H 1.1357347 -0.0439878 -0.0692802  H -2.5929345 -0.2891592 -1.1868616
C 2.3014861 0.4554530 0.7791140  C -2.8901879 2.5961678 -0.0324894
C 3.7673862 2.3791980 0.9809288  H -2.9083742 3.3260575 0.7812026
C -0.1518758 -0.2957877 0.6827553  H -1.8536952 2.4136280 -0.3036501
N 1.4443200 -1.3396112 -0.7213888  H -3.4441225 2.9934137 -0.8886993
H 2.8949383 -1.631978 1.8690277  C -4.1324147 0.4066388 -1.7660380
C 4.3691221 1.7585679 2.0788921  C -2.8901879 2.5961678 -0.0324894
H 4.1078782 3.3550507 0.6468743  C -4.1324147 0.4066388 -1.7660380
C -0.5121569 -1.6384159 0.4080661  N -0.0817497 -4.5430030 3.0041731
C 0.8976489 0.5060177 1.4934776  C -1.6331587 -3.4626474 2.9207740
N 0.4790582 -2.1534626 -0.4074597  C 0.2707217 -4.7152415 2.0630035
C 3.9415532 0.5092632 2.5194834  H -0.8571136 -5.2612246 3.8113435
H 2.5609823 -1.1373302 2.2149244  C -1.5144761 -2.5244199 1.8888909
H 5.1811571 2.2588666 2.5982335  H -2.4205000 -3.3523164 3.6599865
C -1.6466677 -2.2179798 1.0274482  C 0.3944027 -3.7836325 1.0315825
C -2.1751811 0.0101422 1.9680835  H 0.9490087 -5.5602334 2.1361396

TS1m+  TS for tBu+ transfer from 1+ to PMe3
Energy = -1460.207369706
C -0.7479769 -4.5430030 3.0041731
C -1.6331587 -3.4626474 2.9207740
C 0.2707217 -4.7152415 2.0630035
C -0.8571136 -5.2612246 3.8113435
C -1.5144761 -2.5244199 1.8888909
C -2.4205000 -3.3523164 3.6599865
C 0.3944027 -3.7836325 1.0315825
H 0.9490087 -5.5602334 2.1361396
| Atoms | X Position | Y Position | Z Position |
|-------|------------|------------|------------|
| C     | -0.5022213 | -2.7003936 | 0.9577805  |
| H     | -2.2055373 | -1.6887760 | 1.8220182  |
| C     | 1.3312944  | -3.7021346 | -0.0941260 |
| C     | -0.1632842 | -1.8270091 | -0.2460340 |
| C     | 1.0166327  | -2.5683560 | -0.8676116 |
| C     | 2.3860760  | -4.5309225 | -0.4785667 |
| C     | -1.2880350 | -1.4336198 | -1.1555685 |
| N     | 0.3315109  | -0.4828296 | 0.2587588  |
| C     | 1.7308059  | -2.2414110 | -2.0103961 |
| C     | 3.1090969  | -4.2066610 | -1.629892  |

**TS1**b+ 1,2-tBu-shift of cation 1+

Energy = -998.9725514649

| Atoms | X Position | Y Position | Z Position |
|-------|------------|------------|------------|
| C     | -3.2930475 | 0.4540018  | 3.2314115  |
| H     | -2.0197555 | 0.8004530  | 3.6975970 |
| C     | -3.5046132 | 0.1322077  | 1.8880607 |
| C     | -4.1297152 | 0.4399265  | 3.9236781 |
| C     | -0.9247835 | 0.8272141  | 2.8260167 |
| C     | -1.8802719 | 1.0533182  | 4.7442708 |
| C     | -2.4173846 | 0.1618728  | 1.0135582 |
| C     | -4.4980975 | -0.1304639 | 1.5361832 |
| C     | -1.1385261 | 0.5100216  | 1.4925497 |
| C     | -0.629782  | 1.0971115  | 3.1890637 |
| C     | -2.3273721 | -0.0948432 | -0.4281551|
| C     | -0.1225042 | 0.4399441  | 0.3648700 |
| C     | -0.9953789 | 0.1031081  | -0.8404327|
| C     | -3.2973549 | -0.4507406 | -1.3673990|
| C     | 0.8648144  | 1.5490305  | 0.2000956 |
| C     | 0.7865219  | -0.7695713 | 0.5863073 |
| C     | -0.6155928 | -0.0350167 | -2.1682623|
| C     | -2.9174634 | -0.5995314 | -2.7042380|
| H     | -4.3308466 | -0.6050182 | -1.0710445|
| C     | 0.4095049  | 0.1467408  | -2.4816713|
| C     | 0.7388460  | 2.9149678  | -0.0039893|
| C     | 2.1359201  | 0.9656211  | 0.2798943 |
| C     | 3.3138571  | 1.6972140  | 0.1561206 |
| C     | 1.9140748  | 3.667154   | -0.1303292|
| C     | 3.3138571  | 1.6972140  | 0.1561206 |
| C     | 3.1810370  | 3.0708234  | -0.0535724|

S53
TS1+  TS for direct N..P adition of 1+ and PMe3
Energy = -1460.244926139

P    -0.0971382  -2.5925921   -0.0788750
C    -1.4696593  -2.6604232   -1.2723650
H    -2.3863453  -2.2963123   -0.8031260
H    -1.229908   -2.0260933   -2.1292310
H    -1.6174136  -3.6917456   -1.6077291
C    -0.6075231   -3.7005813   -1.3064958
H    -0.6400177  -4.7299103   -0.9313674
C    -0.1208780  -3.6257109   -0.8287339
H    -1.6109835  -3.1900441   -1.7426920
H    -2.0181805  -3.7756508   -0.1085556
H    -0.7724623  -4.6009796   -1.0669808

TS2m+  TS for tBu+ transfer from 2+ to PMe3 59
Energy = -1460.210374701
C    -0.9464297  -2.6578112   3.0156867
C    -0.9719045  -1.3083373   3.3856215
C    -1.1165163  -3.0430547   1.6831528
TS2*  
direct P..C addition of 2+ and PMe3
59

Energy = -1460.24923091

S55
| Atom | X    | Y    | Z    |
|------|------|------|------|
| C    | -2.5784023 | -1.0080151 | 1.7347908 |
| H    | -1.2485746 | -2.3859301 | 0.7313834 |
| C    | 2.5994855  | -1.6332007 | -1.4443181 |
| H    | 3.6576255  | 0.3205566 | 3.9415006 |
| C    | 2.6427117  | -1.6332007 | -1.4443181 |
| H    | 3.6576255  | 0.3205566 | 3.9415006 |
| H    | 3.1625844  | -3.9629822 | 0.1536245 |
| C    | 3.3318316  | -0.2985976 | 1.9153613 |
| C    | 2.5994855  | -1.6332007 | -1.4443181 |
| H    | 3.6576255  | 0.3205566 | 3.9415006 |
| C    | -1.029651 | 3.074389 | 3.4877651 |
| C    | 1.0401572 | 2.7167450 | 4.5720618 |
| TS3b^*      |  |  |  |

TS3b^* TS for 3p protonation with PMe3H^+ 72
TS3p+  deprotonation TS of 3a+ with PMe3

Energy = -1921.438040190

H  6.2841987  -1.8390078  -0.5711882  C  1.5392116  2.2526341  -1.1976011
H  7.2856222  -0.6928192  0.3526658  C  1.5134786  2.4267192  -3.6212369
C  5.2003377  1.0923416  1.7338919  H  1.7370283  0.5885086  -4.7331852
H  4.3904560  1.8271984  1.7452228  C  0.5693909  0.1484792  1.8328014
H  5.1503185  0.4930027  2.6462001  C  -0.8141173  -0.7670854  0.0187657
H  6.1587428  1.6171578  1.6839717  N  1.8950469  0.3925545  1.9613827
C  5.2721788  1.0697535  1.1534990  C  1.4633908  3.0307578  -2.3594840
H  5.2535971  0.4552972  -2.0571552  H  1.5264822  2.7181729  -0.2159438
H  4.4665560  1.8075020  -1.2086052  H  1.4512394  3.0437126  -4.5130743
H  6.2321846  1.5889753  -1.0761970  C  -0.5632295  0.1730984  2.7104367
P  -4.0742952  0.1202287  -0.3356300  C  -2.0230750  -0.6690667  0.8603890
C  -4.1811655  0.8904870  -1.9652805  H  -0.8891928  -1.1303249  -1.0036182
H  -5.1259366  1.4312795  -2.0690822  C  2.6925356  0.8633819  3.1505218
H  -3.3412621  1.5804994  -2.0870546  H  1.3699827  4.1103284  -2.2832654
H  -4.1168129  0.1158211  -2.7336231  C  -1.7784361  -0.2454934  2.2486105
C  -5.4399048  -1.0538910  -0.1473851  H  -0.4919252  0.5098008  3.7341864
H  -5.3693452  -1.819753  -0.9251887  H  -2.6592300  0.5471726  0.2112521
H  -5.3690660  -1.5328406  0.8328780  C  3.7660876  -0.2010749  3.4256906
H  -6.4011990  -0.5393595  -0.2313996  C  3.3381968  2.2019300  2.7581750
C  -4.2288798  1.3917598  0.9385646  C  1.8306181  1.0561308  4.3975899
H  -5.1875241  1.9092551  0.8436630  H  -2.6218377  -0.2089225  2.9330299
H  -4.1594097  0.9184876  1.9213163  H  3.2994003  -1.1532091  3.692212
H  -3.4078299  2.1055403  0.8358716  H  4.3845712  -0.3515074  2.5402475
    H  4.3923870  0.1321054  4.2587965
    H  2.5676277  2.9506169  2.5443219
Energy = -1921.438040190

H  2.4536738  -3.4889407  -2.8364135
C  2.5213869  -3.7415334  -1.4609393
C  2.1897378  -2.2031009  -3.3162449
H  2.6154442  -4.3016038  -0.9251887
C  2.3129855  -2.7109468  -0.5364520
H  2.7402449  -4.7461336  -1.1099787
C  1.9966060  -1.1707312  -2.3953180
H  2.1457458  -2.0150399  -4.3857130
C  2.0543404  -1.4338989  -1.0123126
H  2.3619356  -2.9043589  0.5316289
C  1.7535645  0.2665513  -2.5895055
C  1.7191612  -0.1781161  -0.2144034
C  1.6607408  0.8768039  -1.3242184
C  1.6670705  1.0426333  -3.7483953
C  0.3678909  -0.3066720  0.4838009
N  2.6549190  0.1833052  0.8626843
H  -4.4192759  -2.7720556  -1.3027727
S58

TS4a+  TS for P..N addition of 2+ and PMe3
59

Energy = -1460.24462790

C 1.8516658  -2.9736745  -2.5912803
C 0.4952348  -2.6345728  -2.6229705
C 2.7469078  -2.2683079  -1.7823334
H 2.2157930  -3.7836482  -3.2161207
C 0.0083207  -1.5919258  -1.8265142
H -0.1809303  -3.1752677  -3.2781707
C 2.2590716  -1.2318940  -0.9860508
H 3.8030792  -2.5215590  -1.7835759
C 0.8876634  -0.9155968  -0.9940881
H -1.0382681  -1.3123525  -1.8836939
C 2.9525918  -0.3002664  -0.877446
H 0.6042759  0.2409860  -0.0321989
C 2.0074253  0.5733043  0.4799270
C 4.3097402  -0.1503628  0.2038882
C -0.0710240  1.4394576  -0.6550015
N -0.4077369  -0.0677629  1.0527336
C 2.4006699  1.6320129  1.2863514
C 4.7026106  0.8913963  1.0474614
H 5.0505033  -0.8179566  -0.2264166
C -1.3030019  1.6318954  -0.0380400
C 0.3737399  2.3205618  -1.6327764
N -1.5595345  0.6077232  0.9323351
C 3.7607574  1.7815888  1.5764150
H 1.6717019  2.3282518  1.6907399
H 5.7544974  1.0232770  1.2829118
C -2.1238075  2.7157861  -0.3389659

TS4b+  TS for 4p protonation with PMe3H+
72

Energy = -1921.482073194

C 1.1155843  3.0786877  3.4199546
C 0.2450867  1.9931893  3.576514
C 1.5362535  3.4790074  2.1490414
H 1.4659116  3.6163632  4.2966351
C -0.2204171  1.2908431  2.4597115
H -0.0712395  1.6981442  4.5733990

TS4a+  TS for P..N addition of 2+ and PMe3
59

Energy = -1460.24462790

C 1.8516658  -2.9736745  -2.5912803
C 0.4952348  -2.6345728  -2.6229705
C 2.7469078  -2.2683079  -1.7823334
H 2.2157930  -3.7836482  -3.2161207
C 0.0083207  -1.5919258  -1.8265142
H -0.1809303  -3.1752677  -3.2781707
C 2.2590716  -1.2318940  -0.9860508
H 3.8030792  -2.5215590  -1.7835759
C 0.8876634  -0.9155968  -0.9940881
H -1.0382681  -1.3123525  -1.8836939
C 2.9525918  -0.3002664  -0.877446
H 0.6042759  0.2409860  -0.0321989
C 2.0074253  0.5733043  0.4799270
C 4.3097402  -0.1503628  0.2038882
C -0.0710240  1.4394576  -0.6550015
N -0.4077369  -0.0677629  1.0527336
C 2.4006699  1.6320129  1.2863514
C 4.7026106  0.8913963  1.0474614
H 5.0505033  -0.8179566  -0.2264166
C -1.3030019  1.6318954  -0.0380400
C 0.3737399  2.3205618  -1.6327764
N -1.5595345  0.6077232  0.9323351
C 3.7607574  1.7815888  1.5764150
H 1.6717019  2.3282518  1.6907399
H 5.7544974  1.0232770  1.2829118
C -2.1238075  2.7157861  -0.3389659

TS4b+  TS for 4p protonation with PMe3H+
72

Energy = -1921.482073194

C 1.1155843  3.0786877  3.4199546
C 0.2450867  1.9931893  3.576514
C 1.5362535  3.4790074  2.1490414
H 1.4659116  3.6163632  4.2966351
C -0.2204171  1.2908431  2.4597115
H -0.0712395  1.6981442  4.5733990
| Atm. |  X       |  Y       |  Z       |
|------|----------|----------|----------|
| C    | 1.0695109| 2.7769890| 1.0351580|
| H    | 2.2093299| 4.3247108| 2.0359255|
| C    | 0.1927763| 1.6891569| 1.1975452|
| H    | -0.9021290| 0.4541872| 2.5726319|
| C    | 1.3189933| 2.9676168| -0.3996667|
| C    | -0.1706028| 1.0772949| -0.1482006|
| C    | 0.5841544| 2.0059136| -1.1200334|
| C    | 2.1406938| 3.8783298| -1.0690248|
| C    | 0.3277225| -0.3436628| -0.3550115|
| N    | -1.6473219| 0.8445870| -0.3064477|
| C    | 0.7043514| 1.9125749| -2.5010845|
| C    | 2.2272521| 3.8072269| -2.4612203|
| H    | 2.7111898| 4.6237416| -0.5211911|
| C    | -0.7340661| -1.0637183| -0.9911232|
| N    | -1.8659639| -0.3676837| -1.0708170|
| C    | 1.5210595| 2.8289807| -3.1719160|
| H    | 0.1694281| 1.1458046| -3.0537774|
| C    | -2.5882907| 1.9293286| -3.1719160|
| H    | -3.016039| -0.7396974| 2.6311253|
| C    | 0.7406600| -2.9751698| -1.1555136|
| H    | -1.2683160| -2.9779894| -1.9072800|
| H    | -2.9692833| -1.2528449| -0.2589983|
| C    | -2.2728800| 3.1925178| 0.1068773|
| C    | -2.5773331| 2.2460679| -2.085418|
| C    | -3.9943163| 1.4383308| -0.3135987|
| H    | 0.9126778| -4.000052| -1.4724202|
| H    | -2.921755| 2.9896491| -1.9183545|
| C    | -1.293543| 3.6023457| -0.1550317|
| H    | -3.0271224| 3.9529752| -0.1200447|
| H    | -2.6447781| 1.3152614| -2.7794195|
| H    | -3.4375695| 2.8763994| -2.4984272|
| H    | -1.6695382| 2.7785271| -2.4987697|
| H    | -4.7324825| 2.2240090| -0.5052293|
| H    | -4.2700758| 0.5583409| -0.9020896|
| H    | -4.0214446| 1.1867299| 0.7525183|
| P    | 3.3612161| -2.9583927| -2.363543|
| C    | 3.3967225| -4.6931040| -0.7335014|
| H    | 2.6570550| -5.2611901| -0.1643975|

| Atm. |  X       |  Y       |  Z       |
|------|----------|----------|----------|
| C    | 3.1861194| -4.7804412| -1.8020665|
| H    | 4.3933455| -5.0946273| -0.5312633|
| C    | 3.8444750| -2.8635321| 1.5086769|
| H    | 3.8155781| -1.8196480| 1.8333518|
| C    | 3.1398580| -3.4435260| 2.1097634|
| H    | 3.4857962| -3.2528814| 1.6439083|
| C    | 4.6637068| -2.0946623| -1.1579726|
| C    | 4.4657814| -2.1891788| -2.2286574|
| C    | 4.6498897| -1.0355149| -0.8851888|
| H    | 5.6454491| -2.5155625| -0.9220470|
| C    | -3.6562617| -2.1069444| 0.7685006|
| C    | -5.4323701| -1.7989035| 0.9488734|
| H    | -5.8485626| -2.4470730| 1.7259349|
| C    | -5.5952096| -0.7530789| 2.1290827|
| H    | -6.9321079| -2.0034398| -0.0016436|
| C    | -3.4328984| -3.8631298| 0.3786474|
| C    | -3.9124718| -4.0872693| -0.5781258|
| H    | -2.3639194| -4.0763105| 0.2984876|
| H    | -3.8766263| -4.4853555| 1.1613166|
| C    | -2.8512290| -1.7855033| 2.3578230|
| H    | -3.2581826| -2.4356054| 3.1372174|
| H    | -1.7780545| -1.9655719| 2.2505276|
| C    | -3.016039| -0.7396974| 2.6311253|

TS4c+  TS for 4p protonation at N-tBu

Energy = -1921.48518103

TS4c+  TS for 4p protonation at N-tBu

Energy = -1921.48518103

S59
C  0.4333889  1.4116760 -2.2622085  P  -1.3017464  3.0057163  0.6081665
C  1.7010168  0.8161581 -4.2455618  C  -1.2129594  4.5417507  -0.3710141
H  3.1415977 -0.7778271 -4.0278942  H  -1.0323586  4.3028921  -1.4229219
C  -0.5667538  0.0126159  1.6927350  H  -2.1440541  5.1100259  -0.2876046
C  -1.2644037 -1.2686489 -0.884545  H  -0.3845170  5.1563244  -0.0070137
N  0.3595446  0.8677232  2.1167823  C  -2.7505558  2.0999389  -0.0247158
C  0.7257805  1.5977441 -3.6179086  H  -3.6417402  2.7337454  0.0144397
H  -0.3322122  2.0158143 -1.781160  H  -2.5686817  1.7916296 -1.0575322
H  1.9174889  0.9706579 -5.2986345  H  -2.9014141  1.2050881  0.5851815
C  -1.6994461 -0.4744283  2.4142360  C  -1.7296377  3.5270398  2.2973651
C  -2.4236837 -1.7048433  0.4150315  H  -2.6456284  4.1265928  2.2961152
H  -1.0759357 -1.5903280 -1.3093187  H  -1.8629337  2.6364943  2.9149900
C  2.4216490  1.8736685  1.2352560  H  -0.9084983  4.1187627  2.7095073
H  0.1896520  2.3514305 -4.1872479
C  -2.5949216 -1.3021668  1.7714596  "TS4d+  TS for 4c+ C..N ring opening"
H  -1.8604964 -0.1799740  3.4468480
H  0.0824348  2.1757712  0.5142038  Energy = -1460.260532233
C  3.2815541  1.0394106  2.1955757  C  2.1415842 -3.8586578  0.8524708
C  3.1911417  2.1618402 -0.0557034  C  1.1849168 -3.3136913  1.7168010
C  2.0588190  3.2051829  1.9153910  C  2.5872500 -3.1532740  -0.2728296
H  -3.4665271 -1.6468591  2.3244521  H  2.5383534 -4.8960610  1.0526342
H  2.6835227  0.7199355  3.0526145  C  0.6638749 -2.0366906  1.4844225
C  3.6985997  0.1601991  1.7023729  H  0.8490599 -3.8864655  2.5758072
H  4.114223  1.6575569  2.5539258  C  2.0690808 -1.8840447 -0.5123119
H  2.5867016  2.7352932 -0.7647608  H  3.3137954 -3.5999024  0.9454626
C  4.0786744  2.7505497  0.1961856  C  1.1206372 -1.3224048  0.3799240
H  3.5237886  1.2413397 -0.5410430  H  -0.0748184 -1.6068828  2.1553552
H  2.9771886  3.7207718  2.2106919  C  2.2889266 -0.9254727  1.6034524
C  1.5150185  3.8612750  1.2262729  C  0.7357088  0.0254502 -0.0864477
H  1.4486427  3.0288552  2.8036751  C  1.4626095  0.2007869 -1.3711576
P  -3.6332643 -2.7160087 -0.3453859  C  3.1096690 -0.9701461 -2.7263657
C  -5.2467602 -1.8950809 -0.4506050  C  -0.6193415  0.5410767  0.1442958
H  -5.5680420 -1.6083339  0.5546212  N  1.5048344  1.6212240  0.8715817
H  -5.1519698 -0.9965003 -1.0656634  C  1.4431892  1.2713947  2.2606387
H  -5.9890647 -2.5678392 -0.8890518  C  3.0983032  0.1144735  3.6131469
C  -3.9077160 -4.2515900  0.5748866  H  3.7492511 -1.8267536  2.9193383
H  -2.9803074 -4.8293741  0.5941960  C  -0.7110821  1.8058647  0.8256420
H  -4.1986419 -4.0102020  1.6008615  C  -1.7701945 -0.1562552 -0.1728707
H  -4.7020449 -4.8374954  0.1035685  N  0.4087683  2.2938891  1.3745629
C  -3.1283197 -3.1520996 -2.0225224  C  2.2742218  1.2209412 -3.3874529
H  -3.0112682 -2.2489700 -2.6246325  H  0.7861261  2.1235212 -2.1011837
H  -2.1858739 -3.7045753 -1.9975780  H  3.7349313  0.0926206  4.4925893
H  -3.9018852 -3.7821943 -2.4692812  C  -1.9949757  2.3858502  1.0176399
| Atom | X       | Y       | Z       |
|------|---------|---------|---------|
| C    | -3.042351 | 0.4140318 | 0.0458248 |
| H    | -1.6748090 | -1.1391549 | -0.6301098 |
| C    | 2.6801587 | 1.5471112 | 1.8247098 |
| H    | 2.2727949 | 2.0449922 | -4.0942318 |
| C    | -3.1267891 | 1.7030782 | 0.6298386 |
| H    | -2.0707756 | 3.3628334 | 1.4832637 |
| H    | 1.8323903 | 2.0172941 | -0.0204019 |
| C    | 3.8009107 | 0.7968367 | 1.1027037 |
| C    | 3.1067303 | 2.9921474 | 2.1265440 |
| C    | 2.2362216 | 0.8273008 | 3.0954005 |
| H    | -4.0958604 | 2.1663963 | 0.7871998 |
| H    | 3.5288245 | -0.2446494 | 0.9186526 |
| H    | 4.0462232 | 1.2732905 | 0.1466323 |
| C    | 4.6984333 | 0.8125983 | 1.7267769 |
| H    | 2.9648191 | 3.5357835 | 2.6164341 |
| H    | 3.9805978 | 2.9741573 | 2.7848162 |
| C    | 3.8244611 | 3.5157059 | 1.2053277 |
| C    | 3.0610048 | 0.8306657 | 3.8133845 |
| H    | -4.0958604 | 2.1663963 | 0.7871998 |
| H    | 3.5288245 | -0.2446494 | 0.9186526 |
| H    | 4.0462232 | 1.2732905 | 0.1466323 |
| C    | 4.6984333 | 0.8125983 | 1.7267769 |
| H    | 2.9648191 | 3.5357835 | 2.6164341 |
| H    | 3.9805978 | 2.9741573 | 2.7848162 |
| C    | 3.8244611 | 3.5157059 | 1.2053277 |
| C    | 3.0610048 | 0.8306657 | 3.8133845 |
| H    | -4.0958604 | 2.1663963 | 0.7871998 |
| H    | 3.5288245 | -0.2446494 | 0.9186526 |
| H    | 4.0462232 | 1.2732905 | 0.1466323 |
| C    | 4.6984333 | 0.8125983 | 1.7267769 |
| H    | 2.9648191 | 3.5357835 | 2.6164341 |
| H    | 3.9805978 | 2.9741573 | 2.7848162 |
| C    | 3.8244611 | 3.5157059 | 1.2053277 |
| C    | 3.0610048 | 0.8306657 | 3.8133845 |

**TS4e**

TS for N.H..C H+ transfer

Energy = -1460.248010630
TS4p*  TS for 2p* deprotonation with PMe$_3$

Energy = -1921.463812747
TS4+  TS for final aryl rotation of 4e+

Energy = -1460.257547325

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