

Supporting Information

Single-Electron Transfer in Frustrated Lewis Pair Chemistry

*Flip Holtrop, Andrew R. Jupp, Bastiaan J. Kooij, Nicolaas P. van Leest, Bas de Bruin, and J. Chris Slootweg**

anie_202009717_sm_miscellaneous_information.pdf

SUPPORTING INFORMATION

Table of Contents

| | |
|--|----|
| Experimental Procedures..... | 3 |
| General considerations | 3 |
| Reactivity: H ₂ splitting | 3 |
| Reactivity: Tin hydride reactivity | 6 |
| Reactivity: tetrachloro-1,4-benzoquinone (TCQ) reactivity | 17 |
| Computational details: FLP reactivity with triphenyltin hydride..... | 19 |
| Computational details: Ionisation potentials and electron affinities | 45 |
| References | 74 |

SUPPORTING INFORMATION

Experimental Procedures

General considerations

All manipulations regarding the preparation of air-sensitive compounds were carried out under an atmosphere of dry nitrogen using standard Schlenk and drybox techniques. Solvents were purified, dried and degassed according to standard procedures. NMR spectra were measured on a Bruker DRX 500 or Bruker AMX 400 spectrometer at room temperature. ^1H , ^{11}B , ^{19}F , ^{31}P and ^{119}Sn -NMR spectra were externally referenced (SiMe_4 , $\text{BF}_3\cdot\text{OEt}_2$, CFCl_3 , 85% H_3PO_4 and SnMe_4 , respectively). The EPR spectra were recorded on a Bruker EMX X-band spectrometer and further analyzed and simulated using EasySpin.¹ The following reagents were purchased from commercial sources: $\text{B}(\text{C}_6\text{F}_5)_3$ (>98%, TCI chemicals), PMes_3 (97%, Sigma Aldrich), P^tBu_3 (98%, Sigma Aldrich), $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ (97%, Alfa Aesar), TCQ (99%, Sigma Aldrich), Ph_3SnH (97%, Sigma Aldrich), and used without further purification.

Reactivity: H_2 splitting

Trimesitylphosphine (15.5 mg, 0.04 mmol, 1.0 equiv.) and tris(pentafluorophenyl)borane (20.5 mg, 0.04 mmol, 1.0 equiv.) were added together in 1 mL chlorobenzene to yield a pink solution. A freeze-pump-thaw cycle was employed to degas the solution after which the solution was brought under 1 atm of H_2 . Half the samples were kept in the dark while the other half was irradiated with 530 nm light (High power LEDs: OSRAM Oslon SSL 80). After 2,5 h and 4 h one of each reaction type (dark and irradiated) was quenched via release of H_2 gas and subsequently analysed by ^{31}P -NMR spectroscopy. Spectra recorded for reactions in the dark and under irradiation were identical. This method was chosen after monitoring the reaction in a J-Young NMR tube was found to lead to a very slow reaction, most likely due to the slow diffusion of H_2 into the solution. Therefore using the NMR monitoring method we were not measuring the rate of the reaction but the diffusion speed of H_2 and so a different protocol was designed. For completeness, the approximate conversions obtained using the first method are also given below.

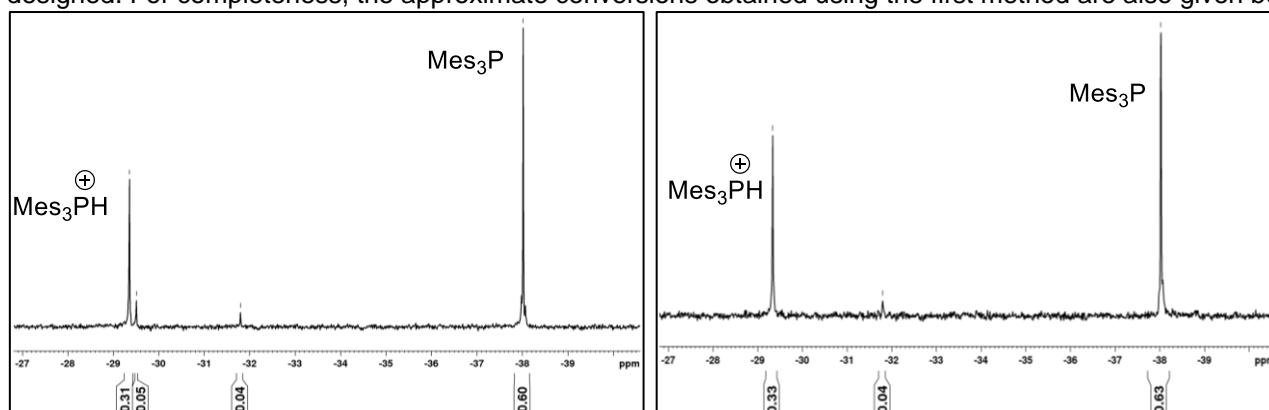


Figure S1. ^{31}P -NMR spectra of $\text{PMes}_3/\text{B}(\text{C}_6\text{F}_5)_3 + \text{H}_2$ after 2.5 h in the dark (left) and irradiated with 530 nm light (right)

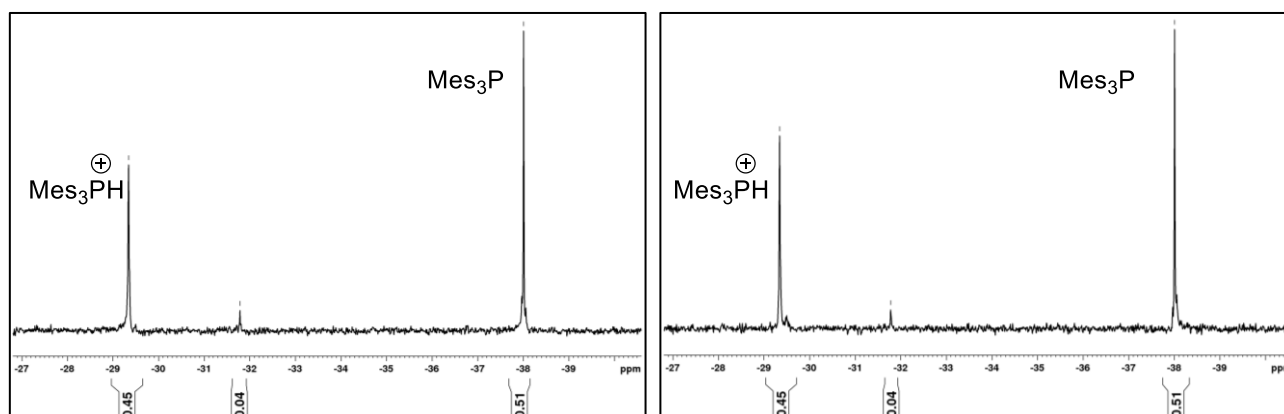


Figure S2. ^{31}P -NMR spectra of $\text{PMes}_3/\text{B}(\text{C}_6\text{F}_5)_3 + \text{H}_2$ after 4 h in the dark (left) and irradiated with 530 nm light (right)

SUPPORTING INFORMATION

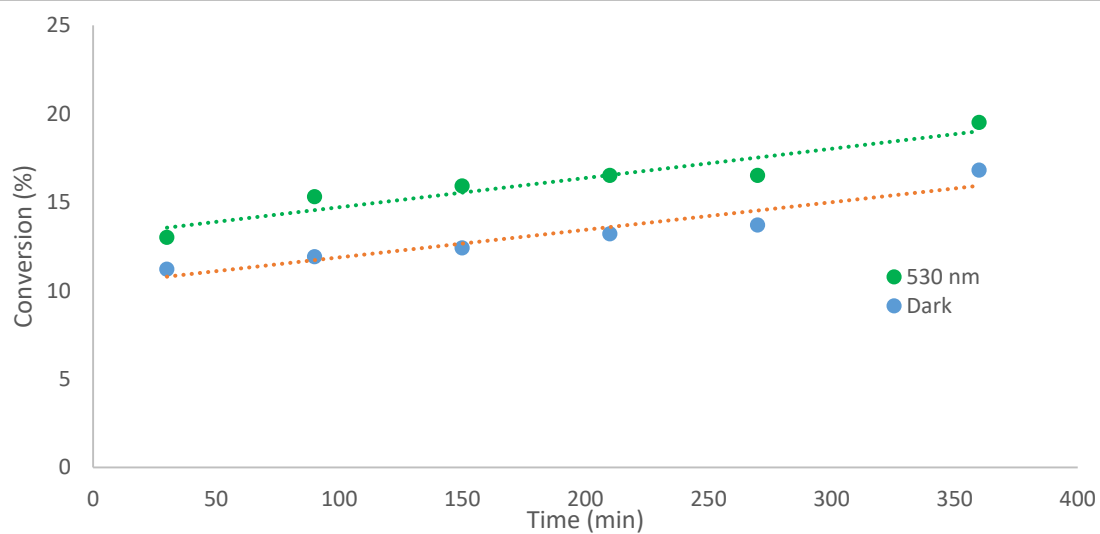


Figure S3. Approximate conversions obtained for the PMes_3/BCF reactions in the dark and under 530 nm irradiation monitored over time in a J-Young NMR tube

SUPPORTING INFORMATION

LED-setup

The LED setup used to irradiate the sample consisted of a LED plate and water-cooled block which keeps the samples at near ambient temperature. The cooling block is mounted on the LED plate after which flat bottomed Schlenks are placed into the holes of the cooling plate. These Schlenks are made to fit exactly so that cooling functions properly.

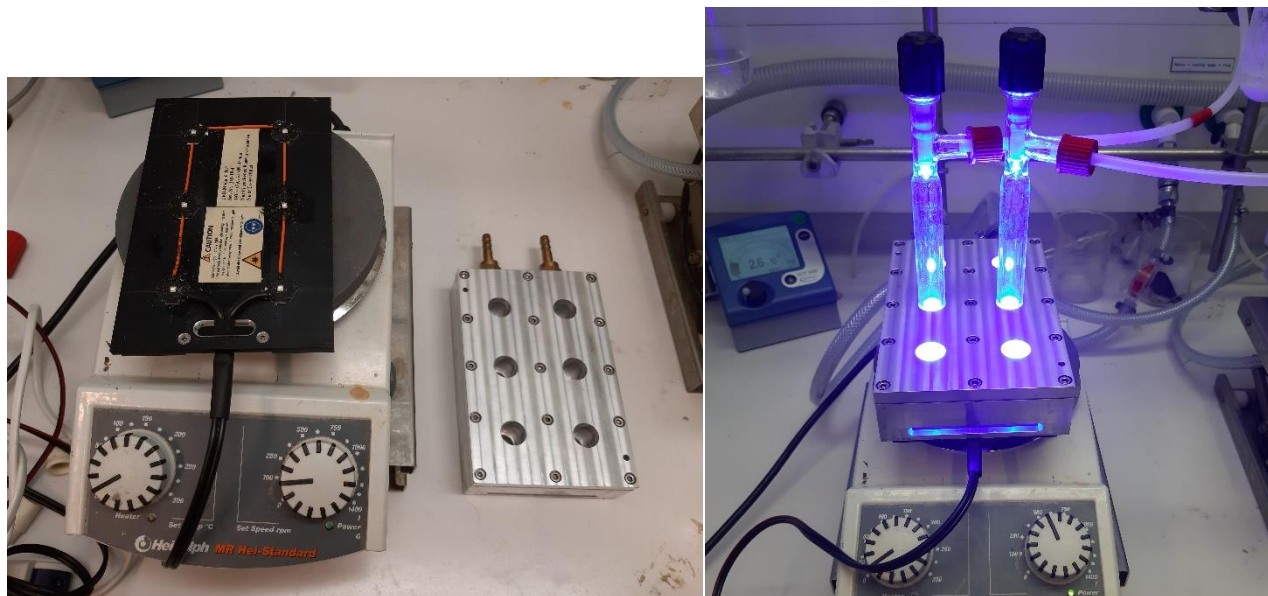


Figure S4. LED plate and water-cooled block (left) used to setup the irradiation setup as shown right. 455 nm irradiation depicted

SUPPORTING INFORMATION

Reactivity: Tin hydride reactivity

PMes₃/BCF + Ph₃SnH

Trimesitylphosphine (23.3 mg, 0.06 mmol, 1.0 equiv.) and tris(pentafluorophenyl)borane (30.4 mg, 0.06 mmol, 1.0 equiv.) were added together in 2 mL chlorobenzene. This solution was added to either 1.0 equiv. or 2.5 equiv. Ph₃SnH (21.2 mg, 0.06 mmol, 1.0 equiv.; 53 mg, 0.15 mmol, 2.5 equiv.). In case of 1.0 equiv., 50% conversion to [Mes₃PH][H(BC₆F₅)₃] was observed. The 2.5 equiv. experiment was performed in both darkness and ambient light for which in both cases full conversion to [Mes₃PH][H(BC₆F₅)₃] was observed.

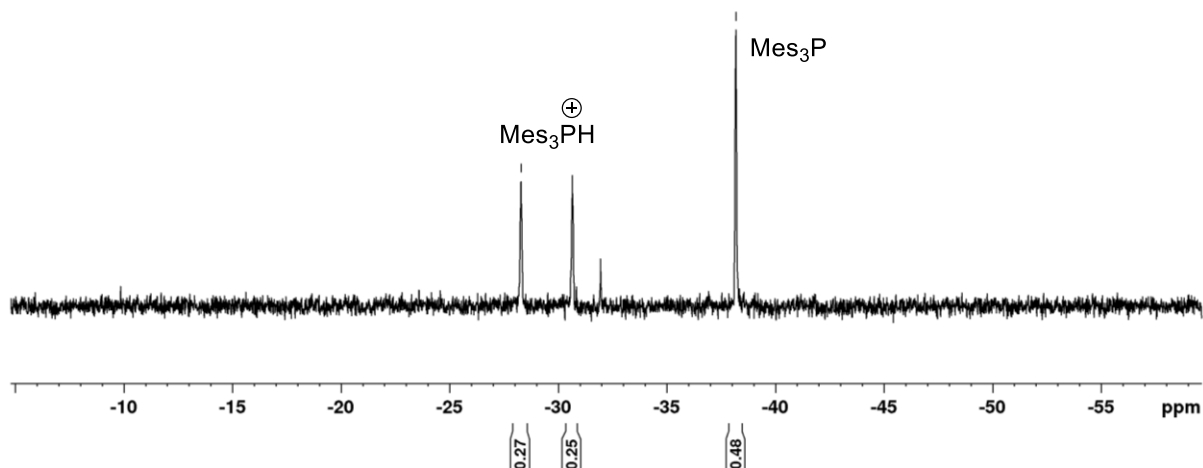


Figure S5. ³¹P-NMR spectra of PMes₃/B(C₆F₅)₃ + 1.0 equiv. Ph₃SnH

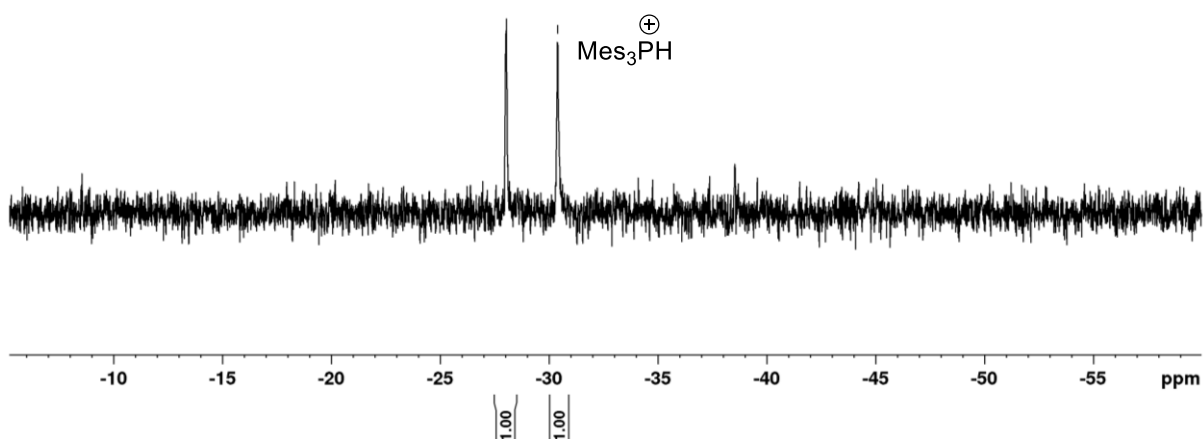


Figure S6. ³¹P-NMR spectrum of PMes₃/B(C₆F₅)₃ + 2.5 equiv. Ph₃SnH in ambient light

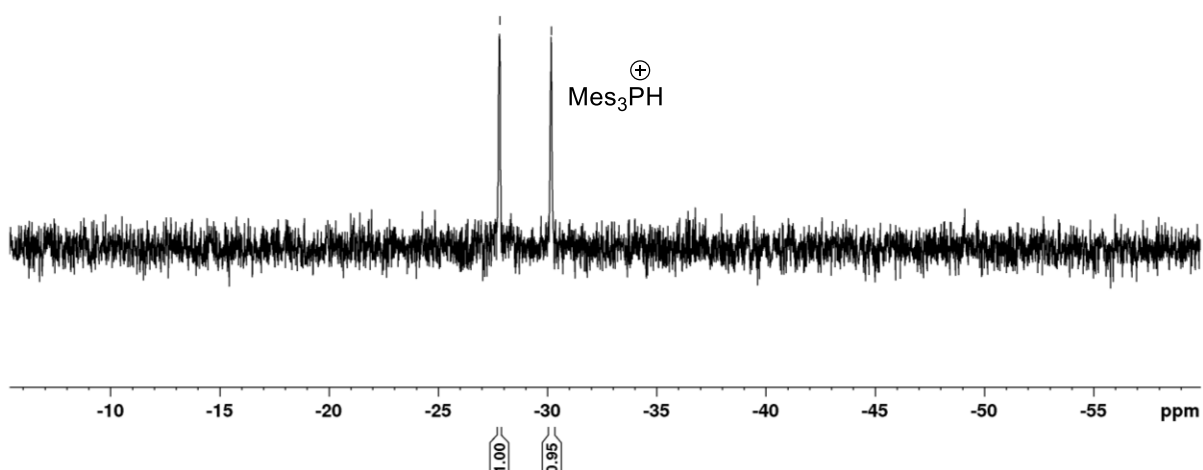


Figure S7. ³¹P-NMR spectrum of PMes₃/B(C₆F₅)₃ + 2.5 equiv. Ph₃SnH in darkness

SUPPORTING INFORMATION

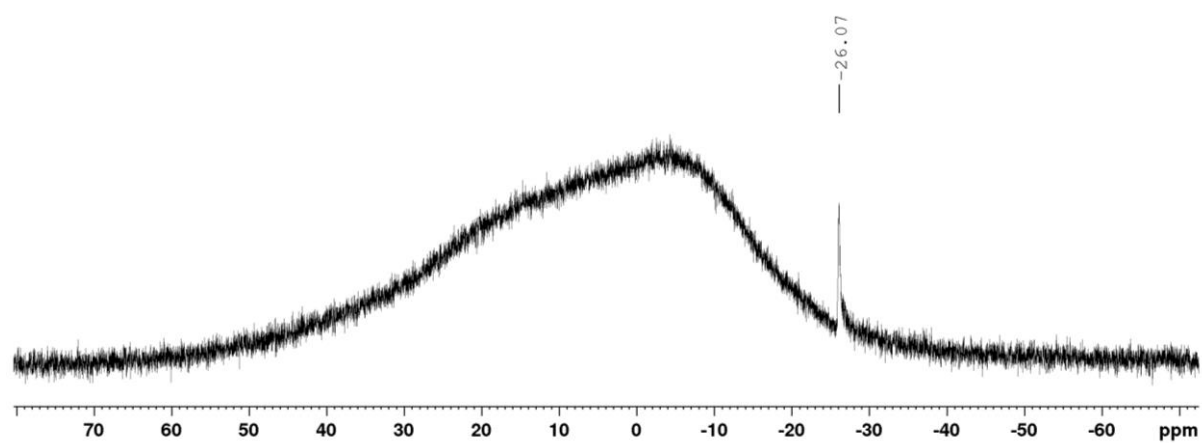


Figure S8. ^{11}B -NMR spectrum of $\text{PMes}_3/\text{B}(\text{C}_6\text{F}_5)_3 + 2.5$ equiv. Ph_3SnH in darkness

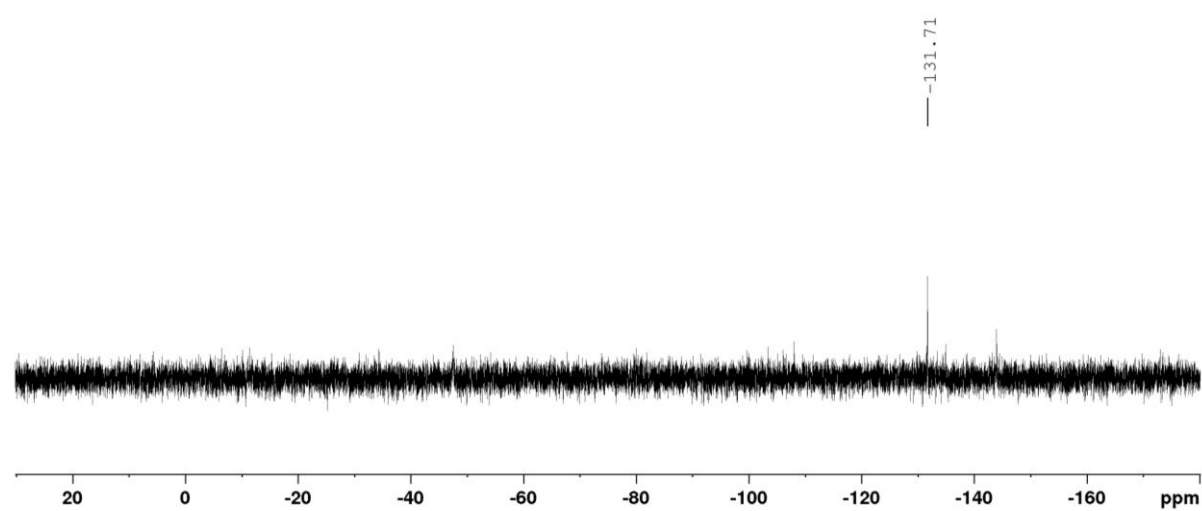


Figure S9. $^{119}\text{Sn}\{^1\text{H}\}$ -NMR spectrum of $\text{PMes}_3/\text{B}(\text{C}_6\text{F}_5)_3 + 2.5$ equiv. Ph_3SnH in darkness

SUPPORTING INFORMATION

PtBu₃/BCF + Ph₃SnH

Tri-*t*-butylphosphine (12.0 mg, 0.06 mmol, 1.0 equiv.) and tris(pentafluorophenyl)borane (30.4 mg, 0.06 mmol, 1.0 equiv.) were added together in 2 mL chlorobenzene. This solution was added to Ph₃SnH (21.2 mg, 0.06 mmol, 1.0 equiv.) or (53 mg, 0.15 mmol, 2.5 equiv.). The 2.5 equiv. Ph₃SnH experiment was stirred overnight.

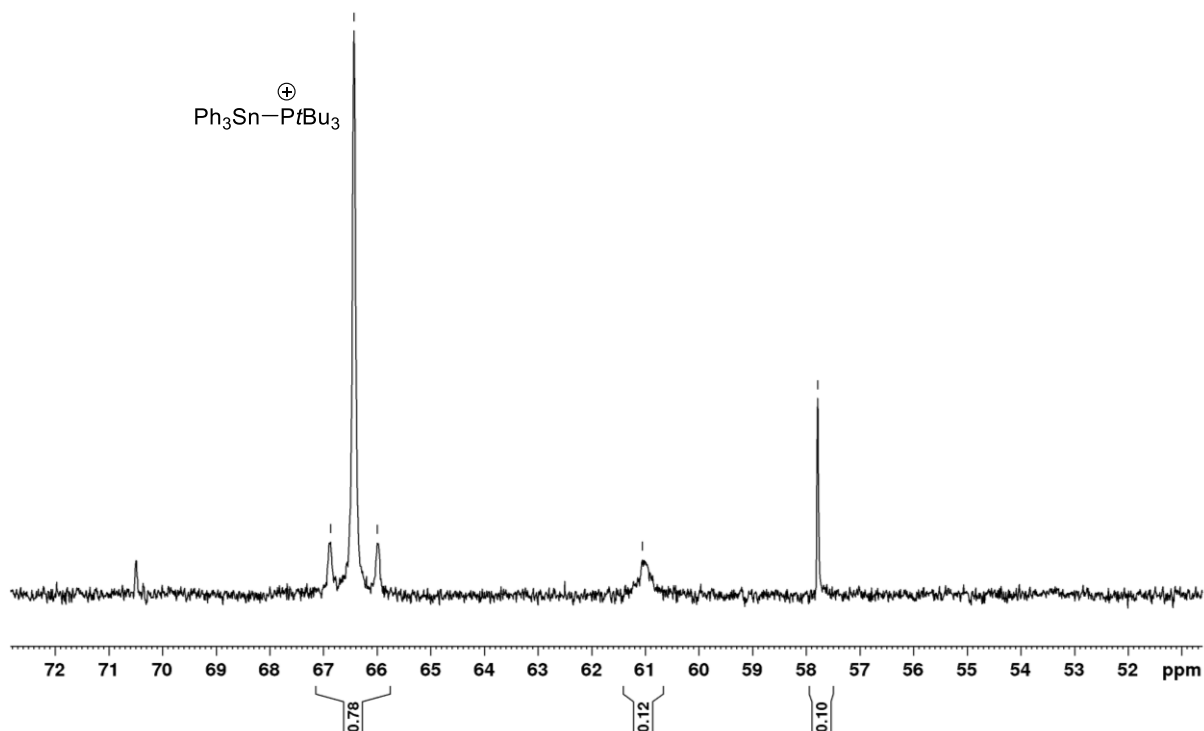


Figure S10. ³¹P-NMR spectrum of 1.0 equiv. PtBu₃/B(C₆F₅)₃ + 1.0 equiv. Ph₃SnH

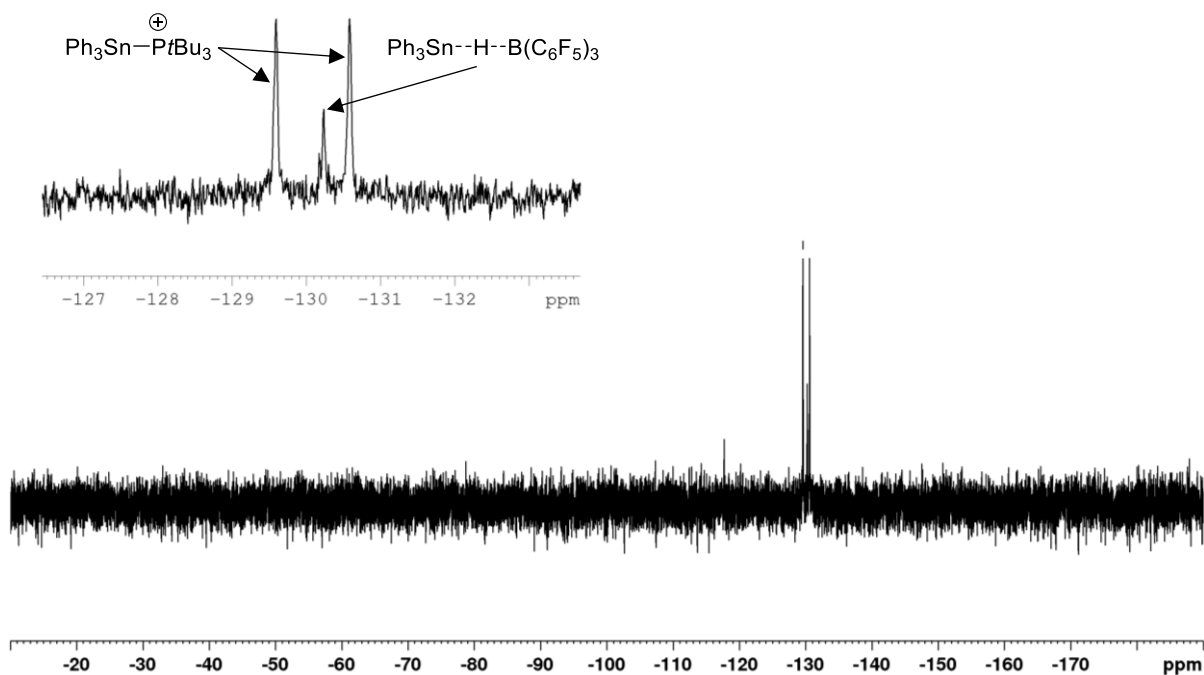


Figure S11. ¹¹⁹Sn{¹H}-NMR spectrum of 1.0 equiv. PtBu₃/B(C₆F₅)₃ + 1.0 equiv. Ph₃SnH

SUPPORTING INFORMATION

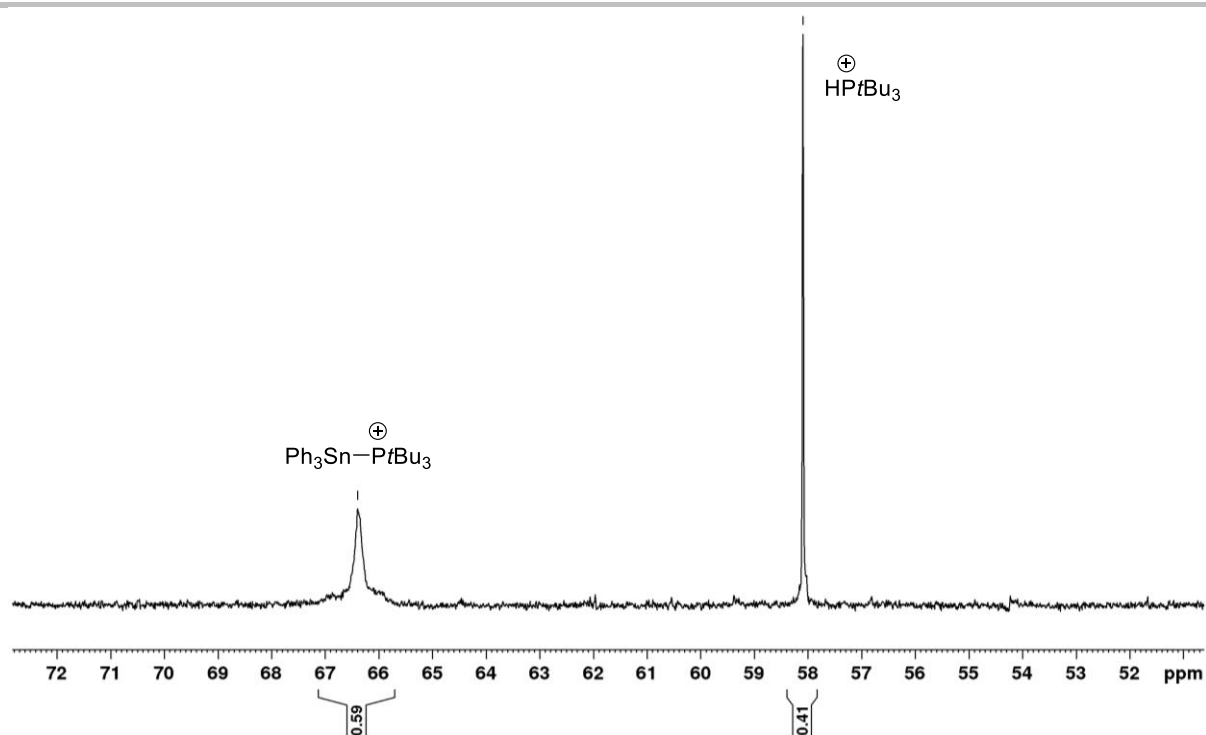


Figure S12. ^{31}P -NMR spectrum of 1.0 equiv. $\text{PtBu}_3/\text{B}(\text{C}_6\text{F}_5)_3 + 2.5$ equiv. Ph_3SnH after overnight stirring

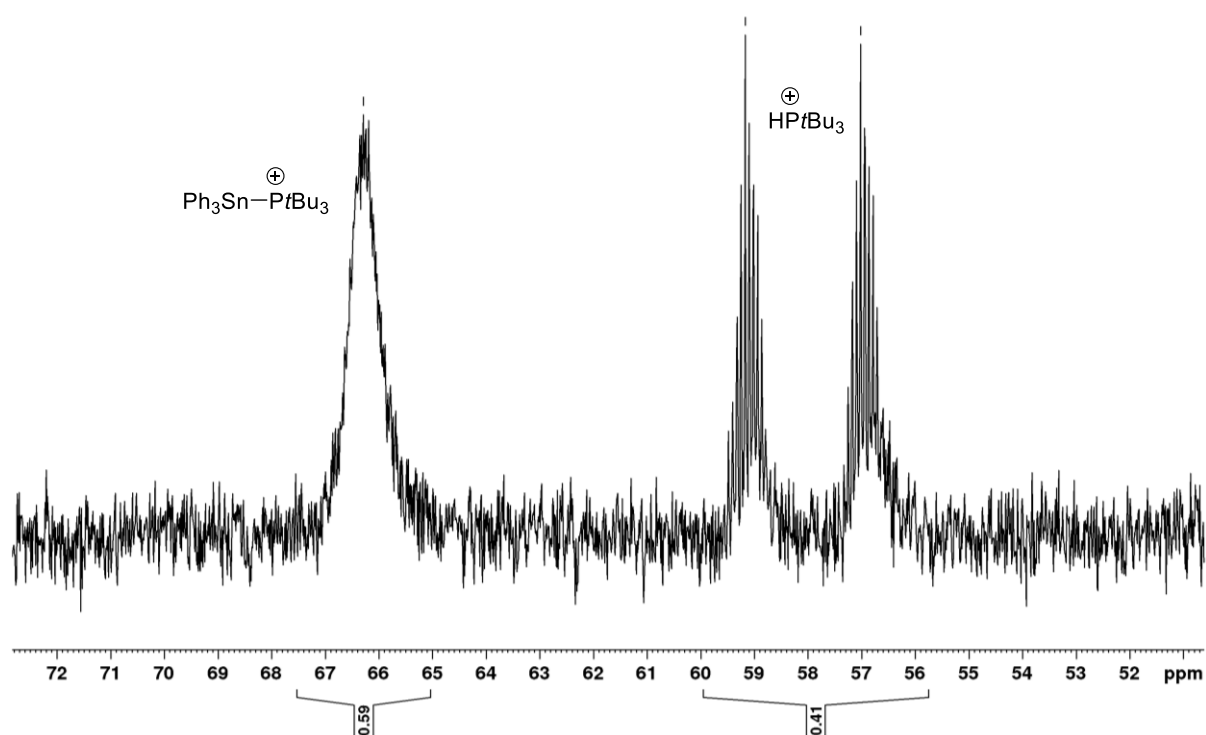


Figure S13. $^{31}\text{P}\{^1\text{H}\}$ -NMR spectrum of 1.0 equiv. $\text{PtBu}_3/\text{B}(\text{C}_6\text{F}_5)_3 + 2.5$ equiv. Ph_3SnH after overnight stirring

SUPPORTING INFORMATION

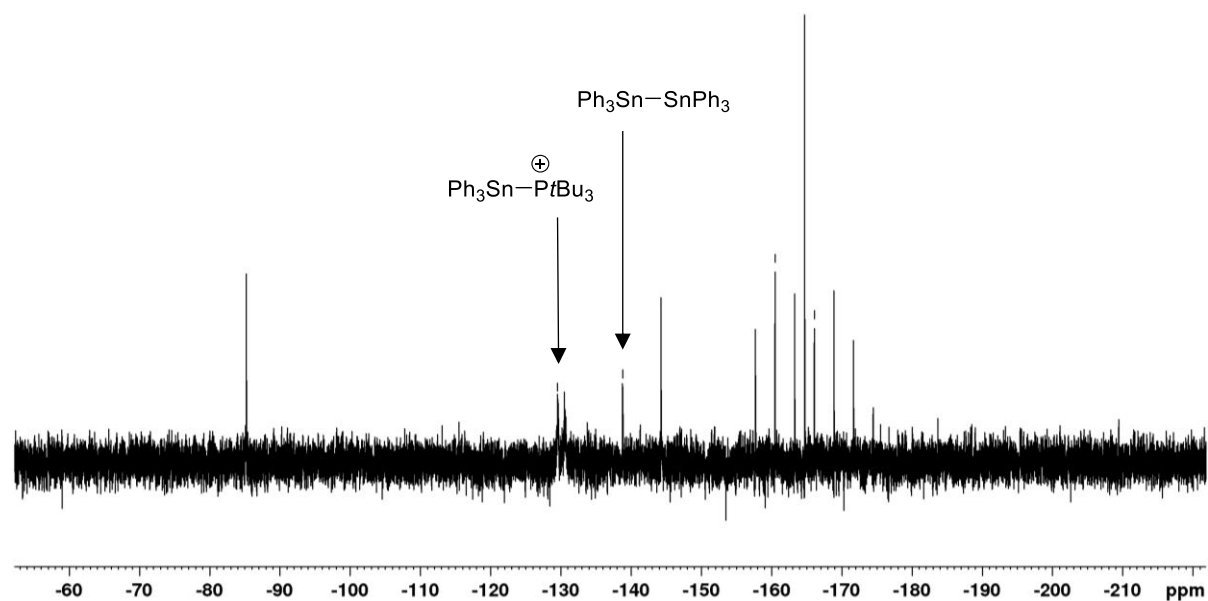


Figure S14. $^{119}\text{Sn}\{^1\text{H}\}$ -NMR spectrum of 1.0 equiv. $\text{PtBu}_3/\text{B}(\text{C}_6\text{F}_5)_3 + 2.5$ equiv. Ph_3SnH after overnight stirring

Control experiment: $\text{Ph}_3\text{SnH} + \text{B}(\text{C}_6\text{F}_5)_3$

Tris(pentafluorophenyl)borane (15.2 mg, 0.03 mmol, 1.0 equiv.) and Ph_3SnH (10.6 mg, 0.03 mmol, 1.0 equiv.) were added together in 1 mL chlorobenzene. NMR analysis shows the tin hydride interacts with the borane causing a significant shift in both ^{119}Sn - (from -163 to -130 ppm) and ^{19}F -NMR (*para*-F peak from -142 to 149 ppm).²

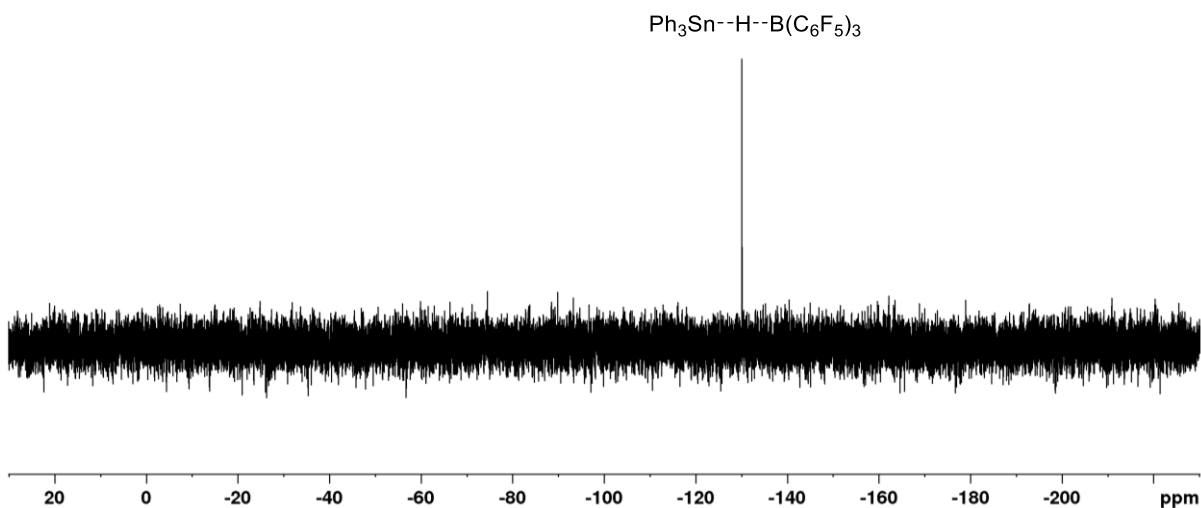
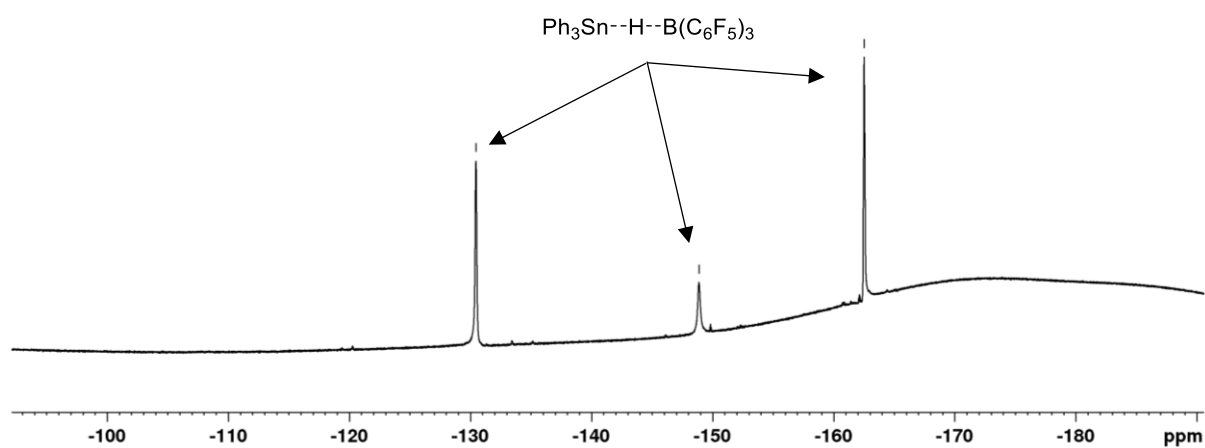
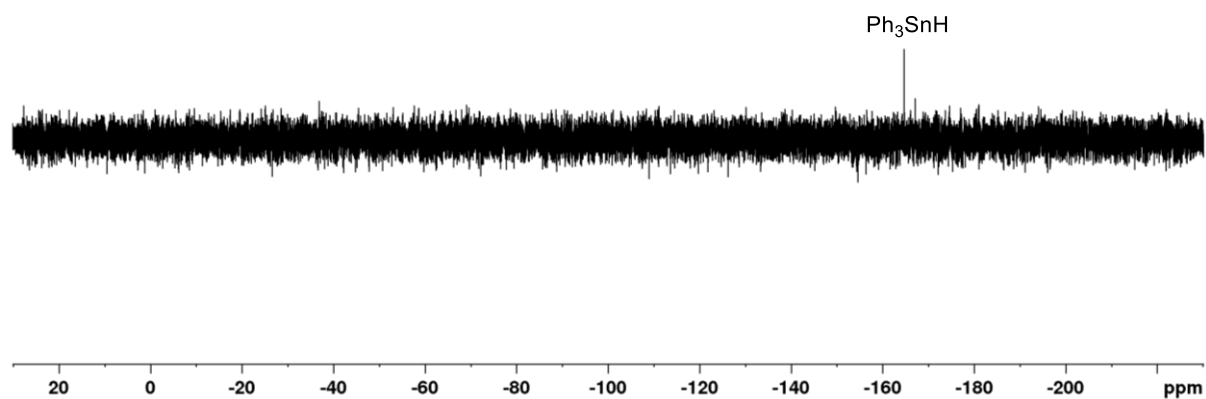
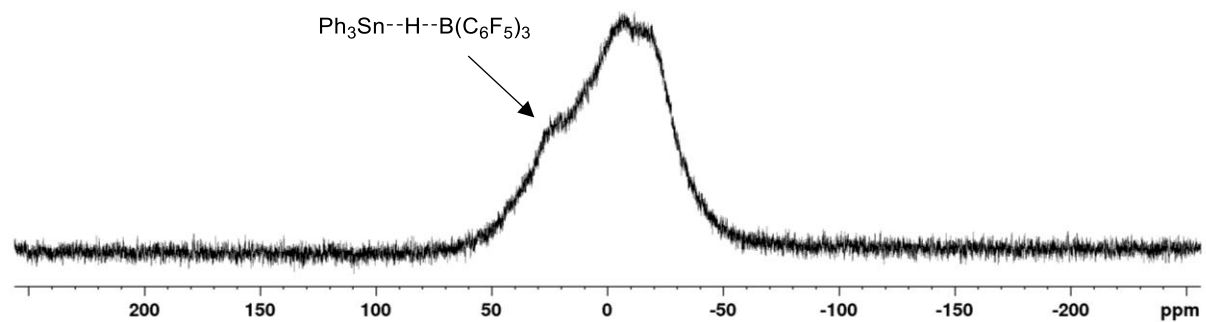
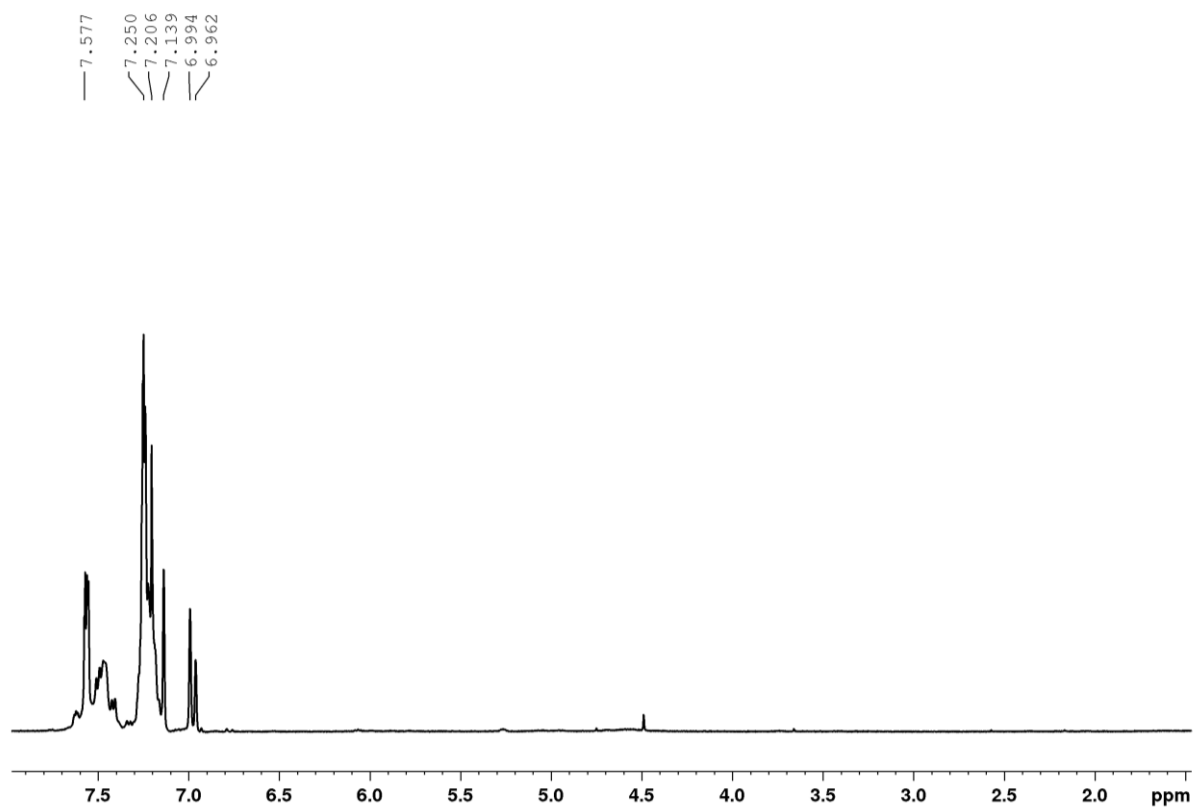
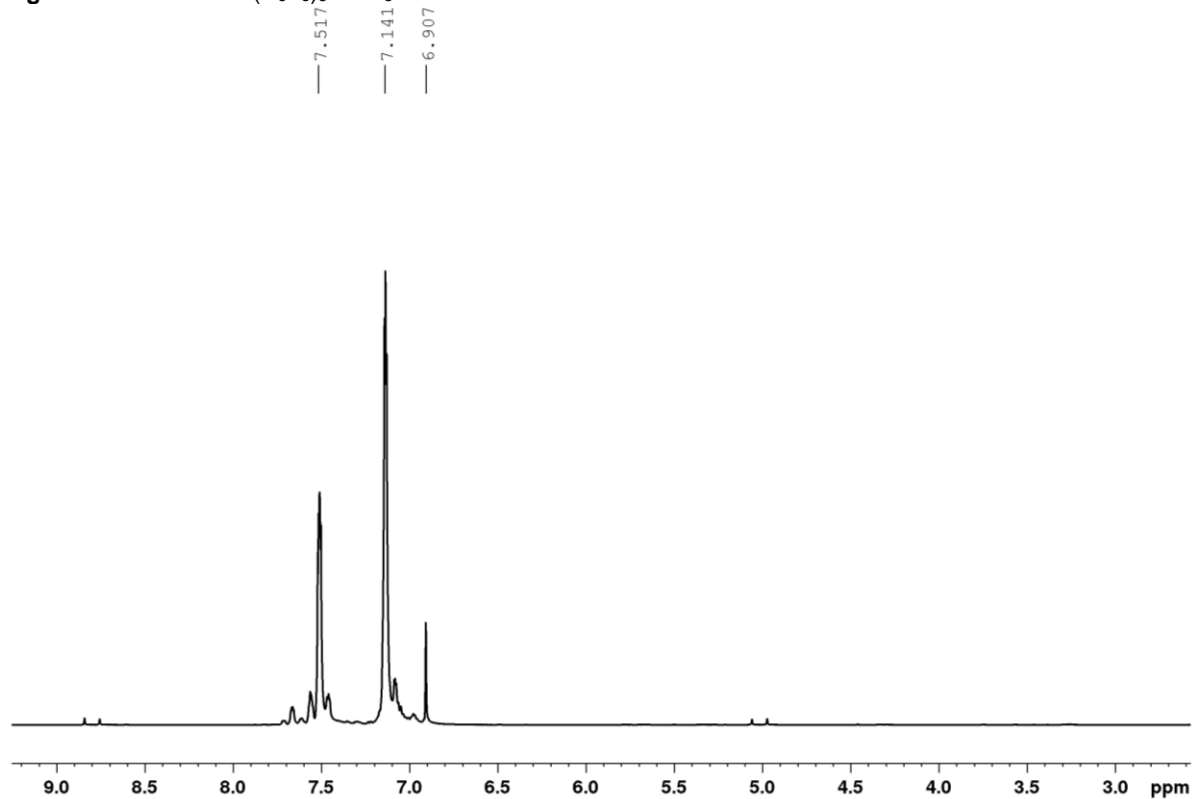


Figure S15. $^{119}\text{Sn}\{^1\text{H}\}$ -NMR $\text{B}(\text{C}_6\text{F}_5)_3 + \text{Ph}_3\text{SnH}$

SUPPORTING INFORMATION

**Figure S16.** ^{19}F -NMR $\text{B}(\text{C}_6\text{F}_5)_3 + \text{Ph}_3\text{SnH}$ **Figure S17.** $^{119}\text{Sn}\{^1\text{H}\}$ -NMR Ph_3SnH in $\text{C}_6\text{D}_5\text{Cl}$ **Figure S18.** ^{11}B -NMR $\text{B}(\text{C}_6\text{F}_5)_3 + \text{Ph}_3\text{SnH}$

SUPPORTING INFORMATION

Figure S19. ¹H-NMR B(C₆F₅)₃ + Ph₃SnHFigure S20. ¹H-NMR Ph₃SnH in C₆D₅Cl

SUPPORTING INFORMATION

[Ph₃C][B(C₆F₅)₄] + Ph₃SnH + PR₃

Triphenyltin hydride (36 mg, 0.1 mmol, 1.0 equiv.) was dissolved in 0.7 mL chlorobenzene. This was added to [Ph₃C][B(C₆F₅)₄] (46 mg, 0.05 mmol, 0.5 equiv.) at -35 °C. During subsequent stirring (30 min) the yellow colour disappeared and a white suspension formed. Subsequent addition of phosphine (PMe₃: 20 mg, 0.05 mmol, 0.5 equiv.; P*t*Bu₃: 10 mg, 0.05 mmol, 0.5 equiv.) was performed at -35 °C after which the reaction mixture was slowly allowed to warm to room temperature over 1 hour.

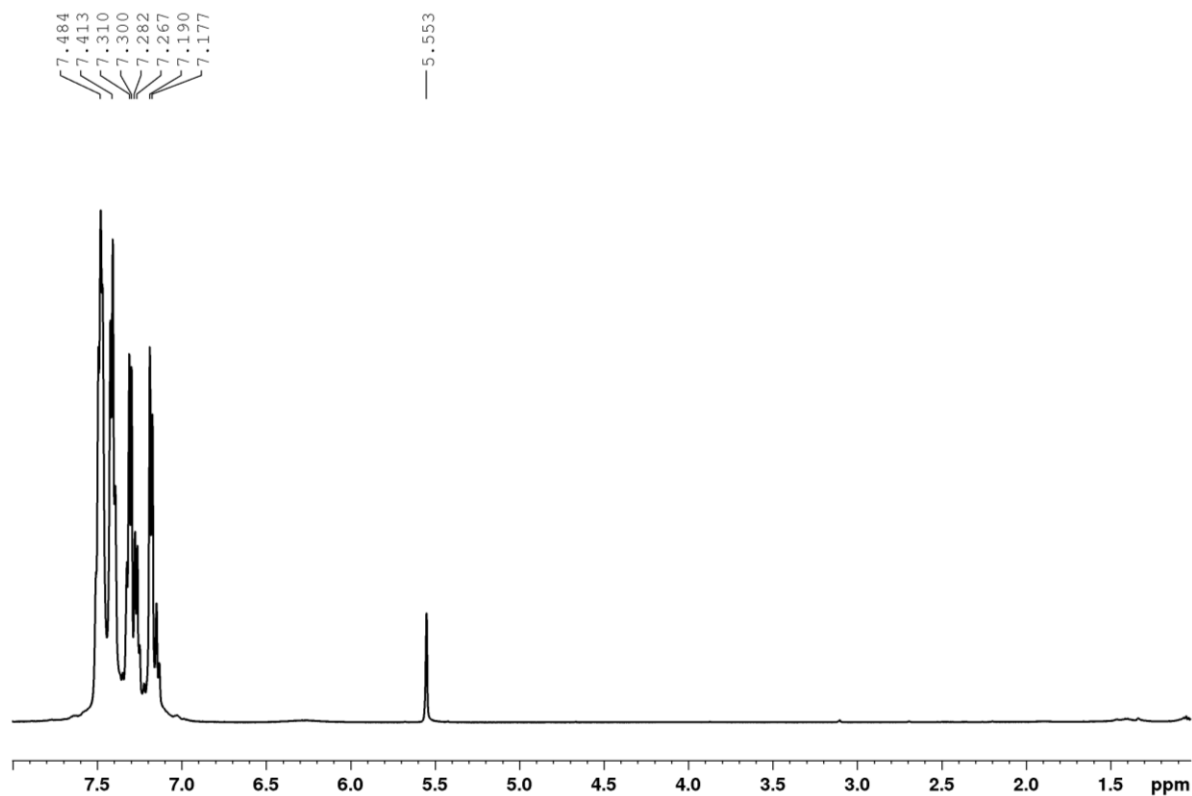


Figure S21. ¹H-NMR [Ph₃C][B(C₆F₅)₄] + 2 equiv. Ph₃SnH in C₆D₅Cl

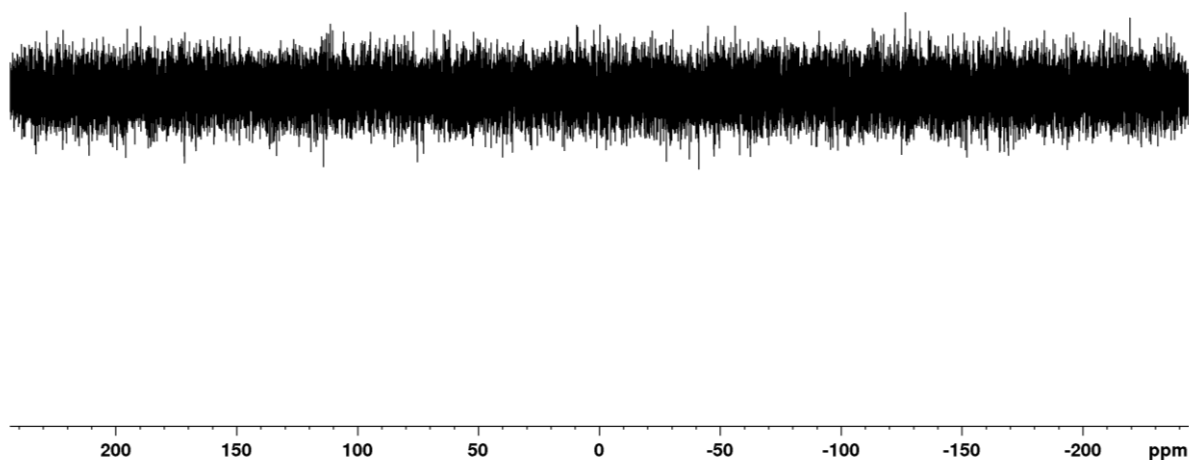


Figure S22. ¹¹⁹Sn{¹H}-NMR [Ph₃C][B(C₆F₅)₄] + 2 equiv. Ph₃SnH in C₆D₅Cl

SUPPORTING INFORMATION

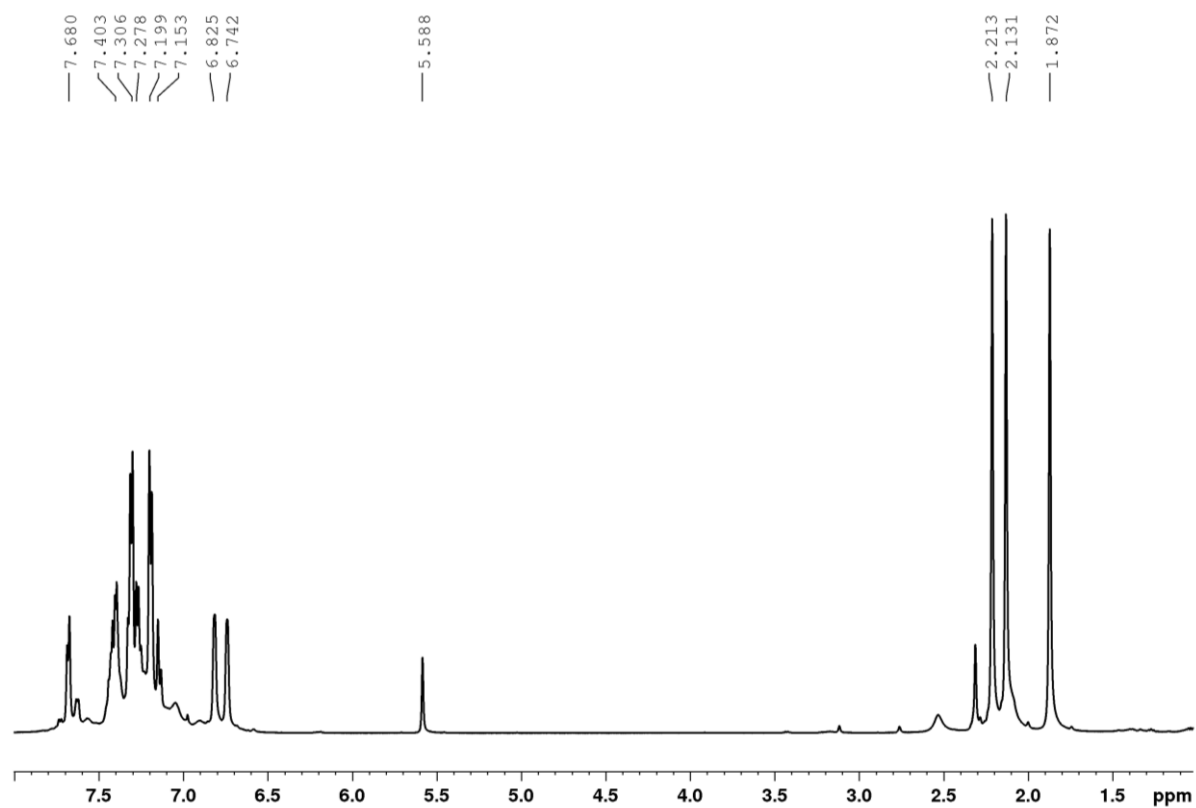
Addition of PMe₃

Figure S23. ¹H-NMR [Ph₃C][B(C₆F₅)₄] + 2 equiv. Ph₃SnH in C₆D₅Cl + PMe₃

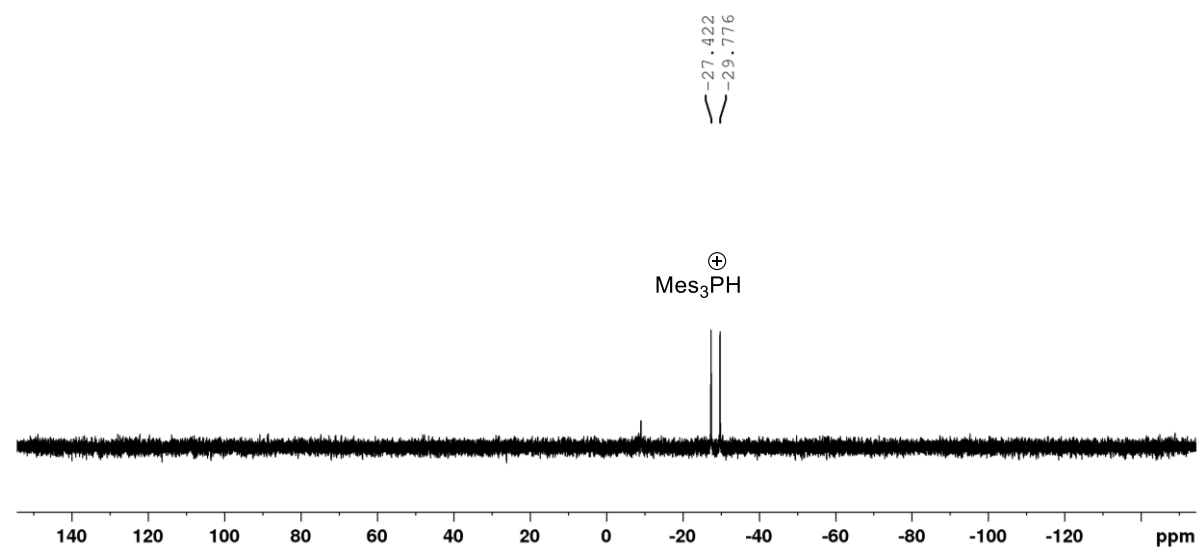


Figure S24. ³¹P-NMR [Ph₃C][B(C₆F₅)₄] + 2 equiv. Ph₃SnH in C₆D₅Cl + PMe₃

SUPPORTING INFORMATION

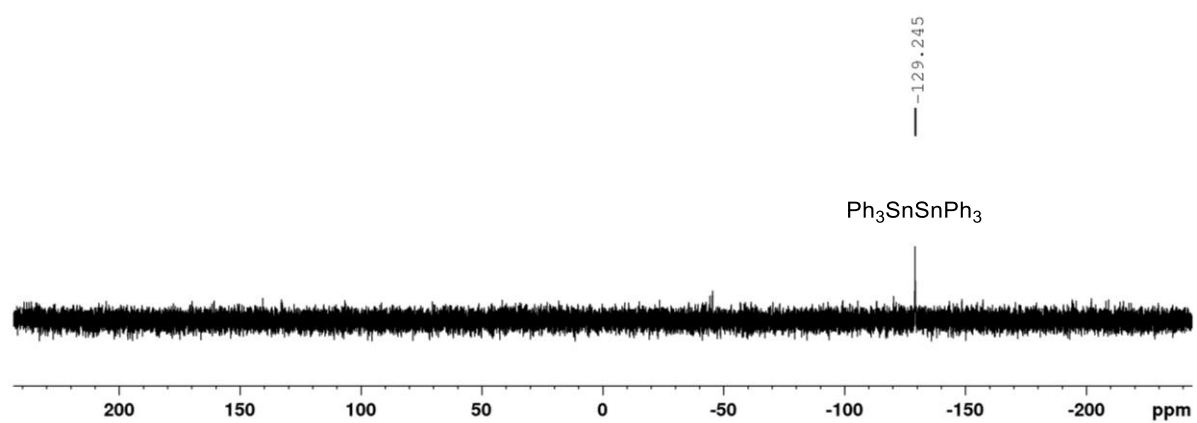


Figure S25. $^{119}\text{Sn}\{^1\text{H}\}$ -NMR $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4] + 2$ equiv. Ph_3SnH in $\text{C}_6\text{D}_5\text{Cl} + \text{PMes}_3$

SUPPORTING INFORMATION

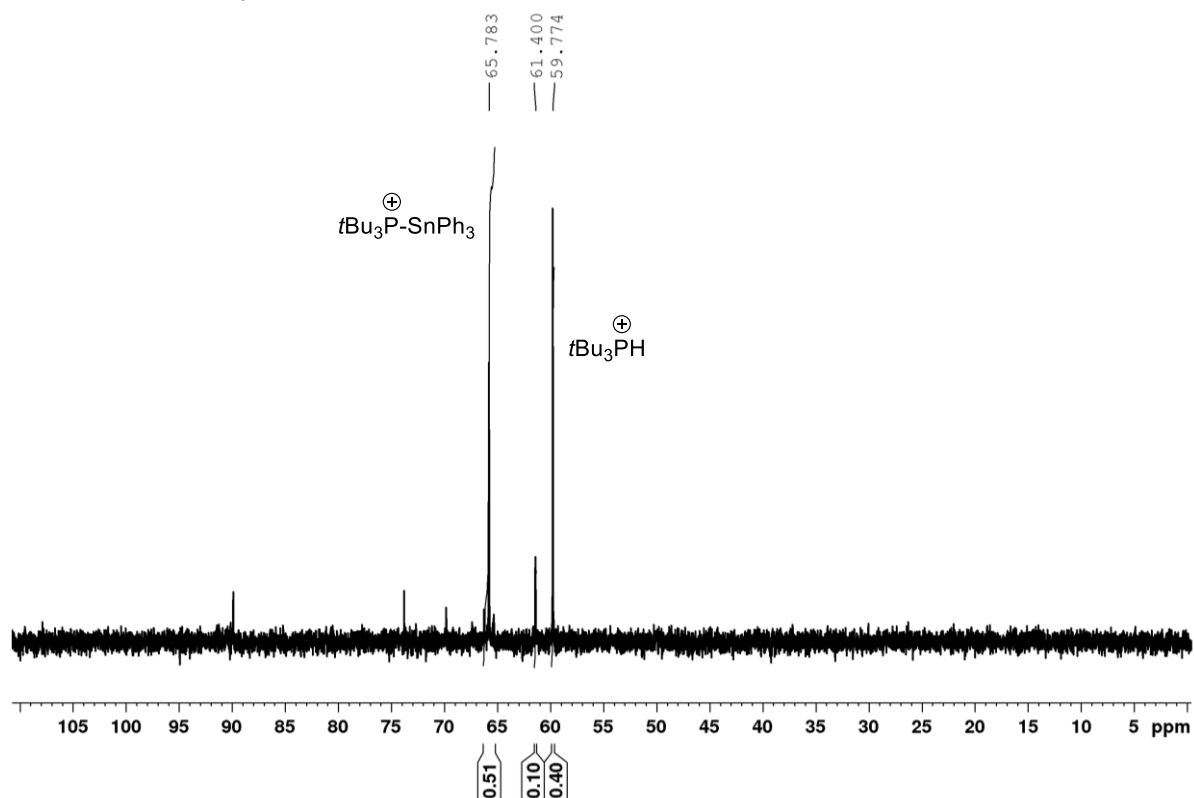
Addition of $PtBu_3$ 

Figure S26. $^{31}P\{^1H\}$ -NMR $[Ph_3C][B(C_6F_5)_4] + 2$ equiv. Ph_3SnH in $C_6D_5Cl + PtBu_3$

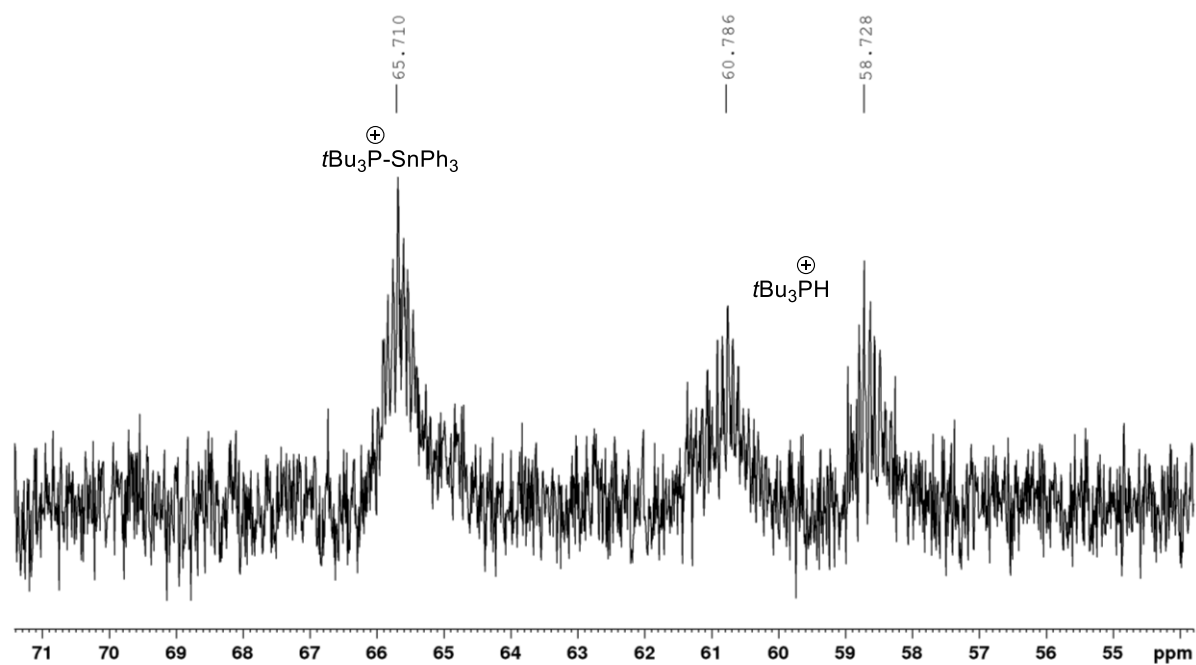


Figure S27. ^{31}P -NMR $[Ph_3C][B(C_6F_5)_4] + 2$ equiv. Ph_3SnH in $C_6D_5Cl + PtBu_3$

SUPPORTING INFORMATION

Reactivity: tetrachloro-1,4-benzoquinone (TCQ) reactivity

TCQ + B(C₆F₅)₃ + PMe₃

Trispentafluorophenylborane (15 mg, 0.03 mmol, 1.0 equiv.) was dissolved in 1.0 mL toluene and added to TCQ (3.7 mg, 0.015 mmol, 0.5 equiv.; 7.4 mg, 0.03 mmol, 1.0 equiv.). This solution was then added to solid trimesitylphosphine (11.7 mg, 0.03 mmol, 1.0 equiv.). The reaction mixtures turned purple immediately. Preparing the sample in the dark yields the same result (Figures S28-29). To enhance the signal, the 2:2:1 experiment was repeated using a higher concentration prepared by mixing trispentafluorophenylborane (30 mg, 0.06 mmol, 1.0 equiv.), TCQ (7.4 mg, 0.03 mmol, 0.5 equiv.) and trimesitylphosphine (23.4 mg, 0.06 mmol, 1.0 equiv.) in 0.5 mL toluene (See Figure 3 of the main manuscript, also given below).

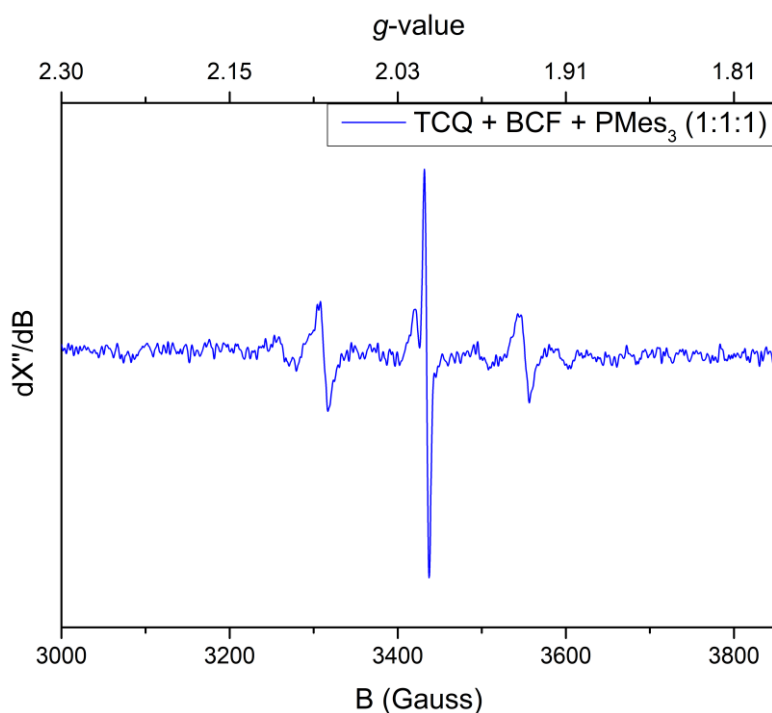


Figure S28. EPR spectrum of TCQ + BCF + PMes₃ (1:1:1) in toluene at ambient temperature.

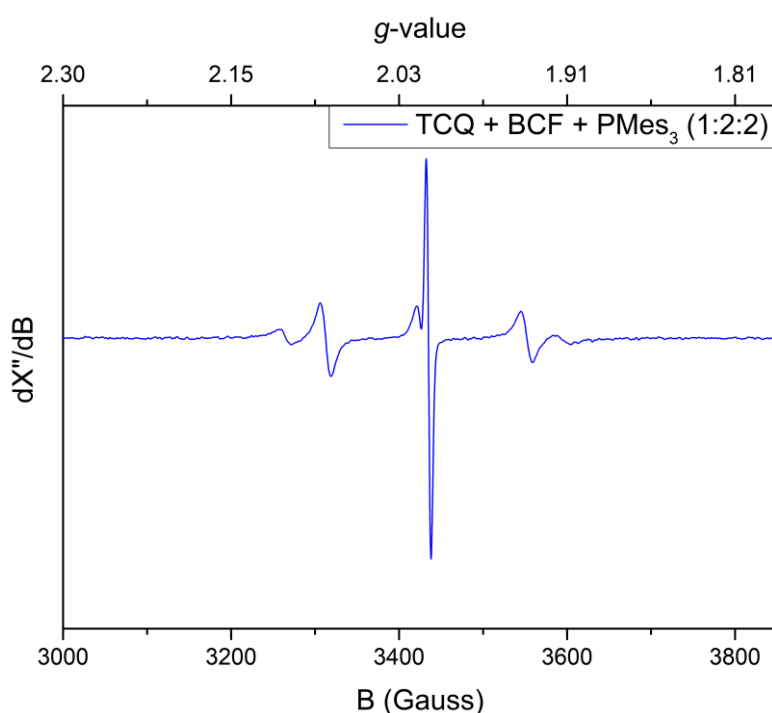


Figure S29. EPR spectrum of TCQ + BCF + PMes₃ (1:2:2) in toluene at ambient temperature.

SUPPORTING INFORMATION

Table S1. EPR experiment acquisition details for TCQ + BCF + PMes₃

| | Microwave frequency (GHz) | Modulation amplitude (G) | Power (mW) |
|-------|---------------------------|--------------------------|------------|
| 1:1:1 | 9.643922 | 4.000 | 0.6325 |
| 1:2:2 | 9.645737 | 4.000 | 0.6325 |

Simulation parameters for Figure 3 in the main text:

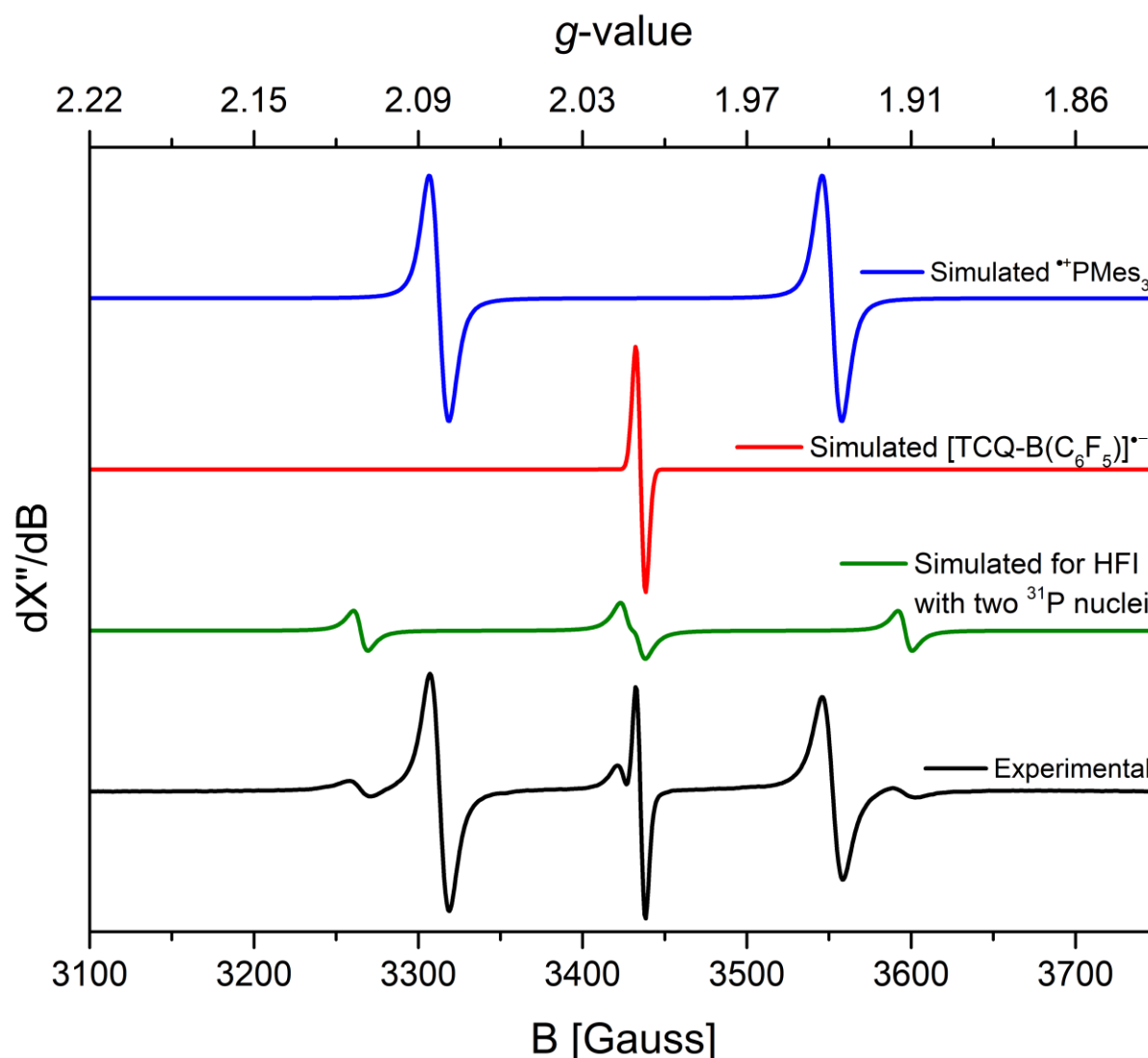


Figure 3. Copy of Figure 3 from the main manuscript: Experimental EPR spectrum (bottom) for reaction of PMes₃, B(C₆F₅)₃ and TCQ (2:2:1) and simulated spectra for PMes₃⁺, TCQ-B(C₆F₅)₃⁻ and the third smaller signal.

Blue line: PMes₃⁺ (hyperfine coupling interaction with one $I = \frac{1}{2}$ nucleus, which we attribute to ³¹P coupling): $g_{\text{iso}} = 2.0050$, $A_{\text{iso}} = 670.00$, 1.00 mT Gaussian and 1.00 mT Lorentzian line width.

Red line: [TCQ-B(C₆F₅)₃]⁻. No hyperfine coupling interactions observed. $g_{\text{iso}} = 2.0058$, 0.70 mT Gaussian line width.

Green line: signals seem to correspond to a species with two ³¹P nuclei coupling to the unpaired electron, or a species with two uncoupled (i.e. non-interacting) unpaired electrons, of which one shows hyperfine coupling to a ³¹P nucleus. Simulation of this species was performed by consideration of hyperfine coupling to two ³¹P nuclei. $g_{\text{iso}} = 2.0060$, $A_{\text{iso}}^1 = A_{\text{iso}}^2 = 465.00$ MHz. 1.50 mT Lorentzian line width.

Table S2. EPR experiment acquisition details for TCQ + BCF + PMes₃ (2:2:1) in toluene at room temperature.

| | Microwave frequency (GHz) | Modulation amplitude (G) | Power (mW) |
|-------|---------------------------|--------------------------|------------|
| 1:1:1 | 9.643975 | 4.000 | 0.6325 |

SUPPORTING INFORMATION

Computational details: FLP reactivity with triphenyltin hydride

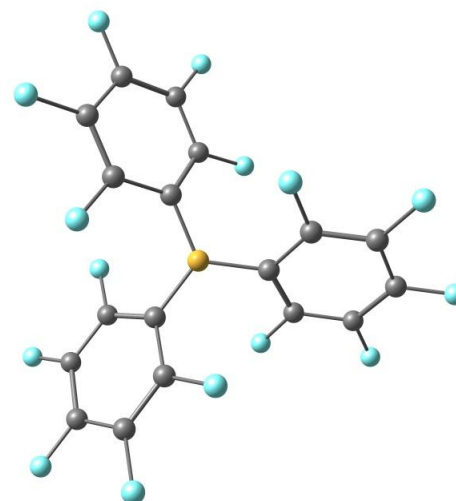
All structures in this section were optimized at ω B97X-D/def2-svp^{3,4} using Gaussian 09, Revision D01.⁵ Zero point energy (ZPE) and Gibbs free energy corrections (G°) were obtained from frequency analyses performed at this level of theory. Energy levels were obtained from single-point calculations at the ω B97X-D/def2-tzvp level of theory.

B(C₆F₅)₃

E: -2208.55591738 a.u

Cartesian coordinates:

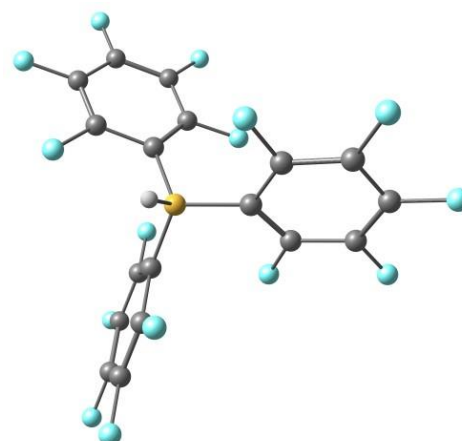
| | | | |
|---|-----------|-----------|----------|
| C | -0.951794 | -1.248713 | -0.00028 |
| C | -2.133513 | -1.275232 | -0.74914 |
| C | -2.984358 | -2.375193 | -0.76814 |
| C | -2.664398 | -3.493974 | -0.00086 |
| C | -1.501017 | -3.507041 | 0.76671 |
| C | -0.665177 | -2.395642 | 0.74833 |
| F | -2.471274 | -0.235721 | -1.50156 |
| F | -4.083664 | -2.370174 | -1.49992 |
| F | -3.462472 | -4.540183 | -0.00109 |
| F | -1.205719 | -4.566170 | 1.49816 |
| F | 0.426386 | -2.446664 | 1.50114 |
| B | 0.000406 | -0.000044 | 0.00013 |
| C | 1.557865 | -0.200079 | 0.00005 |
| C | 2.172065 | -1.211234 | -0.74726 |
| C | 3.550123 | -1.397772 | -0.76594 |
| C | 4.358806 | -0.559804 | -0.00004 |
| C | 3.788170 | 0.455350 | 0.76585 |
| C | 2.407706 | 0.623126 | 0.74721 |
| F | 1.441109 | -2.024825 | -1.49861 |
| F | 4.095710 | -2.353330 | -1.49616 |
| F | 5.663927 | -0.727390 | -0.00011 |
| F | 4.557539 | 1.242082 | 1.49599 |
| F | 1.906073 | 1.595194 | 1.49834 |
| C | -0.605311 | 1.448692 | 0.00039 |
| C | -0.037914 | 2.486011 | -0.74795 |
| C | -0.565909 | 3.772484 | -0.76652 |
| C | -1.695032 | 4.053716 | 0.00080 |
| C | -2.287495 | 3.052109 | 0.76794 |
| C | -1.742218 | 1.772865 | 0.74900 |
| F | 1.031467 | 2.259603 | -1.50025 |
| F | -0.012551 | 4.722701 | -1.49789 |
| F | -2.202805 | 5.267642 | 0.00103 |
| F | -3.352558 | 3.325061 | 1.49946 |
| F | -2.331792 | 0.852419 | 1.50132 |

**[HB(C₆F₅)₃]⁻**

E: -2209.26757804 a.u

Cartesian coordinates:

| | | | |
|---|-----------|-----------|----------|
| C | -1.159031 | -1.061029 | 0.37255 |
| C | -2.003475 | -0.912844 | -0.72565 |
| C | -3.003265 | -1.826977 | -1.05600 |
| C | -3.177568 | -2.961664 | -0.27200 |
| C | -2.349938 | -3.161965 | 0.82719 |
| C | -1.366366 | -2.218954 | 1.12231 |
| F | -1.877759 | 0.131996 | -1.54758 |
| F | -3.784770 | -1.633878 | -2.11760 |
| F | -4.123784 | -3.848837 | -0.57261 |
| F | -2.506841 | -4.249881 | 1.58082 |
| F | -0.600431 | -2.483192 | 2.18190 |
| B | 0.004511 | -0.001241 | 0.82836 |
| C | 1.505353 | -0.477479 | 0.37600 |
| C | 1.805128 | -1.308710 | -0.70103 |



SUPPORTING INFORMATION

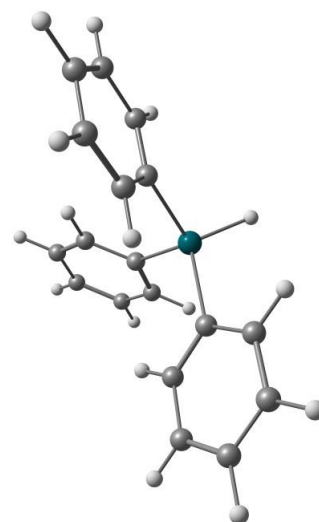
| | | | |
|---|-----------|-----------|----------|
| C | 3.100301 | -1.714098 | -1.02231 |
| C | 4.167352 | -1.266981 | -0.25202 |
| C | 3.920974 | -0.423089 | 0.82540 |
| C | 2.609669 | -0.047664 | 1.11238 |
| F | 0.841099 | -1.754818 | -1.51044 |
| F | 3.329219 | -2.513898 | -2.06293 |
| F | 5.411742 | -1.639265 | -0.54452 |
| F | 4.938821 | 0.014652 | 1.56587 |
| F | 2.448811 | 0.774158 | 2.15075 |
| C | -0.336779 | 1.535232 | 0.37385 |
| C | 0.243972 | 2.217623 | -0.69296 |
| C | -0.059071 | 3.540164 | -1.01592 |
| C | -0.997287 | 4.231209 | -0.25808 |
| C | -1.615597 | 3.588375 | 0.80877 |
| C | -1.278065 | 2.267335 | 1.09804 |
| F | 1.130192 | 1.614885 | -1.48971 |
| F | 0.529731 | 4.145615 | -2.04638 |
| F | -1.303663 | 5.493011 | -0.55255 |
| F | -2.520167 | 4.241804 | 1.53735 |
| F | -1.919409 | 1.709325 | 2.12612 |
| H | 0.004466 | 0.000211 | 2.04867 |

Ph₃SnH

E: -909.900179950 a.u

Cartesian coordinates:

| | | | |
|----|-----------|-----------|----------|
| Sn | 0.000080 | -0.000710 | -0.92054 |
| C | -1.498047 | -1.332604 | -0.16056 |
| C | -1.537953 | -2.680798 | -0.54565 |
| C | -2.444882 | -0.874535 | 0.76608 |
| C | -2.496328 | -3.547270 | -0.02006 |
| H | -0.812434 | -3.072067 | -1.26563 |
| C | -3.406690 | -1.738580 | 1.29163 |
| H | -2.437026 | 0.171964 | 1.08623 |
| C | -3.433141 | -3.075979 | 0.89939 |
| H | -2.512594 | -4.594710 | -0.33051 |
| H | -4.137872 | -1.364716 | 2.01232 |
| H | -4.185131 | -3.753269 | 1.31082 |
| C | 1.902794 | -0.630925 | -0.16001 |
| C | 1.980396 | -1.671673 | 0.77577 |
| C | 3.090378 | 0.003172 | -0.55390 |
| C | 3.210425 | -2.070429 | 1.30096 |
| H | 1.070219 | -2.183701 | 1.10305 |
| C | 4.320906 | -0.391559 | -0.02889 |
| H | 3.066097 | 0.820601 | -1.28127 |
| C | 4.381974 | -1.430471 | 0.89958 |
| H | 3.252879 | -2.884344 | 2.02866 |
| H | 5.236094 | 0.113569 | -0.34675 |
| H | 5.345088 | -1.741399 | 1.31091 |
| C | -0.405035 | 1.962134 | -0.15942 |
| C | -1.547330 | 2.674772 | -0.55278 |
| C | 0.458861 | 2.548772 | 0.77570 |
| C | -1.819120 | 3.937933 | -0.02726 |
| H | -2.244024 | 2.245817 | -1.27968 |
| C | 0.190735 | 3.813466 | 1.30153 |
| H | 1.357044 | 2.015423 | 1.10214 |
| C | -0.948813 | 4.509137 | 0.90088 |
| H | -2.713769 | 4.479060 | -0.34434 |
| H | 0.875373 | 4.256425 | 2.02869 |
| H | -1.159864 | 5.498863 | 1.31245 |
| H | 0.001130 | 0.000611 | -2.63771 |



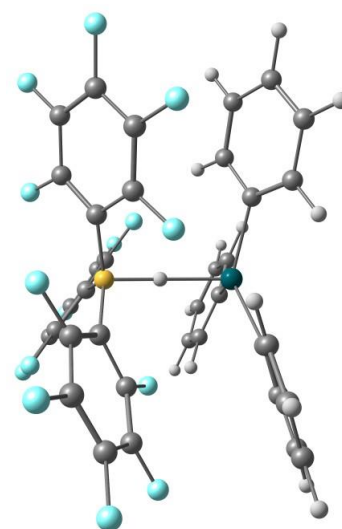
SUPPORTING INFORMATION

Ph₃Sn--H--B(C₆F₅)₃

E: -3118.49000791 a.u

Cartesian coordinates:

| | | | |
|----|-----------|-----------|----------|
| C | 0.285697 | 1.571414 | -1.48122 |
| C | 1.351693 | 2.076221 | -2.22454 |
| C | 1.646125 | 3.437939 | -2.29554 |
| C | 0.843576 | 4.352643 | -1.62103 |
| C | -0.251206 | 3.897808 | -0.89241 |
| C | -0.499153 | 2.532978 | -0.84510 |
| F | 2.153324 | 1.262428 | -2.90535 |
| F | 2.680164 | 3.866946 | -3.00242 |
| F | 1.115331 | 5.644892 | -1.67515 |
| F | -1.029933 | 4.757104 | -0.25363 |
| F | -1.552768 | 2.141030 | -0.11647 |
| B | 0.001441 | -0.000304 | -1.23223 |
| C | -1.501897 | -0.540416 | -1.47949 |
| C | -2.472740 | 0.129234 | -2.22285 |
| C | -3.799002 | -0.297435 | -2.29289 |
| C | -4.189018 | -1.449575 | -1.61747 |
| C | -3.247022 | -2.169251 | -0.88875 |
| C | -1.941461 | -1.700428 | -0.84194 |
| F | -2.169793 | 1.229733 | -2.90506 |
| F | -4.688194 | 0.382750 | -2.99976 |
| F | -5.443815 | -1.861043 | -1.67075 |
| F | -3.600932 | -3.273047 | -0.24901 |
| F | -1.074475 | -2.415582 | -0.11277 |
| C | 1.220338 | -1.032748 | -1.47988 |
| C | 1.123982 | -2.208977 | -2.22208 |
| C | 2.155075 | -3.145986 | -2.29129 |
| C | 3.348221 | -2.908820 | -1.61610 |
| C | 3.502517 | -1.732491 | -0.88893 |
| C | 2.445331 | -0.834226 | -0.84315 |
| F | 0.018699 | -2.495948 | -2.90350 |
| F | 2.008812 | -4.256630 | -2.99704 |
| F | 4.330597 | -3.791360 | -1.66831 |
| F | 4.636026 | -1.488282 | -0.24986 |
| F | 2.633600 | 0.275152 | -0.11612 |
| Sn | -0.001942 | 0.000268 | 1.96604 |
| H | 0.002543 | 0.000572 | 0.13380 |
| C | 0.470413 | 2.042281 | 2.28669 |
| C | -0.500925 | 2.910275 | 2.80486 |
| C | 1.693178 | 2.568600 | 1.84657 |
| C | -0.255704 | 4.279912 | 2.87592 |
| H | -1.466777 | 2.524556 | 3.14271 |
| C | 1.933953 | 3.940258 | 1.91656 |
| H | 2.458534 | 1.917989 | 1.42108 |
| C | 0.958424 | 4.796071 | 2.42503 |
| H | -1.023287 | 4.949416 | 3.26895 |
| H | 2.884664 | 4.342138 | 1.55979 |
| H | 1.141944 | 5.871757 | 2.46381 |
| C | -2.007457 | -0.610208 | 2.28441 |
| C | -2.275103 | -1.886501 | 2.79898 |
| C | -3.073689 | 0.188348 | 1.84696 |
| C | -3.584417 | -2.357577 | 2.86855 |
| H | -1.458975 | -2.532015 | 3.13502 |
| C | -4.382551 | -0.287593 | 1.91550 |
| H | -2.891802 | 1.177707 | 1.42490 |
| C | -4.637493 | -1.561618 | 2.41996 |
| H | -3.781663 | -3.358050 | 3.25844 |
| H | -5.205195 | 0.336903 | 1.56070 |
| H | -5.661266 | -1.939453 | 2.45748 |
| C | 1.530907 | -1.428580 | 2.29011 |
| C | 2.767398 | -1.017831 | 2.80761 |
| C | 1.378175 | -2.751851 | 1.85234 |
| C | 3.833068 | -1.912306 | 2.87976 |



SUPPORTING INFORMATION

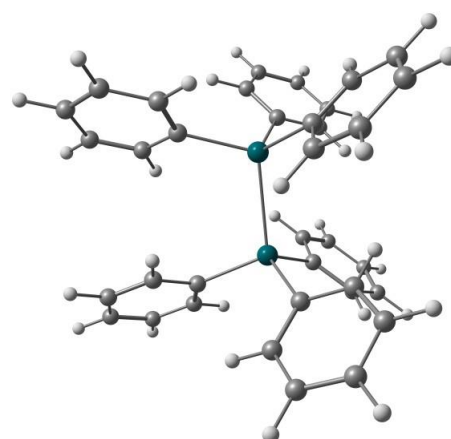
| | | | |
|---|----------|-----------|---------|
| H | 2.913966 | 0.012293 | 3.14393 |
| C | 2.447822 | -3.643542 | 1.92359 |
| H | 0.432733 | -3.092352 | 1.42778 |
| C | 3.675999 | -3.222851 | 2.43082 |
| H | 4.796016 | -1.579432 | 3.27192 |
| H | 2.322842 | -4.668710 | 1.56853 |
| H | 4.517508 | -3.917530 | 2.47026 |

Ph₃Sn–SnPh₃

E: -1818.65554828 a.u

Cartesian coordinates:

| | | | |
|----|-----------|-----------|----------|
| Sn | 1.387736 | 0.003870 | -0.00549 |
| C | 2.114779 | -1.316190 | 1.52224 |
| C | 2.972403 | -2.381244 | 1.21529 |
| C | 1.702386 | -1.149520 | 2.85252 |
| C | 3.408260 | -3.255689 | 2.21193 |
| H | 3.306687 | -2.536630 | 0.18486 |
| C | 2.137671 | -2.021030 | 3.85064 |
| H | 1.020532 | -0.337433 | 3.12353 |
| C | 2.991307 | -3.076435 | 3.53043 |
| H | 4.076609 | -4.081555 | 1.95679 |
| H | 1.802954 | -1.877958 | 4.88076 |
| H | 3.331235 | -3.761905 | 4.31027 |
| C | 2.104634 | -0.667037 | -1.91337 |
| C | 3.001313 | 0.102995 | -2.66655 |
| C | 1.651184 | -1.882090 | -2.44771 |
| C | 3.435543 | -0.331121 | -3.91988 |
| H | 3.367576 | 1.057157 | -2.27532 |
| C | 2.084506 | -2.318697 | -3.69947 |
| H | 0.937792 | -2.499637 | -1.89315 |
| C | 2.977638 | -1.542326 | -4.43742 |
| H | 4.134695 | 0.280439 | -4.49523 |
| H | 1.717276 | -3.265930 | -4.10137 |
| H | 3.316314 | -1.881251 | -5.41925 |
| C | 2.120289 | 1.985517 | 0.36957 |
| C | 3.009912 | 2.245023 | 1.42099 |
| C | 1.682866 | 3.059696 | -0.41930 |
| C | 3.452512 | 3.543788 | 1.67628 |
| H | 3.364032 | 1.425923 | 2.05447 |
| C | 2.124654 | 4.358347 | -0.16703 |
| H | 0.976192 | 2.893941 | -1.23842 |
| C | 3.010250 | 4.601567 | 0.88259 |
| H | 4.145989 | 3.730180 | 2.49980 |
| H | 1.770264 | 5.183289 | -0.78954 |
| H | 3.355362 | 5.618474 | 1.08350 |
| Sn | -1.387720 | 0.004836 | 0.00496 |
| C | -2.116449 | -1.320019 | -1.51780 |
| C | -2.104138 | -0.659212 | 1.91543 |
| C | -2.119059 | 1.985727 | -0.37638 |
| C | -2.976559 | -2.381906 | -1.20685 |
| C | -1.703147 | -1.159706 | -2.84858 |
| C | -2.999980 | 0.113751 | 2.66660 |
| C | -1.651019 | -1.872746 | 2.45349 |
| C | -3.007259 | 2.242729 | -1.42961 |
| C | -1.682077 | 3.061886 | 0.41003 |
| C | -3.413953 | -3.259450 | -2.20009 |
| H | -3.311547 | -2.532383 | -0.17593 |
| C | -2.139959 | -2.034334 | -3.84331 |
| H | -1.019372 | -0.350255 | -3.12263 |
| C | -3.433689 | -0.316020 | 3.92160 |
| H | -3.365990 | 1.066810 | 2.27246 |
| C | -2.083828 | -2.305021 | 3.70692 |
| H | -0.938264 | -2.492484 | 1.90056 |



SUPPORTING INFORMATION

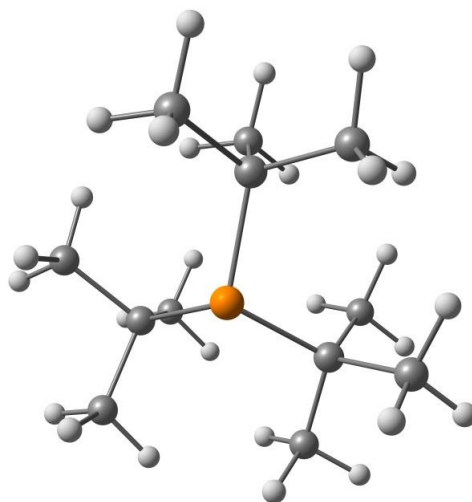
| | | | |
|---|-----------|-----------|----------|
| C | -3.448896 | 3.540994 | -1.68908 |
| H | -3.361023 | 1.422027 | -2.06122 |
| C | -2.122917 | 4.360043 | 0.15360 |
| H | -0.976530 | 2.898052 | 1.23051 |
| C | -2.996075 | -3.086514 | -3.51914 |
| H | -4.084216 | -4.082797 | -1.94185 |
| H | -1.804515 | -1.896210 | -4.87387 |
| C | -2.976110 | -1.525759 | 4.44285 |
| H | -4.132181 | 0.297793 | 4.49536 |
| H | -1.716848 | -3.251122 | 4.11170 |
| C | -3.007088 | 4.600768 | -0.89780 |
| H | -4.141265 | 3.725428 | -2.51397 |
| H | -1.768914 | 5.186547 | 0.77425 |
| H | -3.337216 | -3.774409 | -4.29631 |
| H | -3.314385 | -1.861278 | 5.42598 |
| H | -3.351451 | 5.617278 | -1.10197 |

PtBu₃

E: -814.933636398 a.u

Cartesian coordinates:

| | | | |
|---|-----------|-----------|----------|
| P | -0.000081 | 0.000074 | -0.71579 |
| C | -1.722802 | -0.491050 | -0.00451 |
| C | -1.945751 | -1.998550 | -0.21857 |
| C | -1.997538 | -0.166704 | 1.46999 |
| C | -2.781902 | 0.203751 | -0.88603 |
| H | -1.739543 | -2.299383 | -1.25696 |
| H | -1.342797 | -2.622378 | 0.45324 |
| H | -3.003084 | -2.233209 | -0.01199 |
| H | -2.000420 | 0.913178 | 1.66851 |
| H | -2.995239 | -0.546539 | 1.75021 |
| H | -1.267009 | -0.632230 | 2.14463 |
| H | -3.783499 | -0.167126 | -0.60990 |
| H | -2.798612 | 1.292777 | -0.77162 |
| H | -2.619218 | -0.021631 | -1.95077 |
| C | 1.286586 | -1.246423 | -0.00469 |
| C | 1.142682 | -1.647839 | 1.46949 |
| C | 1.215286 | -2.510405 | -0.88714 |
| C | 2.703518 | -0.685140 | -0.21748 |
| H | 1.179917 | -0.782947 | 2.14489 |
| H | 0.209197 | -2.191050 | 1.66737 |
| H | 1.970847 | -2.321626 | 1.74941 |
| H | 1.329293 | -2.256030 | -1.95166 |
| H | 2.037505 | -3.192192 | -0.61124 |
| H | 0.280756 | -3.069892 | -0.77333 |
| H | 3.435562 | -1.483454 | -0.01132 |
| H | 2.861370 | -0.354968 | -1.25544 |
| H | 2.941508 | 0.148303 | 0.45540 |
| C | 0.436119 | 1.737491 | -0.00456 |
| C | -0.758258 | 2.684106 | -0.21770 |
| C | 0.855285 | 1.812947 | 1.46972 |
| C | 1.566825 | 2.307740 | -0.88652 |
| H | -1.121853 | 2.656647 | -1.25614 |
| H | -1.599961 | 2.472673 | 0.45377 |
| H | -0.433261 | 3.717063 | -0.01016 |
| H | 1.791875 | 1.275083 | 1.66744 |
| H | 1.025728 | 2.866816 | 1.74994 |
| H | 0.087216 | 1.413234 | 2.14492 |
| H | 1.745554 | 3.360916 | -0.61105 |
| H | 2.518807 | 1.778633 | -0.77182 |
| H | 1.290277 | 2.278671 | -1.95123 |



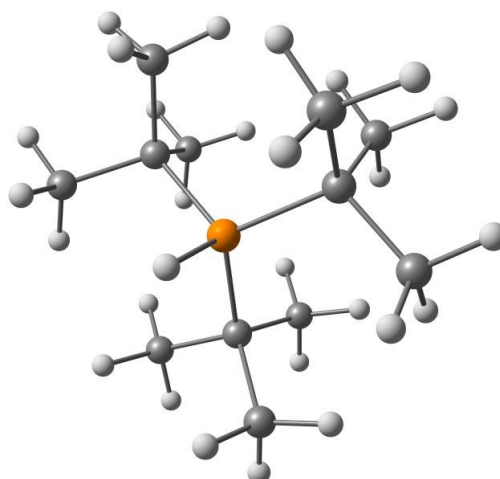
SUPPORTING INFORMATION

 $t\text{Bu}_3\text{PH}^+$

E: -815.340280393 a.u

Cartesian coordinates:

| | | | |
|---|-----------|-----------|----------|
| P | -0.000147 | -0.000153 | -0.45271 |
| C | -1.789303 | -0.390239 | -0.00061 |
| C | -2.091725 | -1.881435 | -0.22851 |
| C | -2.069267 | -0.031306 | 1.46729 |
| C | -2.716590 | 0.399769 | -0.94615 |
| H | -1.902371 | -2.195181 | -1.26500 |
| H | -1.549588 | -2.544762 | 0.45571 |
| H | -3.164394 | -2.032707 | -0.03709 |
| H | -1.979390 | 1.043953 | 1.66802 |
| H | -3.105943 | -0.316741 | 1.70076 |
| H | -1.416793 | -0.572419 | 2.16642 |
| H | -3.750396 | 0.081165 | -0.74551 |
| H | -2.681816 | 1.482738 | -0.79866 |
| H | -2.509951 | 0.180394 | -2.00444 |
| C | 1.232534 | -1.354298 | -0.00073 |
| C | 1.062101 | -1.776544 | 1.46714 |
| C | 1.012339 | -2.552268 | -0.94644 |
| C | 2.675002 | -0.870158 | -0.22856 |
| H | 1.203272 | -0.940826 | 2.16641 |
| H | 0.086673 | -2.237841 | 1.66783 |
| H | 1.828701 | -2.530549 | 1.70054 |
| H | 1.099422 | -2.263566 | -2.00468 |
| H | 1.804989 | -3.288390 | -0.74553 |
| H | 0.056959 | -3.063507 | -0.79936 |
| H | 3.342614 | -1.723040 | -0.03617 |
| H | 2.852321 | -0.550238 | -1.26530 |
| H | 2.977773 | -0.068234 | 0.45508 |
| C | 0.556615 | 1.744459 | -0.00106 |
| C | -0.583698 | 2.751860 | -0.22874 |
| C | 1.007954 | 1.808000 | 1.46670 |
| C | 1.704160 | 2.152364 | -0.94701 |
| H | -0.949964 | 2.745184 | -1.26527 |
| H | -1.429255 | 2.613676 | 0.45542 |
| H | -0.178485 | 3.756423 | -0.03693 |
| H | 1.895065 | 1.193658 | 1.66706 |
| H | 1.278015 | 2.848841 | 1.69994 |
| H | 0.213803 | 1.512695 | 2.16630 |
| H | 1.945839 | 3.206736 | -0.74596 |
| H | 2.624420 | 1.580142 | -0.80035 |
| H | 1.410176 | 2.083768 | -2.00515 |
| H | -0.000230 | -0.000306 | -1.86328 |



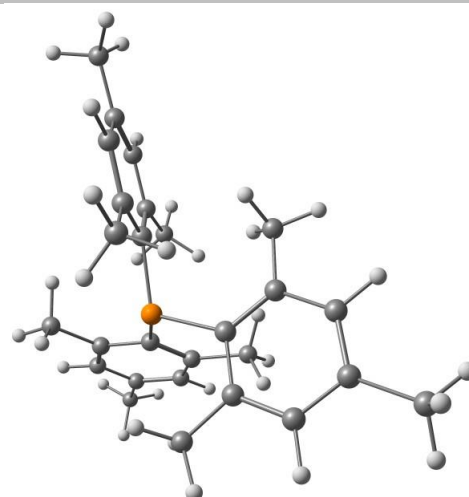
SUPPORTING INFORMATION

PMes₃

E: -1390.16817949 a.u

Cartesian coordinates:

| | | | |
|---|-----------|-----------|----------|
| C | -0.614042 | 1.624000 | 0.23907 |
| C | -1.569159 | 1.846735 | -0.77999 |
| C | -0.112848 | 2.735574 | 0.96383 |
| C | -2.008175 | 3.152626 | -1.02484 |
| C | -0.569664 | 4.020715 | 0.66588 |
| C | -1.529862 | 4.253729 | -0.31747 |
| H | -2.743729 | 3.313890 | -1.81864 |
| H | -0.161747 | 4.867122 | 1.22640 |
| C | -1.099360 | -1.344077 | 0.23898 |
| C | -0.815585 | -2.282445 | -0.78045 |
| C | -2.312351 | -1.465458 | 0.96428 |
| C | -1.727715 | -3.314974 | -1.02517 |
| C | -3.197508 | -2.503197 | 0.66649 |
| C | -2.920132 | -3.451135 | -0.31720 |
| H | -1.500228 | -4.032594 | -1.81916 |
| H | -4.134198 | -2.572970 | 1.22751 |
| C | 1.713906 | -0.280527 | 0.23883 |
| C | 2.384273 | 0.434979 | -0.78047 |
| C | 2.426196 | -1.269694 | 0.96427 |
| C | 3.734729 | 0.162288 | -1.02535 |
| C | 3.767450 | -1.516811 | 0.66598 |
| C | 4.449226 | -0.802307 | -0.31787 |
| H | 4.241933 | 0.718522 | -1.81940 |
| H | 4.296739 | -2.292956 | 1.22674 |
| P | 0.000405 | -0.000215 | 0.85297 |
| C | -2.706619 | -0.474958 | 2.03189 |
| H | -1.922174 | -0.379973 | 2.79820 |
| H | -2.857252 | 0.532965 | 1.61248 |
| H | -3.642158 | -0.779444 | 2.52068 |
| C | 0.399852 | -2.218631 | -1.67161 |
| H | 0.569780 | -1.205260 | -2.05939 |
| H | 1.321144 | -2.509700 | -1.14666 |
| H | 0.274724 | -2.892939 | -2.52984 |
| C | -3.864777 | -4.591396 | -0.59004 |
| H | -3.782426 | -4.943301 | -1.62841 |
| H | -3.641915 | -5.447960 | 0.06699 |
| H | -4.909463 | -4.301015 | -0.40719 |
| C | -2.121377 | 0.761622 | -1.67042 |
| H | -1.328026 | 0.109705 | -2.05985 |
| H | -2.831416 | 0.107530 | -1.14394 |
| H | -2.645435 | 1.206282 | -2.52749 |
| C | -2.045466 | 5.641660 | -0.59089 |
| H | -2.898819 | 5.876915 | 0.06598 |
| H | -1.271944 | 6.401577 | -0.40838 |
| H | -2.391401 | 5.745713 | -1.62933 |
| C | 0.942251 | 2.582500 | 2.03134 |
| H | 0.632691 | 1.855174 | 2.79737 |
| H | 1.890815 | 2.209758 | 1.61205 |
| H | 1.145523 | 3.545004 | 2.52033 |
| C | 1.720336 | 1.455661 | -1.67084 |
| H | 0.758502 | 1.095089 | -2.05917 |
| H | 1.509660 | 2.397987 | -1.14458 |
| H | 2.366886 | 1.686657 | -2.52848 |
| C | 1.766725 | -2.106018 | 2.03289 |
| H | 1.293644 | -1.473809 | 2.79976 |
| H | 0.968454 | -2.740455 | 1.61485 |
| H | 2.498845 | -2.763871 | 2.52079 |
| C | 5.908924 | -1.050192 | -0.59138 |
| H | 6.172924 | -0.798802 | -1.62865 |
| H | 6.539641 | -0.432174 | 0.06839 |
| H | 6.178977 | -2.101066 | -0.41286 |



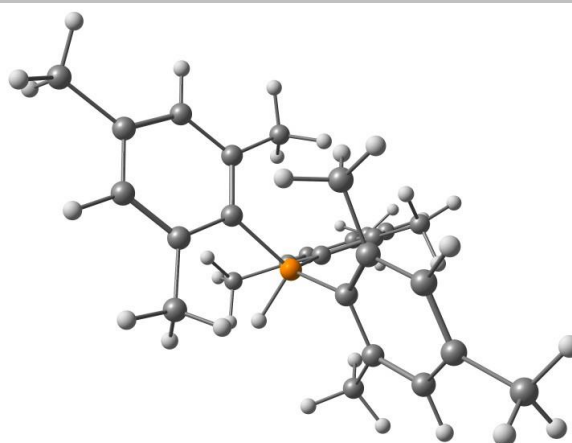
SUPPORTING INFORMATION

Mes₃PH⁺

E: -1390.58266658 a.u

Cartesian coordinates:

| | | | |
|---|-----------|-----------|----------|
| C | 0.170271 | 1.751638 | 0.19181 |
| C | -0.548423 | 2.380087 | -0.85084 |
| C | 1.081531 | 2.483078 | 0.99296 |
| C | -0.341364 | 3.744694 | -1.05437 |
| C | 1.246585 | 3.843192 | 0.73578 |
| C | 0.542392 | 4.496863 | -0.27738 |
| H | -0.887280 | 4.239144 | -1.86177 |
| H | 1.953698 | 4.410919 | 1.34576 |
| C | -1.602873 | -0.729055 | 0.19160 |
| C | -1.788267 | -1.665602 | -0.85104 |
| C | -2.691788 | -0.305124 | 0.99282 |
| C | -3.073824 | -2.168107 | -1.05434 |
| C | -3.952397 | -0.841836 | 0.73582 |
| C | -4.166887 | -1.778536 | -0.27725 |
| H | -3.229426 | -2.888229 | -1.86156 |
| H | -4.797422 | -0.512893 | 1.34586 |
| C | 1.432487 | -1.023800 | 0.19092 |
| C | 2.335296 | -0.715145 | -0.85218 |
| C | 1.611274 | -2.178582 | 0.99211 |
| C | 3.414781 | -1.575571 | -1.05525 |
| C | 2.707406 | -3.000384 | 0.73518 |
| C | 3.625730 | -2.716344 | -0.27778 |
| H | 4.115649 | -1.349458 | -1.86275 |
| H | 2.846301 | -3.896467 | 1.34525 |
| P | 0.000003 | -0.000732 | 0.59400 |
| C | -2.548738 | 0.701941 | 2.10812 |
| H | -1.996579 | 0.280887 | 2.96478 |
| H | -2.027674 | 1.617019 | 1.78789 |
| H | -3.535478 | 1.001868 | 2.48198 |
| C | -0.690475 | -2.145492 | -1.76752 |
| H | -0.100645 | -1.319439 | -2.18874 |
| H | 0.013824 | -2.813726 | -1.25102 |
| H | -1.120479 | -2.701698 | -2.60985 |
| C | -5.529346 | -2.366816 | -0.51109 |
| H | -5.674732 | -2.640966 | -1.56479 |
| H | -5.653651 | -3.282561 | 0.08884 |
| H | -6.325826 | -1.669600 | -0.21790 |
| C | -1.513356 | 1.668944 | -1.76649 |
| H | -1.096298 | 0.741261 | -2.18241 |
| H | -2.445886 | 1.398746 | -1.24979 |
| H | -1.776194 | 2.316783 | -2.61206 |
| C | 0.713729 | 5.970911 | -0.51169 |
| H | -0.020918 | 6.536221 | 0.08387 |
| H | 1.713867 | 6.313577 | -0.21383 |
| H | 0.553994 | 6.232635 | -1.56648 |
| C | 1.882290 | 1.855944 | 2.10825 |
| H | 1.241666 | 1.588848 | 2.96516 |
| H | 2.413778 | 0.946855 | 1.78804 |
| H | 2.635774 | 2.560414 | 2.48160 |
| C | 2.199955 | 0.475148 | -1.76873 |
| H | 1.187794 | 0.575120 | -2.18469 |
| H | 2.430472 | 1.418784 | -1.25302 |
| H | 2.892626 | 0.379312 | -2.61422 |
| C | 0.667230 | -2.559677 | 2.10657 |
| H | 0.755269 | -1.872698 | 2.96460 |
| H | -0.385600 | -2.565346 | 1.78557 |
| H | 0.900523 | -3.564840 | 2.47890 |
| C | 4.817683 | -3.600648 | -0.51068 |
| H | 5.138563 | -3.577189 | -1.56089 |
| H | 5.666998 | -3.259105 | 0.10249 |
| H | 4.607808 | -4.642262 | -0.23214 |
| H | 0.000041 | -0.001274 | 1.99565 |



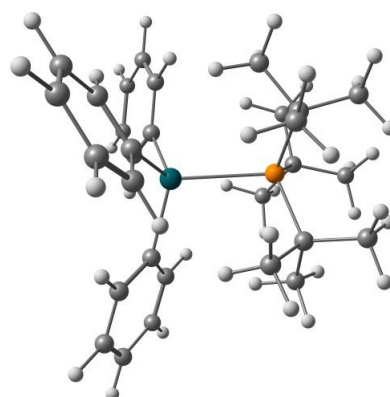
SUPPORTING INFORMATION

[tBu₃P–SnPh₃]⁺

E: -1724.09539125 a.u

Cartesian coordinates:

| | | | |
|----|-----------|-----------|----------|
| P | 1.832010 | -0.001912 | 0.00426 |
| C | 2.432055 | 1.312180 | -1.24989 |
| C | 2.242165 | 2.731413 | -0.68735 |
| C | 3.909592 | 1.124732 | -1.63126 |
| C | 1.562158 | 1.229954 | -2.51771 |
| H | 1.204924 | 2.930198 | -0.38631 |
| H | 2.913518 | 2.959707 | 0.14872 |
| H | 2.481622 | 3.442682 | -1.49242 |
| H | 4.090771 | 0.199574 | -2.19170 |
| H | 4.201357 | 1.958963 | -2.28770 |
| H | 4.581300 | 1.144255 | -0.76442 |
| H | 1.955003 | 1.952562 | -3.24916 |
| H | 1.570297 | 0.246501 | -2.99760 |
| H | 0.522349 | 1.525220 | -2.31515 |
| C | 2.424083 | 0.427964 | 1.77188 |
| C | 3.900902 | 0.853828 | 1.80647 |
| C | 1.550256 | 1.566086 | 2.33045 |
| C | 2.231756 | -0.768805 | 2.71920 |
| H | 4.575363 | 0.094256 | 1.39284 |
| H | 4.082995 | 1.801953 | 1.28618 |
| H | 4.188040 | 1.005671 | 2.85837 |
| H | 0.510100 | 1.241869 | 2.47984 |
| H | 1.938055 | 1.838755 | 3.32381 |
| H | 1.560265 | 2.473337 | 1.71867 |
| H | 2.466704 | -0.426660 | 3.73857 |
| H | 1.194840 | -1.129937 | 2.73675 |
| H | 2.904941 | -1.606331 | 2.50185 |
| C | 2.427192 | -1.747236 | -0.50485 |
| C | 2.240987 | -1.968955 | -2.01569 |
| C | 3.902780 | -1.989397 | -0.14760 |
| C | 1.551075 | -2.800687 | 0.19787 |
| H | 1.205299 | -1.803984 | -2.34137 |
| H | 2.916378 | -1.361483 | -2.62947 |
| H | 2.477393 | -3.022651 | -2.22834 |
| H | 4.081232 | -2.011074 | 0.93427 |
| H | 4.191453 | -2.976850 | -0.53952 |
| H | 4.578693 | -1.252032 | -0.59746 |
| H | 1.940533 | -3.797046 | -0.06115 |
| H | 1.556537 | -2.724581 | 1.28951 |
| H | 0.512346 | -2.768568 | -0.16189 |
| Sn | -0.810392 | 0.001168 | -0.00193 |
| C | -1.447145 | 1.997450 | -0.41192 |
| C | -2.128003 | 2.247636 | -1.61216 |
| C | -1.257217 | 3.057303 | 0.48719 |
| C | -2.589056 | 3.529368 | -1.91405 |
| H | -2.316785 | 1.439691 | -2.32424 |
| C | -1.720070 | 4.337399 | 0.18621 |
| H | -0.744027 | 2.899325 | 1.43817 |
| C | -2.382061 | 4.575853 | -1.01769 |
| H | -3.118093 | 3.707904 | -2.85237 |
| H | -1.565985 | 5.151645 | 0.89729 |
| H | -2.744069 | 5.578526 | -1.25357 |
| C | -1.448175 | -1.350164 | -1.52715 |
| C | -2.134781 | -2.511705 | -1.14471 |
| C | -1.253126 | -1.103486 | -2.89421 |
| C | -2.596271 | -3.413274 | -2.10425 |
| H | -2.327781 | -2.722486 | -0.08935 |
| C | -1.716404 | -2.003466 | -3.85284 |
| H | -0.735382 | -0.203260 | -3.23212 |
| C | -2.384006 | -3.162445 | -3.45829 |
| H | -3.129809 | -4.312775 | -1.79047 |



SUPPORTING INFORMATION

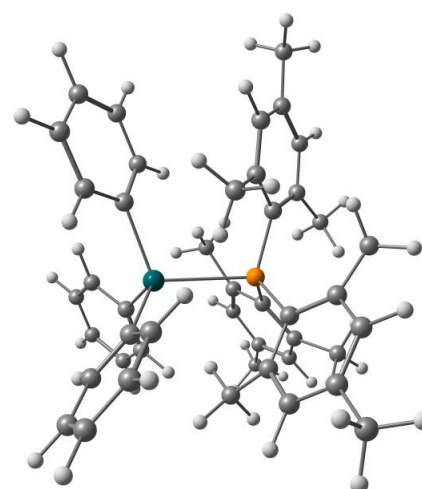
| | | | |
|---|-----------|-----------|----------|
| H | -1.558159 | -1.796485 | -4.91327 |
| H | -2.746312 | -3.867466 | -4.20910 |
| C | -1.456155 | -0.642410 | 1.92878 |
| C | -2.143405 | 0.270917 | 2.74143 |
| C | -1.266627 | -1.950559 | 2.39846 |
| C | -2.611201 | -0.109120 | 3.99971 |
| H | -2.331996 | 1.291156 | 2.39649 |
| C | -1.736125 | -2.330532 | 3.65491 |
| H | -0.748516 | -2.694357 | 1.78932 |
| C | -2.404595 | -1.408172 | 4.45926 |
| H | -3.145255 | 0.613376 | 4.62021 |
| H | -1.582194 | -3.353119 | 4.00565 |
| H | -2.771928 | -1.705707 | 5.44343 |

[Mes₃P–SnPh₃]⁺

E: -2299.31710248 a.u

Cartesian coordinates:

| | | | |
|---|-----------|-----------|----------|
| C | -0.721825 | 1.598939 | -1.72617 |
| C | -1.790509 | 1.688541 | -2.65552 |
| C | -0.249456 | 2.773531 | -1.09297 |
| C | -2.446923 | 2.913276 | -2.79016 |
| C | -0.942392 | 3.970782 | -1.27329 |
| C | -2.071163 | 4.057479 | -2.08369 |
| H | -3.274909 | 2.980965 | -3.50091 |
| H | -0.577075 | 4.865614 | -0.76261 |
| C | -1.029491 | -1.428183 | -1.71988 |
| C | -0.576445 | -2.399975 | -2.64952 |
| C | -2.280845 | -1.604709 | -1.08220 |
| C | -1.310188 | -3.580409 | -2.78025 |
| C | -2.972551 | -2.803298 | -1.25844 |
| C | -2.486711 | -3.825435 | -2.06931 |
| H | -0.957846 | -4.332393 | -3.49135 |
| H | -3.928444 | -2.933080 | -0.74426 |
| C | 1.746282 | -0.181027 | -1.72512 |
| C | 2.358040 | 0.695626 | -2.65833 |
| C | 2.527461 | -1.174890 | -1.08804 |
| C | 3.746900 | 0.651356 | -2.79296 |
| C | 3.910745 | -1.174048 | -1.26852 |
| C | 4.550070 | -0.243074 | -2.08275 |
| H | 4.219336 | 1.331553 | -3.50670 |
| H | 4.503127 | -1.935810 | -0.75494 |
| P | -0.001035 | -0.002521 | -1.20545 |
| C | -2.996947 | -0.522830 | -0.31714 |
| H | -2.344046 | 0.277156 | 0.04703 |
| H | -3.727349 | -0.029201 | -0.97856 |
| H | -3.540087 | -0.935763 | 0.54203 |
| C | 0.590134 | -2.220474 | -3.59362 |
| H | 0.666292 | -1.193200 | -3.97170 |
| H | 1.560189 | -2.466320 | -3.14083 |
| H | 0.457401 | -2.880492 | -4.46076 |
| C | -3.211705 | -5.136060 | -2.19179 |
| H | -3.059281 | -5.591834 | -3.17978 |
| H | -2.838049 | -5.848790 | -1.43897 |
| H | -4.291173 | -5.017466 | -2.02580 |
| C | -2.218270 | 0.585138 | -3.59573 |
| H | -1.366876 | 0.003342 | -3.97066 |
| H | -2.917138 | -0.129801 | -3.14075 |
| H | -2.722344 | 1.027139 | -4.46508 |
| C | -2.844550 | 5.339750 | -2.21013 |
| H | -3.646149 | 5.376089 | -1.45486 |
| H | -2.201834 | 6.216311 | -2.05061 |
| H | -3.318657 | 5.430569 | -3.19708 |
| C | 1.045710 | 2.856311 | -0.32855 |



SUPPORTING INFORMATION

| | | | |
|----|-----------|-----------|----------|
| H | 1.412813 | 1.892532 | 0.03938 |
| H | 1.838095 | 3.239928 | -0.99152 |
| H | 0.959392 | 3.536551 | 0.52788 |
| C | 1.615866 | 1.613476 | -3.60234 |
| H | 0.684235 | 1.166933 | -3.97185 |
| H | 1.349995 | 2.579792 | -3.15280 |
| H | 2.248855 | 1.821923 | -4.47475 |
| C | 1.951798 | -2.335115 | -0.31923 |
| H | 0.933894 | -2.169604 | 0.04864 |
| H | 1.887577 | -3.215629 | -0.97888 |
| H | 2.584319 | -2.597541 | 0.53791 |
| C | 6.047245 | -0.214975 | -2.20930 |
| H | 6.363081 | 0.148603 | -3.19678 |
| H | 6.479707 | 0.462015 | -1.45499 |
| H | 6.484734 | -1.209751 | -2.04824 |
| Sn | 0.001761 | 0.003080 | 1.48094 |
| C | -1.278283 | -1.560932 | 2.16924 |
| C | -1.193808 | -2.899699 | 1.76568 |
| C | -2.265225 | -1.196043 | 3.09770 |
| C | -2.081228 | -3.849499 | 2.26969 |
| H | -0.446041 | -3.224184 | 1.03938 |
| C | -3.150694 | -2.146899 | 3.60420 |
| H | -2.357880 | -0.157475 | 3.42952 |
| C | -3.061898 | -3.474381 | 3.18682 |
| H | -2.005978 | -4.888523 | 1.94195 |
| H | -3.912470 | -1.848704 | 4.32753 |
| H | -3.756094 | -4.219380 | 3.58121 |
| C | 1.998245 | -0.322541 | 2.16390 |
| C | 2.178802 | -1.359472 | 3.09195 |
| C | 3.113845 | 0.420435 | 1.75691 |
| C | 3.446665 | -1.650411 | 3.59460 |
| H | 1.326924 | -1.959185 | 3.42652 |
| C | 4.381768 | 0.127263 | 2.25705 |
| H | 3.018330 | 1.230360 | 1.03102 |
| C | 4.550367 | -0.909471 | 3.17372 |
| H | 3.571811 | -2.459073 | 4.31768 |
| H | 5.242731 | 0.712212 | 1.92661 |
| H | 5.543943 | -1.137863 | 3.56502 |
| C | -0.712664 | 1.896073 | 2.16256 |
| C | -1.915804 | 2.489379 | 1.75907 |
| C | 0.098168 | 2.572959 | 3.08642 |
| C | -2.294675 | 3.734622 | 2.25858 |
| H | -2.571955 | 2.000202 | 1.03645 |
| C | -0.282595 | 3.817046 | 3.58838 |
| H | 1.044912 | 2.136105 | 3.41825 |
| C | -1.478058 | 4.401005 | 3.17106 |
| H | -3.233253 | 4.186703 | 1.93096 |
| H | 0.357600 | 4.331341 | 4.30816 |
| H | -1.776148 | 5.376119 | 3.56189 |

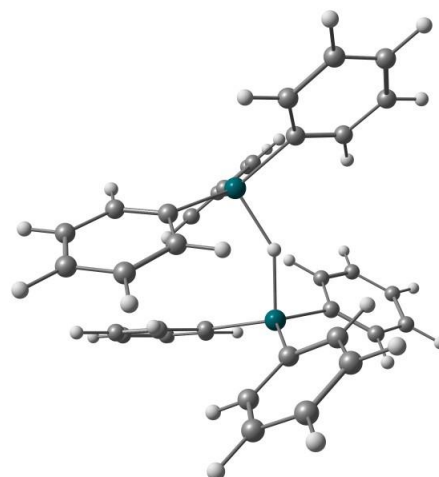
SUPPORTING INFORMATION

[Ph₃Sn--H--SnPh₃]⁺

E: -1819.01983965 a.u

Cartesian coordinates:

| | | | |
|----|-----------|-----------|----------|
| Sn | -0.240860 | -0.999779 | 1.46931 |
| C | -2.114410 | -0.365137 | 2.21324 |
| C | -2.244901 | 0.903177 | 2.79731 |
| C | -3.251280 | -1.163769 | 2.03045 |
| C | -3.499307 | 1.365916 | 3.19086 |
| H | -1.371387 | 1.545214 | 2.94530 |
| C | -4.503909 | -0.697863 | 2.42937 |
| H | -3.171451 | -2.154904 | 1.57541 |
| C | -4.627642 | 0.566029 | 3.00527 |
| H | -3.596812 | 2.353716 | 3.64570 |
| H | -5.386376 | -1.325742 | 2.29041 |
| H | -5.609312 | 0.929643 | 3.31578 |
| C | -0.254737 | -2.595687 | 0.08197 |
| C | 0.829112 | -3.484791 | 0.04814 |
| C | -1.297234 | -2.742128 | -0.84547 |
| C | 0.874245 | -4.499887 | -0.90586 |
| H | 1.651546 | -3.389412 | 0.76257 |
| C | -1.242409 | -3.752420 | -1.80458 |
| H | -2.154715 | -2.063866 | -0.84051 |
| C | -0.156663 | -4.628122 | -1.83675 |
| H | 1.718866 | -5.191662 | -0.92369 |
| H | -2.053947 | -3.855082 | -2.52777 |
| H | -0.118292 | -5.420846 | -2.58687 |
| C | 1.563766 | -0.765286 | 2.54678 |
| C | 1.586823 | -0.555208 | 3.93129 |
| C | 2.768937 | -0.788521 | 1.82656 |
| C | 2.803830 | -0.377386 | 4.58942 |
| H | 0.658982 | -0.529024 | 4.50935 |
| C | 3.981143 | -0.605618 | 2.48960 |
| H | 2.776561 | -0.945259 | 0.74253 |
| C | 3.997825 | -0.402026 | 3.86981 |
| H | 2.818633 | -0.217975 | 5.66943 |
| H | 4.915834 | -0.624776 | 1.92541 |
| H | 4.948522 | -0.261959 | 4.38827 |
| Sn | 0.232227 | 1.177337 | -1.35209 |
| H | 0.051316 | 0.501693 | 0.38292 |
| C | -1.632443 | 0.489333 | -2.07813 |
| C | -1.731132 | -0.249966 | -3.26379 |
| C | -2.771463 | 0.669936 | -1.27890 |
| C | -2.953165 | -0.804892 | -3.64267 |
| H | -0.855416 | -0.408575 | -3.89899 |
| C | -3.988907 | 0.104661 | -1.65563 |
| H | -2.721495 | 1.237913 | -0.34464 |
| C | -4.078246 | -0.634518 | -2.83588 |
| H | -3.025772 | -1.376458 | -4.57025 |
| H | -4.868483 | 0.242539 | -1.02358 |
| H | -5.032429 | -1.075533 | -3.13161 |
| C | 1.972892 | 0.128682 | -1.93520 |
| C | 3.229232 | 0.745875 | -1.84188 |
| C | 1.890380 | -1.217057 | -2.32222 |
| C | 4.387209 | 0.022611 | -2.12267 |
| H | 3.315143 | 1.797241 | -1.55364 |
| C | 3.052113 | -1.935404 | -2.60209 |
| H | 0.923910 | -1.723055 | -2.39911 |
| C | 4.298210 | -1.318166 | -2.49858 |
| H | 5.362374 | 0.508641 | -2.05197 |
| H | 2.979611 | -2.983010 | -2.90096 |
| H | 5.206353 | -1.883119 | -2.71887 |
| C | 0.413074 | 3.207662 | -0.79124 |
| C | 1.435287 | 3.609348 | 0.08164 |
| C | -0.499053 | 4.156163 | -1.27308 |
| C | 1.546004 | 4.946128 | 0.45949 |



SUPPORTING INFORMATION

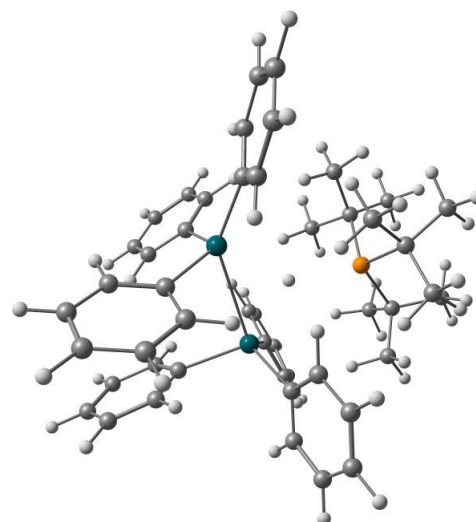
| | | | |
|---|-----------|----------|----------|
| H | 2.149691 | 2.883730 | 0.48234 |
| C | -0.381488 | 5.493199 | -0.89406 |
| H | -1.308599 | 3.862120 | -1.94722 |
| C | 0.639635 | 5.886906 | -0.03036 |
| H | 2.342858 | 5.255121 | 1.13900 |
| H | -1.091533 | 6.229915 | -1.27501 |
| H | 0.729473 | 6.934247 | 0.26489 |

PfBu₃ + [Ph₃Sn--H--SnPh₃]⁺

E: -2633.98040211 a.u

Cartesian coordinates:

| | | | |
|----|-----------|-----------|----------|
| P | -3.637482 | -0.071360 | 0.04869 |
| Sn | 0.651065 | -1.661033 | 0.34820 |
| C | -0.149508 | -2.700322 | -1.31342 |
| C | -1.534018 | -2.829203 | -1.49007 |
| C | 0.722268 | -3.365228 | -2.18904 |
| C | -2.036325 | -3.610565 | -2.52957 |
| H | -2.226906 | -2.299444 | -0.82865 |
| C | 0.213775 | -4.135717 | -3.23348 |
| H | 1.805132 | -3.299405 | -2.06045 |
| C | -1.165035 | -4.259468 | -3.40340 |
| H | -3.116589 | -3.713656 | -2.65475 |
| H | 0.898476 | -4.650725 | -3.91044 |
| H | -1.561686 | -4.870306 | -4.21698 |
| C | 2.753849 | -1.875404 | 0.59012 |
| C | 3.255066 | -2.115162 | 1.87809 |
| C | 3.649141 | -1.830417 | -0.48968 |
| C | 4.622031 | -2.294821 | 2.08318 |
| H | 2.582501 | -2.167745 | 2.73799 |
| C | 5.016350 | -2.003783 | -0.28050 |
| H | 3.295809 | -1.652361 | -1.50735 |
| C | 5.503979 | -2.234099 | 1.00563 |
| H | 4.998249 | -2.482284 | 3.09083 |
| H | 5.701114 | -1.965000 | -1.13028 |
| H | 6.574784 | -2.375941 | 1.16679 |
| C | -0.392685 | -1.733858 | 2.18654 |
| C | -1.529475 | -2.543489 | 2.31470 |
| C | 0.082534 | -1.030763 | 3.30276 |
| C | -2.176949 | -2.650519 | 3.54421 |
| H | -1.921903 | -3.095665 | 1.45759 |
| C | -0.573782 | -1.134338 | 4.52840 |
| H | 0.967629 | -0.393389 | 3.22782 |
| C | -1.701974 | -1.944893 | 4.64918 |
| H | -3.058484 | -3.287895 | 3.63904 |
| H | -0.200758 | -0.581397 | 5.39292 |
| H | -2.213575 | -2.027959 | 5.61017 |
| Sn | 1.676978 | 1.671794 | -0.41686 |
| H | 0.487248 | 0.214376 | -0.10519 |
| C | 2.524484 | 0.857408 | -2.18250 |
| C | 3.875096 | 1.044843 | -2.50525 |
| C | 1.729853 | 0.043799 | -3.00204 |
| C | 4.424966 | 0.410726 | -3.61861 |
| H | 4.517446 | 1.680311 | -1.88963 |
| C | 2.283234 | -0.592952 | -4.11280 |
| H | 0.671683 | -0.119994 | -2.77822 |
| C | 3.632330 | -0.414660 | -4.41688 |
| H | 5.478808 | 0.559720 | -3.86270 |
| H | 1.656291 | -1.233089 | -4.73684 |
| H | 4.067620 | -0.914983 | -5.28430 |
| C | 2.781379 | 1.612126 | 1.38935 |
| C | 2.149253 | 1.942740 | 2.59778 |
| C | 4.124683 | 1.216487 | 1.40454 |
| C | 2.851485 | 1.876361 | 3.80033 |
| H | 1.096401 | 2.240228 | 2.61832 |



SUPPORTING INFORMATION

| | | | |
|---|-----------|-----------|----------|
| C | 4.826810 | 1.161996 | 2.60729 |
| H | 4.631626 | 0.919526 | 0.48300 |
| C | 4.191577 | 1.489122 | 3.80397 |
| H | 2.351824 | 2.132631 | 4.73695 |
| H | 5.873064 | 0.850469 | 2.60862 |
| H | 4.742743 | 1.442429 | 4.74540 |
| C | 0.469003 | 3.384841 | -0.70381 |
| C | 0.244042 | 4.295781 | 0.33694 |
| C | -0.088072 | 3.628620 | -1.96648 |
| C | -0.554297 | 5.417895 | 0.12426 |
| H | 0.689456 | 4.142122 | 1.32270 |
| C | -0.892291 | 4.747215 | -2.17377 |
| H | 0.096302 | 2.944078 | -2.79873 |
| C | -1.131228 | 5.636945 | -1.12632 |
| H | -0.727323 | 6.123948 | 0.93880 |
| H | -1.329669 | 4.927783 | -3.15769 |
| H | -1.761636 | 6.513482 | -1.28932 |
| C | -5.356124 | -0.897603 | 0.26138 |
| C | -5.604519 | -1.175111 | 1.75407 |
| C | -6.564857 | -0.131967 | -0.29451 |
| C | -5.268658 | -2.285530 | -0.40675 |
| H | -4.744274 | -1.671134 | 2.22892 |
| H | -5.842291 | -0.266524 | 2.32164 |
| H | -6.470973 | -1.849251 | 1.84960 |
| H | -6.527909 | -0.014008 | -1.38479 |
| H | -7.488406 | -0.688723 | -0.06355 |
| H | -6.665414 | 0.866871 | 0.14915 |
| H | -6.211981 | -2.830240 | -0.23765 |
| H | -5.112433 | -2.240883 | -1.49018 |
| H | -4.456971 | -2.886742 | 0.03232 |
| C | -3.568472 | 0.675400 | -1.72855 |
| C | -4.294229 | 2.009895 | -1.94768 |
| C | -2.071792 | 0.843559 | -2.05371 |
| C | -4.096010 | -0.327202 | -2.76921 |
| H | -5.363840 | 1.943240 | -1.70754 |
| H | -3.862512 | 2.829885 | -1.35959 |
| H | -4.213390 | 2.299631 | -3.00900 |
| H | -1.555512 | -0.128270 | -2.02081 |
| H | -1.958153 | 1.249974 | -3.07314 |
| H | -1.565309 | 1.531223 | -1.37003 |
| H | -3.871005 | 0.064092 | -3.77484 |
| H | -3.602502 | -1.305056 | -2.68957 |
| H | -5.181359 | -0.474718 | -2.71988 |
| C | -3.529950 | 1.390308 | 1.29401 |
| C | -2.309364 | 2.250663 | 0.93256 |
| C | -4.761656 | 2.295747 | 1.42274 |
| C | -3.197196 | 0.798503 | 2.67819 |
| H | -1.401849 | 1.632312 | 0.84433 |
| H | -2.422911 | 2.830465 | 0.00822 |
| H | -2.130679 | 2.977317 | 1.74186 |
| H | -5.628012 | 1.757381 | 1.82915 |
| H | -4.538723 | 3.116832 | 2.12485 |
| H | -5.060280 | 2.749854 | 0.47005 |
| H | -2.985228 | 1.624289 | 3.37781 |
| H | -4.010873 | 0.211076 | 3.11409 |
| H | -2.305100 | 0.160136 | 2.63268 |

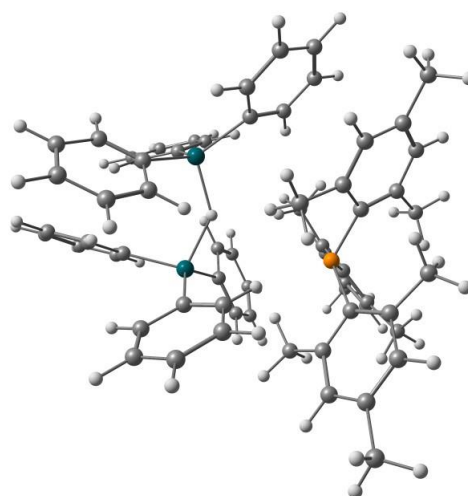
SUPPORTING INFORMATION

Mes₃P--[Ph₃Sn--H--SnPh₃]⁺

E: -3209.22514847 a.u

Cartesian coordinates:

| | | | |
|---|----------|-----------|----------|
| C | 3.131340 | -1.067042 | -1.58326 |
| C | 4.189964 | -1.987334 | -1.76603 |
| C | 2.172885 | -0.911771 | -2.61462 |
| C | 4.202002 | -2.778421 | -2.92031 |
| C | 2.252835 | -1.697320 | -3.76352 |
| C | 3.241694 | -2.665417 | -3.92448 |
| H | 5.019134 | -3.494097 | -3.05070 |
| H | 1.512354 | -1.551041 | -4.55429 |
| C | 3.783250 | -0.746262 | 1.34575 |
| C | 4.806653 | -0.046504 | 2.03426 |
| C | 3.369515 | -2.005484 | 1.84861 |
| C | 5.307890 | -0.582178 | 3.22495 |
| C | 3.913768 | -2.502084 | 3.03479 |
| C | 4.870864 | -1.795467 | 3.75739 |
| H | 6.095860 | -0.032468 | 3.74787 |
| H | 3.573612 | -3.474665 | 3.40178 |
| C | 3.160232 | 1.669848 | -0.33987 |
| C | 4.000575 | 2.198331 | -1.34933 |
| C | 2.519450 | 2.563160 | 0.55293 |
| C | 4.178164 | 3.582789 | -1.42490 |
| C | 2.762493 | 3.934160 | 0.45900 |
| C | 3.588371 | 4.469442 | -0.52488 |
| H | 4.835485 | 3.981191 | -2.20332 |
| H | 2.280183 | 4.605066 | 1.17440 |
| P | 2.767847 | -0.108111 | -0.05815 |
| C | 2.395459 | -2.881152 | 1.10823 |
| H | 1.630107 | -2.286564 | 0.59026 |
| H | 2.905427 | -3.463412 | 0.32294 |
| H | 1.898790 | -3.585306 | 1.79093 |
| C | 5.459023 | 1.220162 | 1.53623 |
| H | 5.710018 | 1.153123 | 0.46956 |
| H | 4.821424 | 2.107212 | 1.65624 |
| H | 6.390548 | 1.401382 | 2.08857 |
| C | 5.419029 | -2.314131 | 5.05938 |
| H | 6.501629 | -2.137685 | 5.13650 |
| H | 4.944705 | -1.804364 | 5.91351 |
| H | 5.238044 | -3.391857 | 5.17348 |
| C | 5.362405 | -2.130811 | -0.82592 |
| H | 5.713346 | -1.158922 | -0.45483 |
| H | 5.127715 | -2.734083 | 0.06302 |
| H | 6.199721 | -2.616932 | -1.34435 |
| C | 3.272445 | -3.560685 | -5.13331 |
| H | 2.842155 | -4.547695 | -4.89609 |
| H | 2.693256 | -3.136859 | -5.96571 |
| H | 4.300648 | -3.731936 | -5.48324 |
| C | 1.113001 | 0.156511 | -2.55374 |
| H | 0.597179 | 0.158184 | -1.58055 |
| H | 1.569471 | 1.153211 | -2.66551 |
| H | 0.367994 | 0.021199 | -3.35026 |
| C | 4.777851 | 1.355611 | -2.32913 |
| H | 5.339078 | 0.558249 | -1.82404 |
| H | 4.131131 | 0.862573 | -3.06882 |
| H | 5.498870 | 1.978051 | -2.87526 |
| C | 1.612012 | 2.088883 | 1.65975 |
| H | 2.152805 | 1.476871 | 2.39987 |
| H | 1.165480 | 2.941287 | 2.18972 |
| H | 0.799561 | 1.462647 | 1.26102 |
| C | 3.853984 | 5.947480 | -0.61380 |
| H | 3.677351 | 6.323471 | -1.63320 |
| H | 3.216423 | 6.515157 | 0.07801 |
| H | 4.902733 | 6.172537 | -0.36447 |



SUPPORTING INFORMATION

| | | | |
|----|-----------|-----------|----------|
| Sn | -1.533978 | -1.687033 | 0.54242 |
| C | -0.778187 | -1.650275 | 2.52073 |
| C | 0.429612 | -1.025584 | 2.84703 |
| C | -1.570992 | -2.199994 | 3.53845 |
| C | 0.846320 | -0.950704 | 4.17399 |
| H | 1.058309 | -0.600422 | 2.06404 |
| C | -1.150163 | -2.124284 | 4.86608 |
| H | -2.522329 | -2.688053 | 3.30967 |
| C | 0.055084 | -1.497940 | 5.18407 |
| H | 1.801715 | -0.476512 | 4.41003 |
| H | -1.767703 | -2.558599 | 5.65497 |
| H | 0.381932 | -1.442687 | 6.22464 |
| C | -3.652776 | -1.859027 | 0.58277 |
| C | -4.300939 | -2.598561 | -0.41737 |
| C | -4.417899 | -1.274031 | 1.60307 |
| C | -5.687950 | -2.736110 | -0.40712 |
| H | -3.727564 | -3.070095 | -1.21990 |
| C | -5.806054 | -1.400624 | 1.60302 |
| H | -3.940147 | -0.706438 | 2.40533 |
| C | -6.441721 | -2.128180 | 0.59638 |
| H | -6.181724 | -3.317598 | -1.18847 |
| H | -6.391232 | -0.931740 | 2.39680 |
| H | -7.529030 | -2.230860 | 0.60100 |
| C | -0.823218 | -2.633872 | -1.21853 |
| C | 0.041250 | -3.734647 | -1.21111 |
| C | -1.385524 | -2.208239 | -2.43170 |
| C | 0.347717 | -4.392911 | -2.40137 |
| H | 0.478184 | -4.098371 | -0.27993 |
| C | -1.078341 | -2.871300 | -3.61757 |
| H | -2.075680 | -1.360122 | -2.46779 |
| C | -0.212178 | -3.963843 | -3.60226 |
| H | 1.028372 | -5.246250 | -2.38670 |
| H | -1.522076 | -2.532209 | -4.55613 |
| H | 0.029867 | -4.481567 | -4.53275 |
| Sn | -2.160417 | 1.720626 | -0.32299 |
| H | -1.182557 | 0.137964 | 0.03379 |
| C | -3.093338 | 1.842373 | 1.57731 |
| C | -4.456861 | 2.133218 | 1.71308 |
| C | -2.335622 | 1.550345 | 2.72067 |
| C | -5.054955 | 2.117655 | 2.97277 |
| H | -5.070231 | 2.363633 | 0.83770 |
| C | -2.938253 | 1.522712 | 3.97767 |
| H | -1.268910 | 1.320642 | 2.64735 |
| C | -4.299239 | 1.802567 | 4.10235 |
| H | -6.118173 | 2.346328 | 3.07170 |
| H | -2.340821 | 1.277307 | 4.85801 |
| H | -4.772716 | 1.780945 | 5.08611 |
| C | -3.332331 | 1.069095 | -1.96415 |
| C | -2.850441 | 1.224875 | -3.27329 |
| C | -4.567266 | 0.438581 | -1.75903 |
| C | -3.582352 | 0.740944 | -4.35550 |
| H | -1.899565 | 1.728235 | -3.46296 |
| C | -5.300383 | -0.037593 | -2.84567 |
| H | -4.966255 | 0.298834 | -0.75099 |
| C | -4.806539 | 0.106267 | -4.14075 |
| H | -3.199589 | 0.866231 | -5.37042 |
| H | -6.260214 | -0.528564 | -2.67373 |
| H | -5.381403 | -0.270550 | -4.98926 |
| C | -0.835502 | 3.327226 | -0.70289 |
| C | -0.098796 | 3.463481 | -1.88699 |
| C | -0.896841 | 4.401922 | 0.19596 |
| C | 0.549814 | 4.661055 | -2.17604 |
| H | -0.024730 | 2.639566 | -2.59802 |
| C | -0.254342 | 5.603201 | -0.10290 |
| H | -1.462739 | 4.318237 | 1.12870 |
| C | 0.458015 | 5.735446 | -1.29244 |
| H | 1.126096 | 4.756355 | -3.09815 |

SUPPORTING INFORMATION

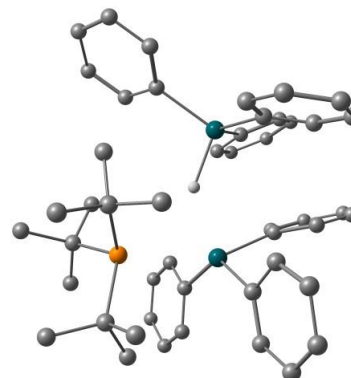
| | | | |
|---|-----------|----------|----------|
| H | -0.318362 | 6.440474 | 0.59515 |
| H | 0.953345 | 6.679012 | -1.52906 |

TS1_{tsu}: [tBu₃P–SnPh₃_HSnPh₃]⁺

E: -2633.97312127 a.u

Cartesian coordinates:

| | | | |
|----|-----------|-----------|----------|
| P | -2.671989 | 1.153620 | -0.15670 |
| Sn | -0.778513 | -1.384325 | -0.22520 |
| C | -1.365235 | -1.718148 | -2.25249 |
| C | -2.445257 | -2.538130 | -2.60023 |
| C | -0.575227 | -1.176201 | -3.27603 |
| C | -2.751272 | -2.776544 | -3.94021 |
| H | -3.070192 | -3.001969 | -1.83454 |
| C | -0.881610 | -1.410820 | -4.61492 |
| H | 0.295858 | -0.558977 | -3.04048 |
| C | -1.977847 | -2.204672 | -4.94873 |
| H | -3.599066 | -3.415383 | -4.19581 |
| H | -0.261262 | -0.973484 | -5.39991 |
| H | -2.222971 | -2.387759 | -5.99673 |
| C | 1.068560 | -2.503255 | -0.10527 |
| C | 1.500398 | -3.032705 | 1.11792 |
| C | 1.749768 | -2.877287 | -1.27337 |
| C | 2.600209 | -3.890071 | 1.17554 |
| H | 0.974693 | -2.794350 | 2.04482 |
| C | 2.842037 | -3.739481 | -1.21827 |
| H | 1.429096 | -2.509283 | -2.24945 |
| C | 3.274603 | -4.241122 | 0.00826 |
| H | 2.920759 | -4.295441 | 2.13810 |
| H | 3.358804 | -4.016609 | -2.13907 |
| H | 4.131570 | -4.916615 | 0.05228 |
| C | -1.748480 | -2.067284 | 1.55528 |
| C | -2.750511 | -3.044392 | 1.50100 |
| C | -1.277075 | -1.648670 | 2.80708 |
| C | -3.307371 | -3.553724 | 2.67428 |
| H | -3.115362 | -3.427596 | 0.54455 |
| C | -1.836888 | -2.155358 | 3.97872 |
| H | -0.460404 | -0.926001 | 2.89230 |
| C | -2.860821 | -3.099833 | 3.91384 |
| H | -4.092447 | -4.310403 | 2.61706 |
| H | -1.463646 | -1.813248 | 4.94626 |
| H | -3.300914 | -3.494622 | 4.83172 |
| Sn | 2.178678 | 0.954160 | 0.23890 |
| H | 0.519521 | 0.387621 | -0.27382 |
| C | 3.528500 | -0.145701 | -0.97627 |
| C | 4.630583 | -0.812157 | -0.42895 |
| C | 3.343308 | -0.169313 | -2.36561 |
| C | 5.520898 | -1.500092 | -1.25364 |
| H | 4.813861 | -0.801507 | 0.64817 |
| C | 4.230167 | -0.858335 | -3.18943 |
| H | 2.498165 | 0.352696 | -2.82567 |
| C | 5.319845 | -1.527439 | -2.63178 |
| H | 6.376635 | -2.016989 | -0.81456 |
| H | 4.074885 | -0.869429 | -4.27035 |
| H | 6.018087 | -2.066060 | -3.27581 |
| C | 2.158330 | 0.559078 | 2.33255 |
| C | 1.477486 | 1.429402 | 3.19726 |
| C | 2.748456 | -0.593819 | 2.86942 |
| C | 1.369406 | 1.144114 | 4.55799 |
| H | 1.010446 | 2.339928 | 2.81471 |
| C | 2.642676 | -0.879166 | 4.23021 |
| H | 3.282214 | -1.294764 | 2.22570 |
| C | 1.947812 | -0.014409 | 5.07499 |
| H | 0.832921 | 1.830711 | 5.21633 |



H-atoms omitted for clarity

SUPPORTING INFORMATION

| | | | |
|---|-----------|-----------|----------|
| H | 3.105954 | -1.782866 | 4.63190 |
| H | 1.865316 | -0.238863 | 6.14053 |
| C | 2.225226 | 3.034476 | -0.23146 |
| C | 2.446613 | 3.997331 | 0.76270 |
| C | 2.063195 | 3.458077 | -1.55786 |
| C | 2.481297 | 5.353951 | 0.44022 |
| H | 2.603387 | 3.698902 | 1.80268 |
| C | 2.094241 | 4.813895 | -1.88023 |
| H | 1.909915 | 2.732233 | -2.36122 |
| C | 2.297522 | 5.763559 | -0.87955 |
| H | 2.657979 | 6.093951 | 1.22362 |
| H | 1.965427 | 5.129847 | -2.91760 |
| H | 2.323575 | 6.825811 | -1.13109 |
| C | -4.454991 | 0.491693 | 0.12230 |
| C | -4.662349 | 0.089659 | 1.59443 |
| C | -5.571321 | 1.471863 | -0.27271 |
| C | -4.621242 | -0.797316 | -0.69872 |
| H | -3.879133 | -0.585477 | 1.96245 |
| H | -4.735462 | 0.950405 | 2.26951 |
| H | -5.617418 | -0.453953 | 1.66701 |
| H | -5.603865 | 1.663854 | -1.35207 |
| H | -6.539296 | 1.021647 | 0.00025 |
| H | -5.503242 | 2.434375 | 0.24721 |
| H | -5.646069 | -1.176533 | -0.55925 |
| H | -4.461823 | -0.665108 | -1.77327 |
| H | -3.941086 | -1.578667 | -0.34028 |
| C | -2.621378 | 2.078686 | -1.83853 |
| C | -3.281632 | 3.466597 | -1.83528 |
| C | -1.143334 | 2.239169 | -2.23602 |
| C | -3.287658 | 1.236363 | -2.94136 |
| H | -4.338305 | 3.435973 | -1.54429 |
| H | -2.765214 | 4.182923 | -1.18505 |
| H | -3.236742 | 3.874432 | -2.85800 |
| H | -0.635818 | 1.268707 | -2.30318 |
| H | -1.091998 | 2.703617 | -3.23400 |
| H | -0.574920 | 2.878754 | -1.55421 |
| H | -3.078124 | 1.715108 | -3.91073 |
| H | -2.891272 | 0.215219 | -2.99402 |
| H | -4.378557 | 1.187929 | -2.84044 |
| C | -2.302710 | 2.418271 | 1.23767 |
| C | -1.076250 | 3.267511 | 0.87531 |
| C | -3.455912 | 3.370435 | 1.58953 |
| C | -1.902475 | 1.620158 | 2.48766 |
| H | -0.223873 | 2.652019 | 0.56793 |
| H | -1.263096 | 4.004587 | 0.08571 |
| H | -0.763226 | 3.832608 | 1.76791 |
| H | -4.317922 | 2.853464 | 2.02711 |
| H | -3.094805 | 4.085572 | 2.34629 |
| H | -3.803399 | 3.955661 | 0.72972 |
| H | -1.668175 | 2.323959 | 3.30277 |
| H | -2.675866 | 0.938492 | 2.85369 |
| H | -0.996257 | 1.031809 | 2.29875 |

SUPPORTING INFORMATION

Approximated transition state TS1_{Mes}

Unfortunately, we were unable to locate the exact transition state for this specific case. However, the linear transit performed (varying the P-Sn distance) shows a clear increase in energy as the distance decreases, after which a sharp drop in energy occurs around 3.09 Å which strongly indicates the presence of a transition state at this point. Attempts to perform transition state searches on this structure were unsuccessful, even after a more detailed linear transit (smaller steps) was performed to zoom in on the region of focus (See Figures S30 and S31). This gave a more detailed indication of the exact position of the transition state, but unfortunately transition search calculations still failed. Attempts to locate the transition state using both QST2 and QST3 algorithms were also unsuccessful. Due to these issues we performed a single-point calculation on the highest point of the linear transit to approximate the energy of the transition state. As the exact energy of this transition state is not of great influence to the mechanistic proposal, we found this approximation to be sufficient.

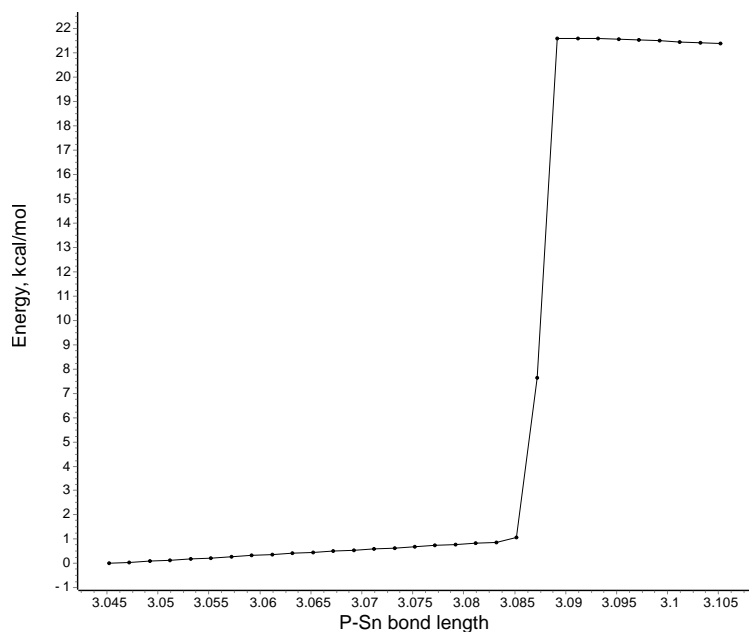


Figure S30. Linear transit shortening the P-Sn bond length; stepsize = 0.002 Å

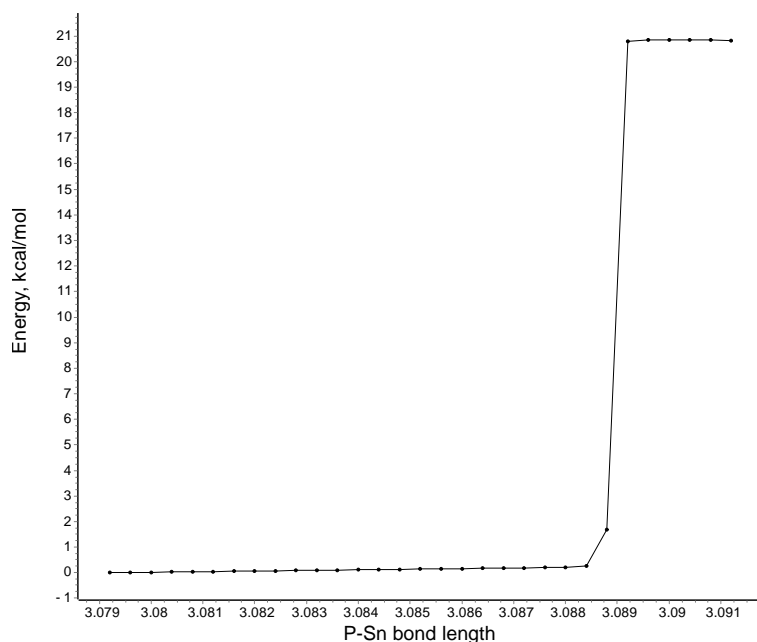


Figure S31. Linear transit shortening the P-Sn bond length; stepsize = 0.0004 Å

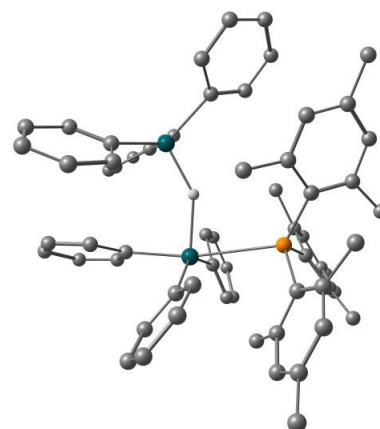
SUPPORTING INFORMATION

TS1_{Mes} estimate: [Mes₃P–SnPh₃_HSnPh₃]⁺

E: -3209.20253773 a.u

Cartesian coordinates:

| | | | |
|---|-----------|-----------|----------|
| C | -2.846341 | 0.894527 | 1.56809 |
| C | -4.066185 | 0.549921 | 2.19394 |
| C | -1.904916 | 1.672972 | 2.29161 |
| C | -4.232044 | 0.846284 | 3.55241 |
| C | -2.136792 | 1.968348 | 3.63188 |
| C | -3.276354 | 1.524425 | 4.30138 |
| H | -5.172804 | 0.559692 | 4.03123 |
| H | -1.393264 | 2.556989 | 4.17570 |
| C | -3.513412 | -0.771201 | -0.93792 |
| C | -4.144682 | -0.511920 | -2.18397 |
| C | -3.668527 | -2.060665 | -0.36711 |
| C | -4.787578 | -1.567458 | -2.84403 |
| C | -4.349556 | -3.061371 | -1.05429 |
| C | -4.885282 | -2.853669 | -2.32070 |
| H | -5.255678 | -1.359689 | -3.80989 |
| H | -4.443808 | -4.044641 | -0.58445 |
| C | -2.198022 | 1.975856 | -1.06244 |
| C | -2.998349 | 3.108900 | -0.74998 |
| C | -1.246999 | 2.097010 | -2.09953 |
| C | -2.750248 | 4.314595 | -1.40875 |
| C | -1.052966 | 3.322935 | -2.74070 |
| C | -1.776208 | 4.457313 | -2.39642 |
| H | -3.372948 | 5.177645 | -1.15634 |
| H | -0.304601 | 3.386045 | -3.53421 |
| P | -2.292793 | 0.374602 | -0.11857 |
| C | -3.164900 | -2.445450 | 0.99871 |
| H | -2.660627 | -1.626293 | 1.51688 |
| H | -4.003943 | -2.741907 | 1.64567 |
| H | -2.491430 | -3.311942 | 0.94021 |
| C | -4.257181 | 0.834418 | -2.86274 |
| H | -4.597065 | 1.614259 | -2.17180 |
| H | -3.315300 | 1.186089 | -3.30243 |
| H | -4.993468 | 0.771121 | -3.67406 |
| C | -5.538671 | -3.973416 | -3.08060 |
| H | -6.100690 | -3.603851 | -3.94886 |
| H | -4.776688 | -4.680211 | -3.44695 |
| H | -6.227291 | -4.543199 | -2.43995 |
| C | -5.283863 | -0.021875 | 1.50237 |
| H | -5.292190 | 0.144837 | 0.42151 |
| H | -5.391172 | -1.103875 | 1.66178 |
| H | -6.183261 | 0.450769 | 1.92114 |
| C | -3.460896 | 1.790525 | 5.76876 |
| H | -2.789971 | 1.147219 | 6.36064 |
| H | -3.217376 | 2.833335 | 6.01950 |
| H | -4.491186 | 1.590588 | 6.09283 |
| C | -0.691816 | 2.302779 | 1.65475 |
| H | -0.211435 | 1.660312 | 0.90572 |
| H | -0.977209 | 3.225775 | 1.12582 |
| H | 0.056527 | 2.558244 | 2.41697 |
| C | -4.180643 | 3.114648 | 0.18898 |
| H | -4.756790 | 2.184392 | 0.13394 |
| H | -3.888069 | 3.257141 | 1.23891 |
| H | -4.856400 | 3.936684 | -0.08202 |
| C | -0.499999 | 0.927243 | -2.67342 |
| H | -1.122730 | 0.398917 | -3.41427 |
| H | 0.408449 | 1.260052 | -3.19268 |
| H | -0.218496 | 0.194687 | -1.91163 |
| C | -1.555273 | 5.779745 | -3.07554 |
| H | -1.188042 | 6.529630 | -2.35769 |
| H | -0.819513 | 5.699452 | -3.88668 |
| H | -2.494006 | 6.167808 | -3.49874 |



H-atoms omitted for clarity

SUPPORTING INFORMATION

| | | | |
|----|-----------|-----------|----------|
| Sn | 0.089423 | -1.460357 | 0.59265 |
| C | -0.606383 | -2.826996 | -0.92909 |
| C | -1.148560 | -2.492763 | -2.17048 |
| C | -0.415039 | -4.181380 | -0.61797 |
| C | -1.503117 | -3.484743 | -3.08386 |
| H | -1.331310 | -1.456131 | -2.43591 |
| C | -0.793201 | -5.174980 | -1.51969 |
| H | 0.042367 | -4.481040 | 0.32955 |
| C | -1.335551 | -4.827748 | -2.75681 |
| H | -1.931122 | -3.200081 | -4.04724 |
| H | -0.647863 | -6.225363 | -1.25901 |
| H | -1.622098 | -5.606071 | -3.46719 |
| C | 2.007089 | -2.473247 | 0.89426 |
| C | 2.513867 | -2.716278 | 2.17936 |
| C | 2.705139 | -3.009453 | -0.19894 |
| C | 3.688291 | -3.447774 | 2.36400 |
| H | 1.996357 | -2.333470 | 3.06134 |
| C | 3.893483 | -3.716741 | -0.02280 |
| H | 2.319926 | -2.888525 | -1.21360 |
| C | 4.390041 | -3.934879 | 1.26287 |
| H | 4.058937 | -3.630856 | 3.37519 |
| H | 4.423454 | -4.109040 | -0.89350 |
| H | 5.315911 | -4.496470 | 1.40576 |
| C | -0.218949 | -0.932967 | 2.66464 |
| C | -1.137273 | -1.492576 | 3.55846 |
| C | 0.764013 | -0.070100 | 3.16985 |
| C | -1.096753 | -1.163771 | 4.91389 |
| H | -1.893557 | -2.203244 | 3.22819 |
| C | 0.802716 | 0.261745 | 4.52144 |
| H | 1.534037 | 0.349082 | 2.51936 |
| C | -0.135137 | -0.280716 | 5.39817 |
| H | -1.825031 | -1.608935 | 5.59512 |
| H | 1.579071 | 0.938575 | 4.88530 |
| H | -0.105747 | -0.029050 | 6.46052 |
| Sn | 2.624607 | 0.950539 | -0.61044 |
| H | 1.014264 | 0.146729 | -0.15495 |
| C | 3.398185 | -0.369371 | -2.08435 |
| C | 4.771199 | -0.648694 | -2.08436 |
| C | 2.574673 | -1.005163 | -3.02331 |
| C | 5.307968 | -1.552136 | -3.00188 |
| H | 5.439130 | -0.174327 | -1.35970 |
| C | 3.110857 | -1.911798 | -3.93556 |
| H | 1.497491 | -0.827687 | -3.03818 |
| C | 4.478303 | -2.187489 | -3.92404 |
| H | 6.379267 | -1.763276 | -2.99065 |
| H | 2.455557 | -2.410606 | -4.65248 |
| H | 4.897610 | -2.900095 | -4.63739 |
| C | 3.696702 | 0.985345 | 1.21677 |
| C | 3.634601 | 2.107760 | 2.05756 |
| C | 4.446038 | -0.129296 | 1.61484 |
| C | 4.294618 | 2.104065 | 3.28489 |
| H | 3.077330 | 2.999829 | 1.75983 |
| C | 5.108917 | -0.127265 | 2.84144 |
| H | 4.509572 | -1.016581 | 0.98000 |
| C | 5.028060 | 0.983613 | 3.67866 |
| H | 4.244039 | 2.981587 | 3.93309 |
| H | 5.684064 | -1.004804 | 3.14359 |
| H | 5.544896 | 0.981412 | 4.64063 |
| C | 2.162631 | 2.879909 | -1.37465 |
| C | 1.607112 | 3.904424 | -0.59738 |
| C | 2.557480 | 3.160315 | -2.69037 |
| C | 1.453655 | 5.185017 | -1.12404 |
| H | 1.282066 | 3.715211 | 0.42763 |
| C | 2.405960 | 4.443836 | -3.21548 |
| H | 2.996970 | 2.377848 | -3.31692 |
| C | 1.857883 | 5.456834 | -2.43045 |
| H | 1.018456 | 5.975542 | -0.50911 |

SUPPORTING INFORMATION

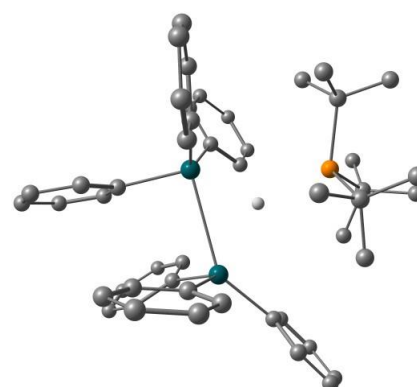
| | | | |
|---|----------|----------|----------|
| H | 2.724234 | 4.653155 | -4.23892 |
| H | 1.743646 | 6.462733 | -2.83973 |

TS2_{tBu}: tBu₃P--[Ph₃Sn--H--SnPh₃]⁺

E: -2633.94631149 a.u

Cartesian coordinates:

| | | | |
|----|-----------|-----------|----------|
| P | -3.018632 | -0.196394 | -0.18679 |
| Sn | 0.733540 | -1.337440 | -0.38542 |
| C | 0.317684 | -1.559637 | -2.46116 |
| C | -0.234973 | -0.529142 | -3.22610 |
| C | 0.686107 | -2.752642 | -3.09821 |
| C | -0.430173 | -0.683364 | -4.59819 |
| H | -0.529851 | 0.410787 | -2.75074 |
| C | 0.481811 | -2.914151 | -4.46858 |
| H | 1.148947 | -3.568966 | -2.53545 |
| C | -0.077213 | -1.880494 | -5.21918 |
| H | -0.863667 | 0.131131 | -5.18273 |
| H | 0.768320 | -3.849664 | -4.95338 |
| H | -0.232056 | -2.006266 | -6.29263 |
| C | 2.855281 | -1.532589 | -0.15754 |
| C | 3.382534 | -2.077014 | 1.02078 |
| C | 3.716512 | -1.248352 | -1.22416 |
| C | 4.754458 | -2.295678 | 1.14314 |
| H | 2.726399 | -2.338479 | 1.85516 |
| C | 5.086293 | -1.473234 | -1.10327 |
| H | 3.326395 | -0.842601 | -2.16032 |
| C | 5.607363 | -1.987192 | 0.08381 |
| H | 5.157104 | -2.718622 | 2.06615 |
| H | 5.748561 | -1.243874 | -1.94055 |
| H | 6.681429 | -2.160001 | 0.17968 |
| C | -0.026086 | -2.766380 | 0.99938 |
| C | -0.339545 | -4.055662 | 0.54812 |
| C | -0.054066 | -2.500877 | 2.37478 |
| C | -0.708620 | -5.051506 | 1.45131 |
| H | -0.314189 | -4.297480 | -0.51837 |
| C | -0.435481 | -3.494397 | 3.27615 |
| H | 0.221480 | -1.516455 | 2.76308 |
| C | -0.768503 | -4.767677 | 2.81504 |
| H | -0.955003 | -6.051190 | 1.08771 |
| H | -0.464583 | -3.272362 | 4.34500 |
| H | -1.064962 | -5.544987 | 3.52227 |
| Sn | 0.820601 | 1.610323 | 0.47414 |
| H | -0.827234 | 0.113496 | -0.09217 |
| C | 2.541847 | 1.800260 | -0.78280 |
| C | 3.795616 | 2.055279 | -0.21306 |
| C | 2.429581 | 1.748719 | -2.17825 |
| C | 4.915920 | 2.235081 | -1.02333 |
| H | 3.916940 | 2.119914 | 0.87110 |
| C | 3.549475 | 1.932597 | -2.98851 |
| H | 1.469080 | 1.545665 | -2.65848 |
| C | 4.795486 | 2.169888 | -2.41060 |
| H | 5.888597 | 2.428074 | -0.56636 |
| H | 3.447026 | 1.885650 | -4.07471 |
| H | 5.674283 | 2.310695 | -3.04320 |
| C | 1.228944 | 1.110664 | 2.50943 |
| C | 0.267096 | 1.304175 | 3.51234 |
| C | 2.448106 | 0.509471 | 2.85459 |
| C | 0.510205 | 0.891479 | 4.82147 |
| H | -0.695560 | 1.766046 | 3.28290 |
| C | 2.691451 | 0.096871 | 4.16427 |
| H | 3.219017 | 0.339584 | 2.10082 |
| C | 1.721207 | 0.281367 | 5.14776 |
| H | -0.249930 | 1.047359 | 5.58981 |
| H | 3.645050 | -0.373107 | 4.41400 |



H-atoms omitted for clarity

SUPPORTING INFORMATION

| | | | |
|---|-----------|-----------|----------|
| H | 1.911068 | -0.044130 | 6.17260 |
| C | -0.205948 | 3.467047 | 0.22475 |
| C | -0.747170 | 4.167275 | 1.30991 |
| C | -0.186022 | 4.079996 | -1.03545 |
| C | -1.300563 | 5.434744 | 1.12893 |
| H | -0.738061 | 3.740107 | 2.31482 |
| C | -0.740855 | 5.344654 | -1.21664 |
| H | 0.268972 | 3.578917 | -1.89344 |
| C | -1.308123 | 6.019499 | -0.13595 |
| H | -1.719261 | 5.969961 | 1.98362 |
| H | -0.722870 | 5.808655 | -2.20487 |
| H | -1.742608 | 7.011189 | -0.27728 |
| C | -3.770665 | -1.936490 | -0.50149 |
| C | -3.601558 | -2.836146 | 0.73443 |
| C | -5.266967 | -1.920309 | -0.85664 |
| C | -2.978531 | -2.599658 | -1.64244 |
| H | -2.577683 | -2.836448 | 1.12305 |
| H | -4.290837 | -2.574807 | 1.54646 |
| H | -3.834496 | -3.871055 | 0.43874 |
| H | -5.479780 | -1.444047 | -1.82028 |
| H | -5.613838 | -2.963414 | -0.93339 |
| H | -5.878531 | -1.431207 | -0.08827 |
| H | -3.406045 | -3.596036 | -1.83740 |
| H | -3.002029 | -2.043010 | -2.58524 |
| H | -1.926795 | -2.743939 | -1.36730 |
| C | -3.733109 | 1.007519 | -1.50143 |
| C | -5.163517 | 1.496789 | -1.22885 |
| C | -2.790885 | 2.219324 | -1.56396 |
| C | -3.703074 | 0.373076 | -2.90290 |
| H | -5.886318 | 0.675301 | -1.15217 |
| H | -5.238170 | 2.108813 | -0.32170 |
| H | -5.480680 | 2.134096 | -2.07007 |
| H | -1.769338 | 1.916704 | -1.83516 |
| H | -3.140855 | 2.914786 | -2.34346 |
| H | -2.732351 | 2.786553 | -0.62990 |
| H | -3.935371 | 1.159647 | -3.63812 |
| H | -2.718068 | -0.033271 | -3.15993 |
| H | -4.447698 | -0.418977 | -3.03904 |
| C | -3.568809 | 0.380708 | 1.55208 |
| C | -3.256883 | 1.875337 | 1.70235 |
| C | -5.043816 | 0.147726 | 1.90865 |
| C | -2.679995 | -0.345522 | 2.57696 |
| H | -2.223688 | 2.106005 | 1.41743 |
| H | -3.918210 | 2.524827 | 1.11641 |
| H | -3.380114 | 2.160437 | 2.75955 |
| H | -5.303350 | -0.916488 | 1.95879 |
| H | -5.232485 | 0.570163 | 2.90904 |
| H | -5.734161 | 0.638118 | 1.21208 |
| H | -2.852746 | 0.090877 | 3.57412 |
| H | -2.879036 | -1.418193 | 2.65267 |
| H | -1.614697 | -0.221320 | 2.34461 |

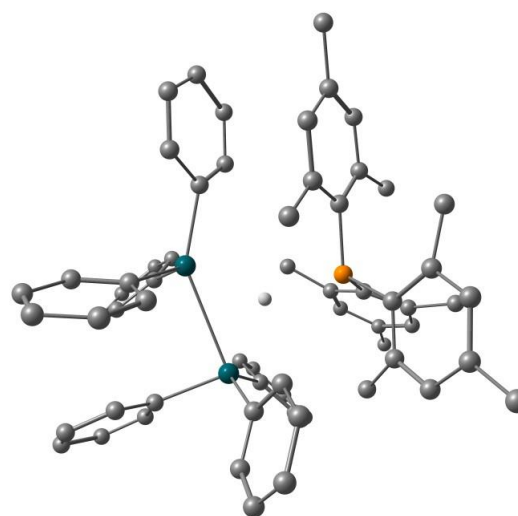
SUPPORTING INFORMATION

TS2_{Mes}: Mes₃P--[Ph₃Sn--H--SnPh₃]⁺

E: -3209.18553379 a.u

Cartesian coordinates:

| | | | |
|----|-----------|-----------|----------|
| C | -2.809632 | -0.929177 | 1.68989 |
| C | -3.887941 | -1.838039 | 1.81954 |
| C | -1.930240 | -0.754247 | 2.78522 |
| C | -3.948866 | -2.643293 | 2.96276 |
| C | -2.052006 | -1.562733 | 3.91208 |
| C | -3.027073 | -2.554642 | 4.00310 |
| H | -4.773744 | -3.356189 | 3.04868 |
| H | -1.358873 | -1.413727 | 4.74344 |
| C | -3.242895 | -0.916153 | -1.26250 |
| C | -4.254168 | -0.335076 | -2.07434 |
| C | -2.827149 | -2.238548 | -1.55033 |
| C | -4.675813 | -1.028454 | -3.21412 |
| C | -3.302788 | -2.894444 | -2.68499 |
| C | -4.198040 | -2.290948 | -3.56236 |
| H | -5.444692 | -0.567860 | -3.84048 |
| H | -2.949920 | -3.909209 | -2.88823 |
| C | -2.854585 | 1.699274 | 0.12653 |
| C | -3.694883 | 2.314368 | 1.08995 |
| C | -2.361812 | 2.470918 | -0.95137 |
| C | -3.977990 | 3.674393 | 0.95526 |
| C | -2.699325 | 3.821359 | -1.04918 |
| C | -3.497714 | 4.449733 | -0.10132 |
| H | -4.622944 | 4.146444 | 1.70159 |
| H | -2.308056 | 4.401081 | -1.88879 |
| P | -2.363351 | -0.067687 | 0.12505 |
| C | -1.957068 | -3.035669 | -0.62318 |
| H | -1.304519 | -2.406787 | -0.01002 |
| H | -2.576719 | -3.601695 | 0.09130 |
| H | -1.336693 | -3.749609 | -1.18132 |
| C | -5.019221 | 0.931775 | -1.76547 |
| H | -5.242100 | 1.032962 | -0.69651 |
| H | -4.493163 | 1.847387 | -2.06759 |
| H | -5.976470 | 0.912873 | -2.30261 |
| C | -4.640564 | -2.981584 | -4.82224 |
| H | -5.590869 | -2.576241 | -5.19559 |
| H | -3.888188 | -2.849949 | -5.61680 |
| H | -4.762677 | -4.062712 | -4.66547 |
| C | -5.042815 | -1.963069 | 0.85336 |
| H | -5.317243 | -1.001110 | 0.40439 |
| H | -4.837351 | -2.654524 | 0.02355 |
| H | -5.923199 | -2.343256 | 1.38872 |
| C | -3.082536 | -3.480889 | 5.18500 |
| H | -2.391060 | -4.326190 | 5.03551 |
| H | -2.780966 | -2.971177 | 6.11102 |
| H | -4.088901 | -3.897031 | 5.32994 |
| C | -0.941522 | 0.375762 | 2.84663 |
| H | -0.411981 | 0.523865 | 1.89780 |
| H | -1.464149 | 1.319372 | 3.07424 |
| H | -0.191786 | 0.206911 | 3.62840 |
| C | -4.385473 | 1.591564 | 2.22126 |
| H | -4.971208 | 0.735933 | 1.85940 |
| H | -3.691825 | 1.199447 | 2.97603 |
| H | -5.078269 | 2.273716 | 2.73044 |
| C | -1.547821 | 1.891600 | -2.07870 |
| H | -2.194812 | 1.421158 | -2.83769 |
| H | -0.956661 | 2.672981 | -2.57456 |
| H | -0.855752 | 1.111733 | -1.73817 |
| C | -3.850972 | 5.906295 | -0.20981 |
| H | -3.708295 | 6.419836 | 0.75250 |
| H | -3.236175 | 6.414596 | -0.96476 |
| H | -4.908077 | 6.031235 | -0.49263 |
| Sn | 1.381031 | -1.506141 | -0.23830 |



H-atoms omitted for clarity

SUPPORTING INFORMATION

| | | | |
|----|-----------|-----------|----------|
| C | 0.796425 | -2.178294 | -2.17829 |
| C | -0.161247 | -1.558660 | -2.98570 |
| C | 1.516129 | -3.266588 | -2.69404 |
| C | -0.402093 | -2.014435 | -4.28094 |
| H | -0.750373 | -0.722578 | -2.61033 |
| C | 1.264260 | -3.733255 | -3.98374 |
| H | 2.293306 | -3.756172 | -2.09959 |
| C | 0.307160 | -3.104769 | -4.78020 |
| H | -1.158742 | -1.519676 | -4.89365 |
| H | 1.827020 | -4.585161 | -4.37099 |
| H | 0.117392 | -3.465195 | -5.79343 |
| C | 3.523193 | -1.576091 | -0.34348 |
| C | 4.256153 | -2.107288 | 0.72603 |
| C | 4.200627 | -1.184974 | -1.50625 |
| C | 5.643597 | -2.219619 | 0.64453 |
| H | 3.753560 | -2.433311 | 1.63943 |
| C | 5.588872 | -1.285942 | -1.58137 |
| H | 3.653330 | -0.792511 | -2.36617 |
| C | 6.312285 | -1.796719 | -0.50349 |
| H | 6.203792 | -2.636605 | 1.48418 |
| H | 6.105130 | -0.966564 | -2.48905 |
| H | 7.399866 | -1.876545 | -0.56376 |
| C | 0.917811 | -2.465267 | 1.61945 |
| C | 0.283206 | -3.709675 | 1.71575 |
| C | 1.444737 | -1.884716 | 2.78321 |
| C | 0.150842 | -4.344661 | 2.95043 |
| H | -0.106872 | -4.209285 | 0.82745 |
| C | 1.314732 | -2.521630 | 4.01589 |
| H | 1.972395 | -0.928144 | 2.74302 |
| C | 0.662452 | -3.750657 | 4.10218 |
| H | -0.347425 | -5.314745 | 3.00807 |
| H | 1.732862 | -2.055047 | 4.91073 |
| H | 0.562571 | -4.251433 | 5.06763 |
| Sn | 1.483231 | 1.554292 | 0.06478 |
| H | -0.202511 | 0.029275 | -0.05021 |
| C | 2.560635 | 1.702283 | -1.77609 |
| C | 3.851575 | 2.248278 | -1.75552 |
| C | 2.036559 | 1.253228 | -2.99459 |
| C | 4.607957 | 2.321761 | -2.92485 |
| H | 4.286713 | 2.617698 | -0.82284 |
| C | 2.793674 | 1.322332 | -4.16375 |
| H | 1.036132 | 0.820770 | -3.04891 |
| C | 4.083399 | 1.851064 | -4.12821 |
| H | 5.613991 | 2.745403 | -2.89391 |
| H | 2.374429 | 0.955344 | -5.10289 |
| H | 4.679428 | 1.901816 | -5.04181 |
| C | 2.788603 | 1.408442 | 1.76007 |
| C | 2.319131 | 1.779773 | 3.02905 |
| C | 4.117912 | 0.984879 | 1.63134 |
| C | 3.146289 | 1.694761 | 4.14734 |
| H | 1.299865 | 2.148862 | 3.16003 |
| C | 4.948204 | 0.907176 | 2.74965 |
| H | 4.522056 | 0.700880 | 0.65787 |
| C | 4.461572 | 1.250274 | 4.00920 |
| H | 2.765511 | 1.985817 | 5.12869 |
| H | 5.980326 | 0.571071 | 2.63066 |
| H | 5.111345 | 1.183750 | 4.88436 |
| C | 0.405336 | 3.384218 | 0.30688 |
| C | -0.326127 | 3.738945 | 1.44553 |
| C | 0.677928 | 4.363727 | -0.65748 |
| C | -0.767206 | 5.047840 | 1.62265 |
| H | -0.574966 | 2.996257 | 2.20306 |
| C | 0.231902 | 5.674162 | -0.48012 |
| H | 1.254535 | 4.117969 | -1.55400 |
| C | -0.483148 | 6.019417 | 0.66380 |
| H | -1.338537 | 5.308781 | 2.51589 |
| H | 0.456724 | 6.429306 | -1.23648 |

SUPPORTING INFORMATION

H -0.822913 7.047085 0.80818

SUPPORTING INFORMATION

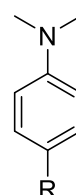
Computational details: Ionisation potentials and electron affinities

All structures in this section were optimized at the ω B97X-D/6-31G(d) level of theory after which single point calculations were performed using Gaussian 09, Revision D01⁵ at the ω B97X-D/6-311+G(d,p) level of theory.^{4,6} Solvent was taken into account where specified by applying Self-Consistent Reaction Field (SCRF) method using the polarizable continuum model. Minimum-energy crossing points (MECPs) were calculated using the method developed by Harvey *et al.* after which a frequency analysis was performed applying another method developed within the same group.^{7,8}

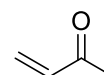
Table S3. Ionization potentials and electron affinities for different donors and acceptors calculating using different functionals and PCM solvent corrections

| Functional | ω B97X-D | ω B97X-D | ω B97X-D | ω B97X-D |
|--|----------------------------------|-----------------|-----------------|-----------------|
| Solvent | C ₆ H ₅ Cl | Toluene | THF | DCE |
| Ionization potentials | | | | |
| PMes ₃ | 5.25 | 5.54 | 5.20 | |
| PtBu ₃ | 5.55 | 5.95 | | |
| Me ₂ N-Ph-Me | 5.36 | | | 5.23 |
| Me ₂ N-Ph-Br | 5.66 | | | 5.51 |
| Electron affinities | | | | |
| TCQ | 4.45 | 4.02 | | |
| TCQ-B(C ₆ F ₅) ₃ | 5.57 | 5.34 | | |
| (C ₆ F ₅) ₃ B-TCQ-B(C ₆ F ₅) ₃ | 4.75 | 4.54 | | |
| [(C ₆ F ₅) ₃ B-TCQ-B(C ₆ F ₅) ₃] ⁻ | 6.11 | 5.39 | | |
| MVK | 1.08 | | | 1.26 |
| MVK-B(C ₆ F ₅) ₃ | 2.58 | | | 2.65 |
| 9 | 2.24 | | 2.31 | |
| 9 -B(C ₆ F ₅) ₃ | 3.42 | | 3.45 | |
| B(C ₆ F ₅) ₃ | 3.31 | 3.03 | | |

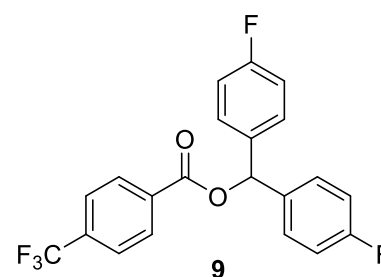
ΔE in eV



Me₂N-Ph-R



MVK



9

SUPPORTING INFORMATION

Table S4. Calculated energy for adduct formation between the substrate and $B(C_6F_5)_3$

| | | ΔE | ΔG |
|-----|------------------------------------|------------|------------|
| BCF | TCQ | -4.6 | 10.7 |
| | TCQ- $B(C_6F_5)_3$ | -16.0 | -2.9 |
| | [TCQ- $B(C_6F_5)_3$] ⁻ | 2.7 | 18.8 |
| | MVK | -16.3 | 0.88 |
| | 9 | -19.1 | -0.2 |

 ΔE and ΔG in kcal/mol

SUPPORTING INFORMATION

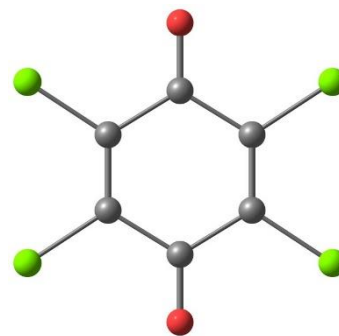
TCQ

E: -2219.83477667 a.u

G: -2219.825316 a.u

Cartesian coordinates:

| | | | |
|----|-----------|-----------|----------|
| C | -1.279690 | 0.672135 | 0.00002 |
| C | 0.000008 | 1.455500 | 0.00002 |
| C | 1.279680 | 0.672133 | -0.00002 |
| C | 1.279678 | -0.672135 | 0.00001 |
| C | 0.000000 | -1.455501 | 0.00014 |
| C | -1.279693 | -0.672135 | -0.00002 |
| Cl | 2.711196 | -1.609801 | -0.00007 |
| Cl | 2.711203 | 1.609793 | -0.00011 |
| Cl | -2.711192 | 1.609822 | 0.00001 |
| Cl | -2.711200 | -1.609816 | -0.00019 |
| O | -0.000004 | -2.661108 | 0.00042 |
| O | 0.000004 | 2.661115 | 0.00024 |

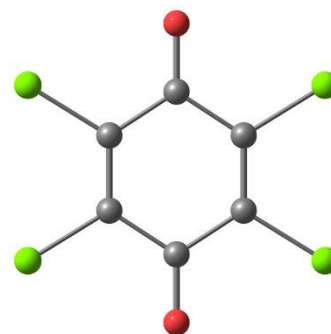
TCQ⁻

E: -2219.99790560 a.u

G: -2219.98983 a.u

Cartesian coordinates:

| | | | |
|----|-----------|-----------|----------|
| C | 1.223264 | 0.684440 | 0.00014 |
| C | -0.000009 | 1.481304 | 0.00033 |
| C | -1.223255 | 0.684446 | 0.00014 |
| C | -1.223254 | -0.684447 | 0.00013 |
| C | -0.000007 | -1.481304 | 0.00027 |
| C | 1.223265 | -0.684439 | 0.00014 |
| Cl | -2.704875 | -1.597274 | -0.00008 |
| Cl | -2.704877 | 1.597271 | -0.00009 |
| Cl | 2.704872 | 1.597278 | -0.00010 |
| Cl | 2.704873 | -1.597277 | -0.00007 |
| O | 0.000008 | -2.721893 | -0.00009 |
| O | 0.000004 | 2.721896 | -0.00008 |

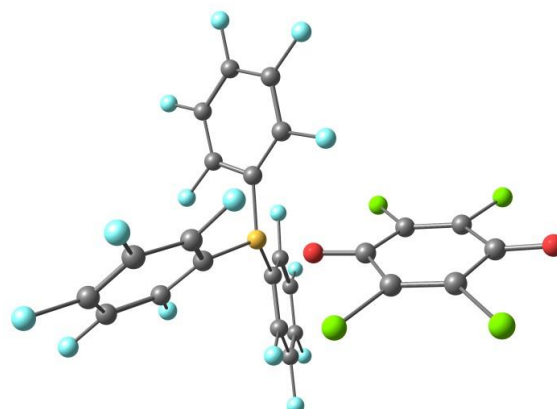
TCQ-B(C₆F₅)₃

E: -4428.11564972 a.u

G: -4427.985938 a.u

Cartesian coordinates:

| | | | |
|----|-----------|-----------|----------|
| C | 2.735762 | 1.716491 | 0.13594 |
| C | 1.969883 | 0.449429 | -0.01891 |
| C | 2.711638 | -0.816950 | -0.22980 |
| C | 4.050232 | -0.792788 | -0.39550 |
| C | 4.834855 | 0.488398 | -0.34299 |
| C | 4.071662 | 1.740852 | -0.03270 |
| Cl | 4.971574 | -2.195920 | -0.67301 |
| Cl | 1.818603 | -2.271350 | -0.25539 |
| Cl | 1.816494 | 3.107113 | 0.50224 |
| Cl | 5.002807 | 3.160523 | 0.08651 |
| O | 6.024245 | 0.502651 | -0.52800 |
| O | 0.752836 | 0.531138 | 0.04012 |
| B | -0.849912 | -0.115057 | 0.07263 |
| C | -0.773788 | -0.983192 | 1.42862 |
| C | -0.467418 | -0.348508 | 2.63306 |
| C | -0.988350 | -2.355889 | 1.52322 |
| C | -0.400950 | -1.003879 | 3.85274 |
| C | -0.937636 | -3.050529 | 2.72691 |
| C | -0.645449 | -2.370318 | 3.89951 |



SUPPORTING INFORMATION

| | | | |
|---|-----------|-----------|----------|
| C | -1.705925 | 1.252674 | 0.12989 |
| C | -1.466247 | 2.265114 | -0.79745 |
| C | -2.766247 | 1.481434 | 1.00219 |
| C | -2.189358 | 3.447734 | -0.84422 |
| C | -3.522805 | 2.648063 | 0.98124 |
| C | -3.229758 | 3.638964 | 0.05560 |
| C | -1.121651 | -0.849732 | -1.33914 |
| C | -2.382878 | -1.421554 | -1.49506 |
| C | -0.324830 | -0.860764 | -2.47641 |
| C | -2.821813 | -2.007327 | -2.67172 |
| C | -0.723318 | -1.436837 | -3.67770 |
| C | -1.979291 | -2.015196 | -3.77669 |
| F | -0.488018 | 2.121469 | -1.70596 |
| F | -1.901741 | 4.388503 | -1.74224 |
| F | -3.940234 | 4.760926 | 0.02695 |
| F | -4.523988 | 2.820142 | 1.84123 |
| F | -0.102385 | -0.341443 | 4.96808 |
| F | -0.584126 | -3.021175 | 5.05451 |
| F | -1.148449 | -4.364287 | 2.75680 |
| F | -3.114933 | 0.568171 | 1.91413 |
| F | -0.206662 | 0.966965 | 2.64372 |
| F | -1.221877 | -3.097454 | 0.43449 |
| F | -3.230253 | -1.414825 | -0.45712 |
| F | -4.033303 | -2.550187 | -2.75376 |
| F | -2.374845 | -2.568979 | -4.91739 |
| F | 0.092063 | -1.428719 | -4.73069 |
| F | 0.902511 | -0.305262 | -2.47828 |

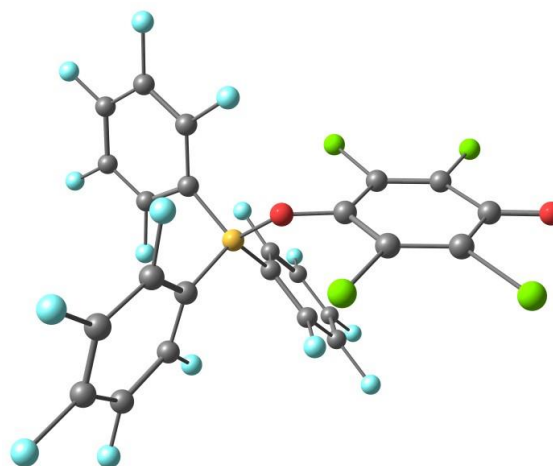
TCQ-B(C₆F₅)₃⁻

E: -4428.31974880 a.u

G: -4428.190662 a.u

Cartesian coordinates:

| | | | |
|----|-----------|-----------|----------|
| C | 2.366321 | 1.462496 | -1.34667 |
| C | 1.622401 | 0.248273 | -1.14886 |
| C | 2.354847 | -0.982504 | -1.11814 |
| C | 3.727703 | -0.992587 | -1.18288 |
| C | 4.516834 | 0.230797 | -1.32397 |
| C | 3.733442 | 1.462699 | -1.42286 |
| Cl | 4.627700 | -2.461306 | -1.13156 |
| Cl | 1.464347 | -2.463115 | -1.06179 |
| Cl | 1.455272 | 2.924980 | -1.46258 |
| Cl | 4.637592 | 2.915300 | -1.63031 |
| O | 5.748994 | 0.222165 | -1.37559 |
| O | 0.337976 | 0.327262 | -1.06985 |
| B | -0.689825 | -0.050517 | -0.00036 |
| C | 0.130772 | -0.598359 | 1.31115 |
| C | 1.033722 | 0.250960 | 1.94895 |
| C | 0.062982 | -1.877693 | 1.85375 |
| C | 1.812388 | -0.114168 | 3.03701 |
| C | 0.818881 | -2.286031 | 2.94806 |
| C | 1.699848 | -1.399770 | 3.54503 |
| C | -1.525761 | 1.344826 | 0.28551 |
| C | -1.997657 | 2.082668 | -0.79990 |
| C | -1.877867 | 1.852412 | 1.53163 |
| C | -2.723033 | 3.260353 | -0.67273 |
| C | -2.605860 | 3.025541 | 1.70297 |
| C | -3.027910 | 3.738423 | 0.59291 |
| C | -1.790421 | -1.082683 | -0.63819 |
| C | -2.871904 | -1.475864 | 0.14631 |
| C | -1.836480 | -1.516068 | -1.95951 |
| C | -3.915427 | -2.265601 | -0.30961 |
| C | -2.867618 | -2.309717 | -2.45871 |
| C | -3.912056 | -2.687512 | -1.63189 |
| F | -1.778060 | 1.662576 | -2.05222 |



SUPPORTING INFORMATION

| | | | |
|---|-----------|-----------|----------|
| F | -3.141396 | 3.929057 | -1.75312 |
| F | -3.728075 | 4.866798 | 0.73903 |
| F | -2.905905 | 3.469077 | 2.92900 |
| F | 2.656397 | 0.753993 | 3.60095 |
| F | 2.433813 | -1.778686 | 4.59291 |
| F | 0.711206 | -3.532029 | 3.42034 |
| F | -1.531630 | 1.223016 | 2.66405 |
| F | 1.183314 | 1.512579 | 1.51445 |
| F | -0.726433 | -2.822195 | 1.32507 |
| F | -2.929767 | -1.088569 | 1.43121 |
| F | -4.919581 | -2.619324 | 0.50036 |
| F | -4.906204 | -3.447781 | -2.10011 |
| F | -2.860677 | -2.705940 | -3.73650 |
| F | -0.885779 | -1.193435 | -2.84273 |

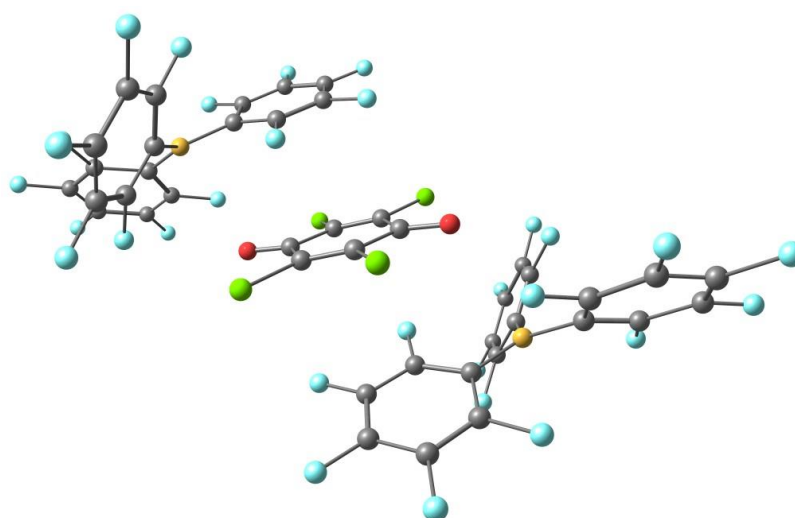
(C₆F₅)₃B-TCQ-B(C₆F₅)₃

E: -6636.41473264 a.u

G: -6636.168245 a.u

Cartesian coordinates:

| | | | |
|----|-----------|-----------|----------|
| C | -0.547373 | -1.246312 | 0.47981 |
| C | -1.256035 | 0.050462 | 0.72455 |
| C | -0.586601 | 1.298231 | 0.23401 |
| C | 0.546452 | 1.247182 | -0.48607 |
| C | 1.253910 | -0.049867 | -0.73307 |
| C | 0.585640 | -1.297407 | -0.24032 |
| Cl | 1.311368 | 2.637548 | -1.12052 |
| Cl | -1.382852 | 2.763199 | 0.61275 |
| Cl | -1.310661 | -2.636465 | 1.11664 |
| Cl | 1.383008 | -2.762282 | -0.61706 |
| O | 2.333589 | -0.084648 | -1.27232 |
| O | -2.337494 | 0.084857 | 1.26031 |
| B | -4.824279 | 0.069130 | -0.72791 |
| C | -3.972953 | 1.055231 | -1.60608 |
| C | -2.720823 | 0.706388 | -2.12262 |
| C | -4.402645 | 2.348680 | -1.92393 |
| C | -1.930933 | 1.568419 | -2.86447 |
| C | -3.643689 | 3.238492 | -2.67205 |
| C | -2.394260 | 2.848661 | -3.13792 |
| C | -4.681733 | -1.479081 | -0.93925 |
| C | -4.632101 | -2.364717 | 0.13850 |
| C | -4.594391 | -2.052978 | -2.20885 |
| C | -4.467959 | -3.732632 | -0.02616 |
| C | -4.457087 | -3.416903 | -2.41107 |
| C | -4.384663 | -4.259995 | -1.30773 |
| C | -5.832028 | 0.589487 | 0.35309 |
| C | -7.039908 | -0.071107 | 0.60151 |
| C | -5.574758 | 1.703206 | 1.15743 |
| C | -7.936444 | 0.336927 | 1.57751 |
| C | -6.438805 | 2.128130 | 2.15518 |
| C | -7.627742 | 1.440112 | 2.36338 |
| F | -4.706254 | -1.911972 | 1.38903 |
| F | -4.373359 | -4.535597 | 1.03019 |
| F | -4.233430 | -5.564795 | -1.48012 |
| F | -4.387581 | -3.922509 | -3.63876 |
| F | -0.731343 | 1.180890 | -3.29345 |
| F | -1.653137 | 3.688211 | -3.84076 |
| F | -4.100520 | 4.455064 | -2.94506 |
| F | -4.657644 | -1.278386 | -3.29634 |
| F | -2.188413 | -0.499074 | -1.87765 |
| F | -5.598800 | 2.779435 | -1.52781 |
| F | -7.394725 | -1.129213 | -0.13123 |
| F | -9.079827 | -0.314292 | 1.76677 |
| F | -8.468588 | 1.839198 | 3.30516 |
| F | -6.144343 | 3.185261 | 2.90535 |



SUPPORTING INFORMATION

| | | | |
|---|-----------|-----------|----------|
| F | -4.455059 | 2.405594 | 0.99689 |
| B | 4.825728 | -0.069612 | 0.73054 |
| C | 4.684353 | 1.479276 | 0.93732 |
| C | 4.595048 | 2.056624 | 2.20520 |
| C | 4.637267 | 2.361902 | -0.14297 |
| C | 4.458561 | 3.421194 | 2.40346 |
| C | 4.473925 | 3.730407 | 0.01766 |
| C | 4.388844 | 4.261315 | 1.29767 |
| C | 3.969656 | -1.052222 | 1.60786 |
| C | 4.395391 | -2.346006 | 1.92970 |
| C | 2.716510 | -0.699538 | 2.11932 |
| C | 3.631911 | -3.232603 | 2.67701 |
| C | 1.922315 | -1.558243 | 2.86044 |
| C | 2.381790 | -2.838998 | 3.13790 |
| C | 5.835648 | -0.593865 | -0.34643 |
| C | 5.578511 | -1.708515 | -1.14951 |
| C | 7.045313 | 0.064223 | -0.59274 |
| C | 6.444593 | -2.136873 | -2.14402 |
| C | 7.943861 | -0.347268 | -1.56544 |
| C | 7.635381 | -1.451399 | -2.35009 |
| F | 2.187590 | 0.506494 | 1.86995 |
| F | 0.722214 | -1.167092 | 3.28478 |
| F | 1.636408 | -3.675473 | 3.83985 |
| F | 4.084994 | -4.449679 | 2.95393 |
| F | 5.591872 | -2.780159 | 1.53835 |
| F | 7.399764 | 1.123150 | 0.13897 |
| F | 9.088915 | 0.301557 | -1.75275 |
| F | 4.713044 | 1.905477 | -1.39208 |
| F | 4.381834 | 4.530589 | -1.04100 |
| F | 4.238400 | 5.566703 | 1.46623 |
| F | 4.387200 | 3.930211 | 3.62963 |
| F | 4.655317 | 1.284719 | 3.29477 |
| F | 4.456792 | -2.408202 | -0.99110 |
| F | 6.150274 | -3.194752 | -2.89317 |
| F | 8.478143 | -1.853735 | -3.28875 |

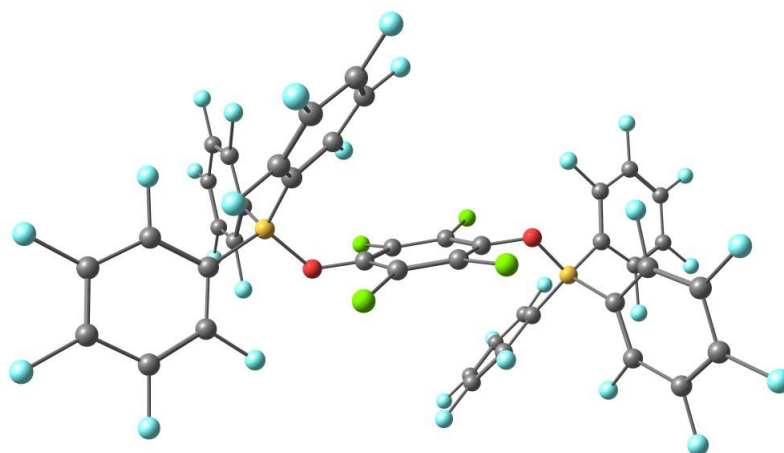
(C₆F₅)₃B-TCQ-B(C₆F₅)₃⁻

E: -6636.58907516 a.u

G: -6636.338304 a.u

Cartesian coordinates:

| | | | |
|----|-----------|-----------|----------|
| C | 0.635455 | 1.224114 | 0.17834 |
| C | 1.416378 | 0.077182 | 0.39233 |
| C | 0.738527 | -1.148861 | 0.26134 |
| C | -0.635166 | -1.224078 | -0.17784 |
| C | -1.416070 | -0.077157 | -0.39187 |
| C | -0.738245 | 1.148911 | -0.26073 |
| Cl | -1.344045 | -2.737881 | -0.47133 |
| Cl | 1.550608 | -2.569331 | 0.71212 |
| Cl | 1.344447 | 2.737894 | 0.47170 |
| Cl | -1.550402 | 2.569411 | -0.71125 |
| O | -2.660690 | -0.164206 | -0.76895 |
| O | 2.661059 | 0.164219 | 0.76922 |
| B | 3.894087 | -0.079665 | -0.11166 |
| C | 3.387946 | -0.828664 | -1.49001 |
| C | 2.565231 | -0.154720 | -2.39197 |
| C | 3.631338 | -2.156981 | -1.82786 |
| C | 2.014709 | -0.722824 | -3.53226 |
| C | 3.111569 | -2.768259 | -2.96600 |
| C | 2.297139 | -2.048703 | -3.82572 |
| C | 4.597082 | 1.390394 | -0.36838 |
| C | 4.791737 | 2.238905 | 0.72148 |
| C | 5.108057 | 1.864178 | -1.57228 |
| C | 5.399087 | 3.484739 | 0.62894 |
| C | 5.726169 | 3.103006 | -1.70842 |



SUPPORTING INFORMATION

| | | | |
|---|-----------|-----------|----------|
| C | 5.869489 | 3.922405 | -0.60042 |
| C | 4.984555 | -0.934964 | 0.76214 |
| C | 6.227548 | -1.202752 | 0.19250 |
| C | 4.844507 | -1.349858 | 2.08262 |
| C | 7.265186 | -1.839623 | 0.85379 |
| C | 5.863314 | -1.991882 | 2.78501 |
| C | 7.079546 | -2.237691 | 2.17081 |
| F | 4.392718 | 1.870300 | 1.94587 |
| F | 5.544083 | 4.258498 | 1.70930 |
| F | 6.459005 | 5.114344 | -0.71238 |
| F | 6.186499 | 3.507550 | -2.89614 |
| F | 1.229077 | -0.011105 | -4.34044 |
| F | 1.788230 | -2.623190 | -4.91350 |
| F | 3.380680 | -4.048602 | -3.22765 |
| F | 5.033707 | 1.134018 | -2.69444 |
| F | 2.245198 | 1.132831 | -2.17144 |
| F | 4.363340 | -2.957462 | -1.04220 |
| F | 6.456061 | -0.849637 | -1.08372 |
| F | 8.431257 | -2.074282 | 0.24404 |
| F | 8.061143 | -2.852993 | 2.83407 |
| F | 5.674485 | -2.372678 | 4.05240 |
| F | 3.711383 | -1.163246 | 2.76865 |
| B | -3.893914 | 0.079677 | 0.11168 |
| C | -4.597171 | -1.390344 | 0.36794 |
| C | -5.108874 | -1.864009 | 1.57157 |
| C | -4.791500 | -2.238803 | -0.72203 |
| C | -5.727383 | -3.102675 | 1.70741 |
| C | -5.399212 | -3.484482 | -0.62978 |
| C | -5.870340 | -3.922040 | 0.59933 |
| C | -3.387950 | 0.828294 | 1.49031 |
| C | -3.631222 | 2.156591 | 1.82838 |
| C | -2.565657 | 0.154000 | 2.39238 |
| C | -3.111843 | 2.767486 | 2.96688 |
| C | -2.015539 | 0.721727 | 3.53305 |
| C | -2.297893 | 2.047559 | 3.82675 |
| C | -4.984074 | 0.935273 | -0.76223 |
| C | -4.843734 | 1.350173 | -2.08268 |
| C | -6.227130 | 1.203245 | -0.19280 |
| C | -5.862303 | 1.992409 | -2.78521 |
| C | -7.264534 | 1.840338 | -0.85425 |
| C | -7.078601 | 2.238409 | -2.17122 |
| F | -2.245703 | -1.133525 | 2.17161 |
| F | -1.230334 | 0.009679 | 4.34139 |
| F | -1.789353 | 2.621669 | 4.91491 |
| F | -3.380836 | 4.047808 | 3.22876 |
| F | -4.362755 | 2.957398 | 1.04260 |
| F | -6.455968 | 0.850108 | 1.08336 |
| F | -8.430669 | 2.075173 | -0.24469 |
| F | -4.391834 | -1.870288 | -1.94623 |
| F | -5.543846 | -4.258203 | -1.71023 |
| F | -6.460202 | -5.113839 | 0.71098 |
| F | -6.188410 | -3.507095 | 2.89489 |
| F | -5.034922 | -1.133887 | 2.69379 |
| F | -3.710532 | 1.163362 | -2.76851 |
| F | -5.673192 | 2.373209 | -4.05256 |
| F | -8.059967 | 2.853911 | -2.83463 |

SUPPORTING INFORMATION

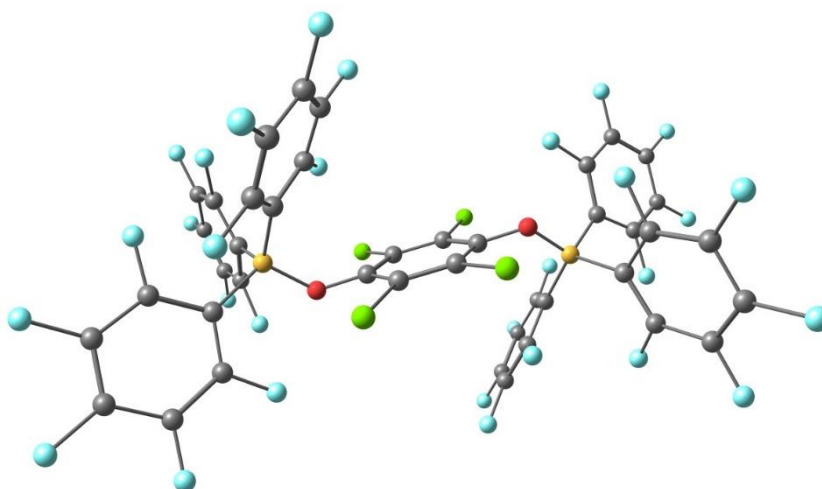
 $(C_6F_5)_3B-TCQ-B(C_6F_5)_3^{2-}$

E: -6636.81307005 a.u

G: -6636.559595 a.u

Cartesian coordinates:

| | | | |
|----|-----------|-----------|----------|
| C | -0.627566 | -1.233472 | 0.04371 |
| C | -1.393060 | -0.091684 | 0.33899 |
| C | -0.720602 | 1.143404 | 0.30533 |
| C | 0.627646 | 1.233429 | -0.04400 |
| C | 1.393141 | 0.091651 | -0.33924 |
| C | 0.720672 | -1.143440 | -0.30562 |
| Cl | 1.408284 | 2.780577 | -0.14583 |
| Cl | -1.601809 | 2.566123 | 0.76796 |
| Cl | -1.408229 | -2.780612 | 0.14537 |
| Cl | 1.601868 | -2.566127 | -0.76836 |
| O | 2.661692 | 0.203374 | -0.70554 |
| O | -2.661611 | -0.203470 | 0.70529 |
| B | -3.889389 | 0.084452 | -0.09248 |
| C | -3.481826 | 0.869270 | -1.48575 |
| C | -2.768809 | 0.199593 | -2.47888 |
| C | -3.712546 | 2.214355 | -1.75775 |
| C | -2.318765 | 0.791046 | -3.65063 |
| C | -3.284933 | 2.848545 | -2.91971 |
| C | -2.581831 | 2.133614 | -3.87374 |
| C | -4.674198 | -1.361791 | -0.35714 |
| C | -4.824670 | -2.241243 | 0.71562 |
| C | -5.284976 | -1.780203 | -1.53436 |
| C | -5.479000 | -3.463772 | 0.62545 |
| C | -5.950751 | -2.994977 | -1.66736 |
| C | -6.045015 | -3.847066 | -0.58052 |
| C | -4.960501 | 0.920169 | 0.85108 |
| C | -6.209976 | 1.253137 | 0.33280 |
| C | -4.786369 | 1.236792 | 2.19608 |
| C | -7.217886 | 1.870246 | 1.05702 |
| C | -5.776032 | 1.855746 | 2.96052 |
| C | -6.996560 | 2.175142 | 2.39191 |
| F | -4.350934 | -1.926278 | 1.92634 |
| F | -5.585929 | -4.269009 | 1.69184 |
| F | -6.686105 | -5.018734 | -0.68850 |
| F | -6.510823 | -3.345744 | -2.83470 |
| F | -1.651098 | 0.083266 | -4.56752 |
| F | -2.168108 | 2.728514 | -4.99767 |
| F | -3.543820 | 4.147837 | -3.12225 |
| F | -5.276629 | -1.016654 | -2.63822 |
| F | -2.493651 | -1.104832 | -2.34230 |
| F | -4.363855 | 3.006511 | -0.89215 |
| F | -6.488589 | 0.984069 | -0.95530 |
| F | -8.395938 | 2.172318 | 0.49022 |
| F | -7.953035 | 2.769291 | 3.11927 |
| F | -5.558698 | 2.141808 | 4.25197 |
| F | -3.657438 | 0.966127 | 2.85201 |
| B | 3.889400 | -0.084408 | 0.09243 |
| C | 4.674121 | 1.361854 | 0.35716 |
| C | 5.284799 | 1.780327 | 1.53440 |
| C | 4.824672 | 2.241284 | -0.71562 |
| C | 5.950470 | 2.995149 | 1.66746 |
| C | 5.478898 | 3.463868 | -0.62541 |
| C | 6.044779 | 3.847226 | 0.58060 |
| C | 3.481716 | -0.869237 | 1.48566 |
| C | 3.712360 | -2.214352 | 1.75760 |
| C | 2.768710 | -0.199576 | 2.47880 |
| C | 3.284758 | -2.848561 | 2.91954 |
| C | 2.318693 | -0.791045 | 3.65055 |
| C | 2.581695 | -2.133632 | 3.87361 |
| C | 4.960657 | -0.920120 | -0.85097 |
| C | 4.786715 | -1.236791 | -2.19598 |



SUPPORTING INFORMATION

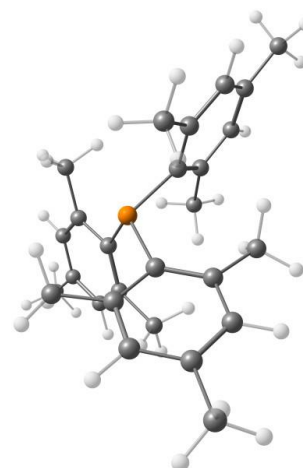
| | | | |
|---|----------|-----------|----------|
| C | 6.210034 | -1.253114 | -0.33249 |
| C | 5.776463 | -1.855842 | -2.96024 |
| C | 7.218021 | -1.870328 | -1.05651 |
| C | 6.996887 | -2.175275 | -2.39142 |
| F | 2.493531 | 1.104846 | 2.34224 |
| F | 1.651054 | -0.083271 | 4.56747 |
| F | 2.167957 | -2.728549 | 4.99753 |
| F | 3.543574 | -4.147877 | 3.12202 |
| F | 4.363592 | -3.006507 | 0.89193 |
| F | 6.488425 | -0.984053 | 0.95567 |
| F | 8.395952 | -2.172479 | -0.48951 |
| F | 4.351129 | 1.926258 | -1.92640 |
| F | 5.585881 | 4.269080 | -1.69181 |
| F | 6.685782 | 5.018936 | 0.68862 |
| F | 6.510424 | 3.345963 | 2.83483 |
| F | 5.276413 | 1.016787 | 2.63828 |
| F | 3.657888 | -0.966166 | -2.85211 |
| F | 5.559299 | -2.141992 | -4.25170 |
| F | 7.953432 | -2.769549 | -3.11859 |

PMes₃

E: -1390.06157057 a.u.
G: -1389.593190 a.u.

Cartesian coordinates:

| | | | |
|---|-----------|-----------|----------|
| C | -1.540148 | 0.799661 | -0.24153 |
| C | -1.649075 | 1.773216 | 0.77540 |
| C | -2.703500 | 0.433040 | -0.96229 |
| C | -2.892221 | 2.360932 | 1.02291 |
| C | -3.924436 | 1.033558 | -0.66224 |
| C | -4.040005 | 2.013418 | 0.31911 |
| H | -2.965171 | 3.107524 | 1.81141 |
| H | -4.810066 | 0.728411 | -1.21611 |
| C | 1.462501 | 0.934444 | -0.24130 |
| C | 2.360964 | 0.540379 | 0.77462 |
| C | 1.726294 | 2.125931 | -0.96047 |
| C | 3.492084 | 1.322073 | 1.02160 |
| C | 2.857513 | 2.882156 | -0.66037 |
| C | 3.764951 | 2.490535 | 0.31889 |
| H | 4.175710 | 1.010995 | 1.80923 |
| H | 3.035592 | 3.802322 | -1.21330 |
| C | 0.077429 | -1.733150 | -0.24193 |
| C | -0.712202 | -2.314385 | 0.77441 |
| C | 0.976863 | -2.557218 | -0.96190 |
| C | -0.600135 | -3.684870 | 1.02140 |
| C | 1.067189 | -3.914964 | -0.66169 |
| C | 0.275523 | -4.505159 | 0.31859 |
| H | -1.210506 | -4.121733 | 1.80942 |
| H | 1.774901 | -4.529109 | -1.21506 |
| P | -0.000029 | 0.000519 | -0.86021 |
| C | 0.789254 | 2.643088 | -2.02715 |
| H | 0.623162 | 1.895979 | -2.81091 |
| H | -0.195483 | 2.892327 | -1.61406 |
| H | 1.195299 | 3.547147 | -2.49024 |
| C | 2.159450 | -0.663060 | 1.66517 |
| H | 1.140362 | -0.713541 | 2.05780 |
| H | 2.340759 | -1.606590 | 1.14122 |
| H | 2.844377 | -0.615511 | 2.51702 |
| C | 5.007751 | 3.296847 | 0.59643 |
| H | 5.353394 | 3.157184 | 1.62553 |
| H | 5.825480 | 2.994840 | -0.06944 |
| H | 4.833822 | 4.365916 | 0.43730 |
| C | -0.506527 | 2.199661 | 1.66670 |
| H | 0.048166 | 1.342366 | 2.05738 |
| H | 0.218406 | 2.831327 | 1.14424 |



SUPPORTING INFORMATION

| | | | |
|---|-----------|-----------|----------|
| H | -0.891031 | 2.766440 | 2.51985 |
| C | -5.360281 | 2.685277 | 0.59743 |
| H | -5.508312 | 3.545238 | -0.06727 |
| H | -6.198606 | 1.999544 | 0.43747 |
| H | -5.412391 | 3.053006 | 1.62704 |
| C | -2.681680 | -0.636138 | -2.02979 |
| H | -1.949735 | -0.406686 | -2.81180 |
| H | -2.406619 | -1.613893 | -1.61642 |
| H | -3.666877 | -0.735315 | -2.49470 |
| C | -1.653270 | -1.538062 | 1.66540 |
| H | -1.186014 | -0.631972 | 2.06051 |
| H | -2.560296 | -1.220806 | 1.14169 |
| H | -1.956249 | -2.156037 | 2.51581 |
| C | 1.891992 | -2.003720 | -2.02922 |
| H | 1.326836 | -1.487648 | -2.81300 |
| H | 2.599219 | -1.274190 | -1.61683 |
| H | 2.472821 | -2.806889 | -2.49206 |
| C | 0.353614 | -5.984350 | 0.59743 |
| H | 0.070090 | -6.211912 | 1.62983 |
| H | -0.324249 | -6.541788 | -0.06062 |
| H | 1.364321 | -6.369584 | 0.42861 |

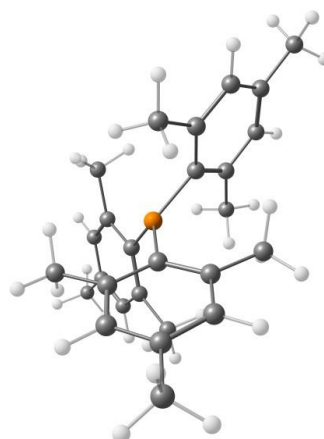
SUPPORTING INFORMATION

PMe₃⁺⁺

E: -1389.86930013 a.u.
G: -1389.404301 a.u.

Cartesian coordinates:

| | | | |
|---|-----------|-----------|----------|
| C | -0.351725 | 1.724314 | 0.12666 |
| C | -1.277616 | 2.167291 | -0.85038 |
| C | 0.331630 | 2.648448 | 0.95658 |
| C | -1.487291 | 3.536566 | -0.97339 |
| C | 0.081797 | 4.003744 | 0.78020 |
| C | -0.825793 | 4.469495 | -0.17281 |
| H | -2.183809 | 3.891250 | -1.72856 |
| H | 0.603283 | 4.720070 | 1.40953 |
| C | -1.317524 | -1.166896 | 0.12690 |
| C | -1.238237 | -2.189996 | -0.85039 |
| C | -2.459654 | -1.037235 | 0.95683 |
| C | -2.319144 | -3.056288 | -0.97343 |
| C | -3.508432 | -1.931209 | 0.78023 |
| C | -3.457919 | -2.949962 | -0.17290 |
| H | -2.278049 | -3.836652 | -1.72881 |
| H | -4.389609 | -1.837858 | 1.40946 |
| C | 1.669228 | -0.557707 | 0.12681 |
| C | 2.515233 | 0.022363 | -0.85083 |
| C | 2.128485 | -1.611322 | 0.95697 |
| C | 3.805995 | -0.480409 | -0.97411 |
| C | 3.427157 | -2.072222 | 0.78017 |
| C | 4.283830 | -1.519262 | -0.17336 |
| H | 4.461053 | -0.054532 | -1.72963 |
| H | 3.787331 | -2.881591 | 1.40972 |
| P | -0.000013 | -0.000115 | 0.38730 |
| C | -2.580984 | 0.038807 | 2.00881 |
| H | -1.698029 | 0.079307 | 2.65759 |
| H | -2.704331 | 1.030903 | 1.56012 |
| H | -3.448289 | -0.146069 | 2.64646 |
| C | -0.064546 | -2.365377 | -1.78289 |
| H | 0.243536 | -1.420710 | -2.24336 |
| H | 0.810508 | -2.773009 | -1.26630 |
| H | -0.325489 | -3.054571 | -2.58907 |
| C | -4.593036 | -3.925685 | -0.31691 |
| H | -4.665917 | -4.307210 | -1.33896 |
| H | -4.438721 | -4.784980 | 0.34647 |
| H | -5.549552 | -3.469405 | -0.04785 |
| C | -2.017489 | 1.238787 | -1.78218 |
| H | -1.355057 | 0.496839 | -2.24046 |
| H | -2.810576 | 0.688380 | -1.26565 |
| H | -2.481114 | 1.809210 | -2.59006 |
| C | -1.103358 | 5.940440 | -0.31618 |
| H | -1.921944 | 6.236847 | 0.35039 |
| H | -0.228712 | 6.540436 | -0.05059 |
| H | -1.401197 | 6.194258 | -1.33711 |
| C | 1.324452 | 2.214903 | 2.00800 |
| H | 0.918891 | 1.428651 | 2.65568 |
| H | 2.245411 | 1.826867 | 1.55846 |
| H | 1.597539 | 3.057719 | 2.64683 |
| C | 2.080391 | 1.127032 | -1.78270 |
| H | 1.105207 | 0.925235 | -2.23834 |
| H | 2.002752 | 2.089589 | -1.26678 |
| H | 2.804533 | 1.241763 | -2.59233 |
| C | 1.257887 | -2.254678 | 2.00938 |
| H | 0.781638 | -1.510945 | 2.65913 |
| H | 0.460242 | -2.857585 | 1.56097 |
| H | 1.852147 | -2.913597 | 2.64631 |
| C | 5.696600 | -2.013917 | -0.31711 |
| H | 6.064296 | -1.884404 | -1.33861 |
| H | 6.362931 | -1.451739 | 0.34789 |
| H | 5.779674 | -3.070879 | -0.04984 |



SUPPORTING INFORMATION

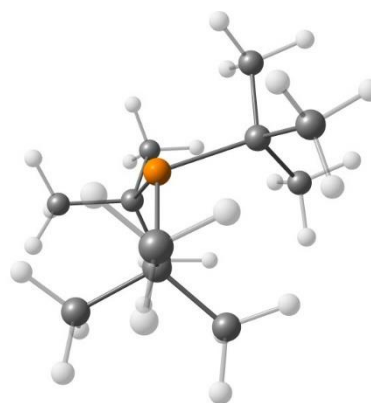
PtBu₃

E: -814.891306377 a.u

G: -814.5567012 a.u

Cartesian coordinates:

| | | | |
|---|-----------|-----------|----------|
| P | -0.000007 | -0.000091 | -0.71393 |
| C | 0.746102 | -1.625766 | -0.00571 |
| C | 2.271755 | -1.621507 | -0.22079 |
| C | 0.473226 | -1.951481 | 1.47073 |
| C | 0.222971 | -2.783467 | -0.88493 |
| H | 2.536089 | -1.370439 | -1.25362 |
| H | 2.795293 | -0.937821 | 0.45085 |
| H | 2.658516 | -2.628465 | -0.01771 |
| H | -0.587191 | -2.125231 | 1.66963 |
| H | 1.006075 | -2.872321 | 1.74527 |
| H | 0.816794 | -1.159722 | 2.14132 |
| H | 0.738118 | -3.710821 | -0.60082 |
| H | -0.846405 | -2.963418 | -0.77467 |
| H | 0.426554 | -2.595171 | -1.94429 |
| C | 1.034993 | 1.458941 | -0.00576 |
| C | 1.453384 | 1.386004 | 1.47079 |
| C | 2.299378 | 1.584396 | -0.88476 |
| C | 0.268530 | 2.778017 | -0.22131 |
| H | 0.595867 | 1.288322 | 2.14136 |
| H | 2.133807 | 0.554481 | 1.67043 |
| H | 1.984641 | 2.307901 | 1.74486 |
| H | 2.034769 | 1.666226 | -1.94420 |
| H | 2.844885 | 2.494277 | -0.60083 |
| H | 2.989893 | 0.748295 | -0.77405 |
| H | 0.947269 | 3.616540 | -0.01883 |
| H | -0.081422 | 2.880916 | -1.25407 |
| H | -0.585099 | 2.889963 | 0.45054 |
| C | -1.781075 | 0.166754 | -0.00579 |
| C | -2.540293 | -1.156614 | -0.22087 |
| C | -1.927072 | 0.566019 | 1.47062 |
| C | -2.521855 | 1.198778 | -0.88505 |
| H | -2.455015 | -1.511150 | -1.25368 |
| H | -2.210110 | -1.951901 | 0.45079 |
| H | -3.605730 | -0.988038 | -0.01784 |
| H | -1.547040 | 1.571075 | 1.66976 |
| H | -2.991090 | 0.565364 | 1.74469 |
| H | -1.413761 | -0.127597 | 2.14143 |
| H | -3.582690 | 1.216127 | -0.60146 |
| H | -2.143148 | 2.214834 | -0.77422 |
| H | -2.460021 | 0.928718 | -1.94448 |



SUPPORTING INFORMATION

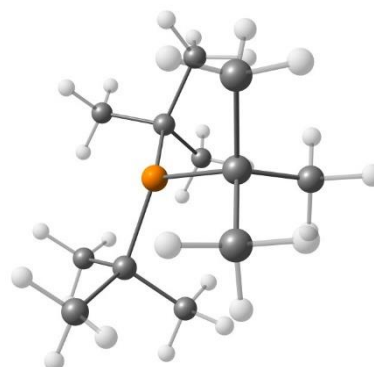
PtBu₃⁺⁺

E: -814.687971452 a.u

G: -814.3550137 a.u

Cartesian coordinates:

| | | | |
|---|-----------|-----------|----------|
| P | 0.000128 | -0.000122 | -0.41324 |
| C | -0.330240 | 1.817491 | -0.02122 |
| C | -1.811671 | 2.171381 | -0.23996 |
| C | 0.051350 | 2.106003 | 1.44527 |
| C | 0.489928 | 2.698125 | -0.98854 |
| H | -2.132950 | 1.994446 | -1.27001 |
| H | -2.486459 | 1.655103 | 0.44473 |
| H | -1.920952 | 3.243581 | -0.04602 |
| H | 1.113900 | 1.955577 | 1.64698 |
| H | -0.170449 | 3.160172 | 1.64757 |
| H | -0.527870 | 1.505694 | 2.15271 |
| H | 0.201776 | 3.740250 | -0.81387 |
| H | 1.565274 | 2.632753 | -0.83316 |
| H | 0.269257 | 2.468114 | -2.03567 |
| C | -1.409118 | -1.194742 | -0.02116 |
| C | -1.850046 | -1.008116 | 1.44517 |
| C | -2.581460 | -0.924474 | -0.98886 |
| C | -0.975404 | -2.654866 | -0.23957 |
| H | -1.040633 | -1.209294 | 2.15283 |
| H | -2.251325 | -0.012711 | 1.64637 |
| H | -2.652025 | -1.727334 | 1.64750 |
| H | -2.271565 | -1.000694 | -2.03587 |
| H | -3.340149 | -1.694867 | -0.81437 |
| H | -3.062218 | 0.039680 | -0.83366 |
| H | -1.849741 | -3.285198 | -0.04624 |
| H | -0.660889 | -2.844765 | -1.26942 |
| H | -0.191630 | -2.981655 | 0.44565 |
| C | 1.739472 | -0.622853 | -0.02124 |
| C | 2.786706 | 0.483107 | -0.23993 |
| C | 1.798524 | -1.097514 | 1.44531 |
| C | 2.091821 | -1.773412 | -0.98866 |
| H | 2.793138 | 0.850752 | -1.26966 |
| H | 2.677832 | 1.324998 | 0.44564 |
| H | 3.769986 | 0.041297 | -0.04725 |
| H | 1.137819 | -1.943166 | 1.64696 |
| H | 2.822624 | -1.431563 | 1.64790 |
| H | 1.567391 | -0.295909 | 2.15268 |
| H | 3.138012 | -2.045918 | -0.81319 |
| H | 1.496610 | -2.671594 | -0.83432 |
| H | 2.004142 | -1.466709 | -2.03572 |



SUPPORTING INFORMATION

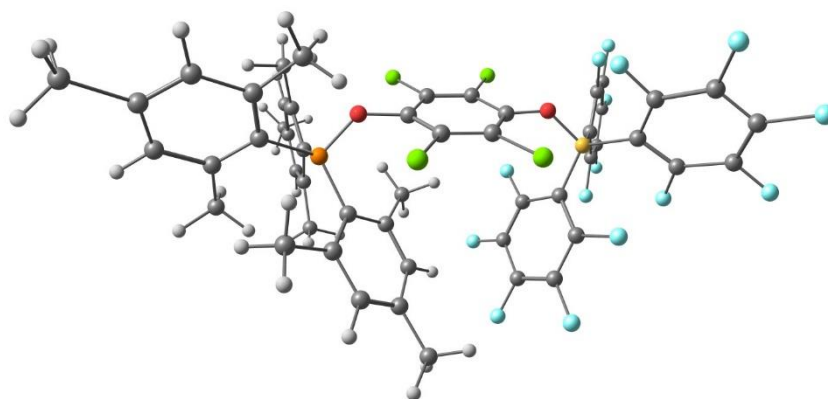
Mes₃P-TCQ-B(C₆F₅)₃

E: -5818.26697272 a.u.

G: -5817.627509 a.u.

Cartesian coordinates:

| | | | |
|----|-----------|-----------|----------|
| Cl | 1.776498 | -2.658131 | -1.04965 |
| P | 4.240791 | -0.102523 | -0.16793 |
| Cl | -1.317266 | -2.515611 | -0.95331 |
| Cl | 2.001408 | 2.714387 | -1.70168 |
| Cl | -1.144234 | 2.810602 | -1.71692 |
| F | -3.568254 | -2.653594 | 1.31451 |
| F | -1.745340 | 1.724177 | 1.29226 |
| F | -5.793186 | -0.932896 | 1.15589 |
| F | -4.371477 | 1.542927 | -2.50720 |
| O | 3.127059 | 0.040068 | -1.33616 |
| F | -3.511958 | -1.384523 | -2.97350 |
| F | -0.620008 | 1.241903 | 3.66392 |
| F | -0.942882 | -1.160104 | 4.87310 |
| F | -4.553472 | 1.493215 | 2.23354 |
| F | -2.386134 | -3.113964 | 3.63647 |
| F | -7.723860 | -2.550425 | 0.24816 |
| O | -2.387205 | 0.271873 | -1.25738 |
| F | -5.734545 | 3.825915 | -2.51812 |
| F | -5.429102 | -2.979200 | -3.84381 |
| F | -5.927965 | 3.751196 | 2.18738 |
| F | -6.538315 | 4.965618 | -0.17563 |
| F | -7.562485 | -3.594464 | -2.26860 |
| C | 3.480176 | -1.025460 | 1.18646 |
| C | 5.643236 | -0.888597 | -1.02850 |
| C | 5.607564 | 3.714639 | -0.56923 |
| H | 5.878676 | 4.346198 | -1.41117 |
| C | 5.661836 | 4.243974 | 0.71645 |
| C | 5.581661 | -1.386078 | -2.35669 |
| C | 6.879141 | -0.897034 | -0.33431 |
| C | 5.223978 | 2.402406 | -0.82381 |
| C | 4.975702 | 2.064396 | 1.59111 |
| C | 4.840450 | 1.570802 | 0.26858 |
| C | 1.741104 | 0.056123 | -1.27413 |
| C | -5.666326 | -1.424766 | -0.08852 |
| C | 0.991942 | -1.112758 | -1.12707 |
| C | 3.847205 | -2.364937 | 1.49311 |
| C | 1.074581 | 1.269329 | -1.47614 |
| C | -4.543449 | -1.090273 | -0.84145 |
| C | -0.404098 | -1.059338 | -1.08761 |
| C | 6.765586 | -1.846879 | -2.93705 |
| H | 6.720244 | -2.228323 | -3.95355 |
| C | 8.019077 | -1.373138 | -0.97392 |
| H | 8.957351 | -1.382932 | -0.42474 |
| C | 2.423333 | -0.402858 | 1.90450 |
| C | 5.372666 | 3.390964 | 1.77112 |
| H | 5.461265 | 3.761622 | 2.78973 |
| C | -1.098835 | 0.164858 | -1.22993 |
| C | 5.307376 | 1.963382 | -2.26898 |
| H | 4.432133 | 1.407705 | -2.59992 |
| H | 5.394863 | 2.840822 | -2.91357 |
| H | 6.193484 | 1.340476 | -2.43136 |
| C | -2.885741 | -1.635024 | 1.84551 |
| C | -4.333630 | 1.417159 | -0.13770 |
| C | -0.313897 | 1.324763 | -1.45795 |
| C | -2.774398 | -0.411145 | 1.19073 |
| C | 1.845802 | 0.971018 | 1.64522 |
| H | 2.419775 | 1.599976 | 0.96643 |
| H | 0.837550 | 0.872215 | 1.23231 |
| H | 1.738189 | 1.513425 | 2.58740 |
| C | 7.991130 | -1.841581 | -2.28225 |
| C | 3.187764 | -3.005421 | 2.53838 |



SUPPORTING INFORMATION

| | | | |
|---|-----------|-----------|----------|
| H | 3.461240 | -4.031583 | 2.76788 |
| C | -1.382463 | 0.304684 | 3.07966 |
| C | 4.358428 | -1.468465 | -3.24213 |
| H | 3.526627 | -1.980659 | -2.76119 |
| H | 4.001344 | -0.480781 | -3.54374 |
| H | 4.609319 | -2.020228 | -4.15090 |
| C | -1.975246 | 0.522819 | 1.84728 |
| C | -4.700863 | 2.063567 | -1.31837 |
| C | -4.795676 | 2.025752 | 1.02450 |
| C | 4.791233 | 1.310993 | 2.89423 |
| H | 4.741291 | 0.231068 | 2.80604 |
| H | 5.630129 | 1.551159 | 3.55462 |
| H | 3.878974 | 1.638827 | 3.40167 |
| C | -4.513735 | -1.634602 | -2.12173 |
| C | 7.059048 | -0.451621 | 1.09881 |
| H | 6.213448 | -0.716003 | 1.73757 |
| H | 7.940148 | -0.937191 | 1.52612 |
| H | 7.207382 | 0.630148 | 1.16869 |
| C | 4.855632 | -3.207391 | 0.74366 |
| H | 4.687480 | -3.195563 | -0.33509 |
| H | 5.888787 | -2.896404 | 0.91775 |
| H | 4.769933 | -4.244391 | 1.07582 |
| C | -6.680461 | -2.258107 | -0.53261 |
| C | 1.820307 | -1.100280 | 2.94603 |
| H | 1.045987 | -0.599775 | 3.51614 |
| C | -1.544587 | -0.922148 | 3.70129 |
| C | 6.025334 | 5.685021 | 0.94852 |
| H | 6.770087 | 6.030053 | 0.22505 |
| H | 5.139107 | 6.320667 | 0.83721 |
| H | 6.421817 | 5.842246 | 1.95553 |
| C | -2.281709 | -1.907363 | 3.07099 |
| C | 2.177096 | -2.401009 | 3.28019 |
| C | -5.512510 | -2.475358 | -2.60878 |
| C | 9.243540 | -2.315054 | -2.96909 |
| H | 9.022418 | -3.077404 | -3.72148 |
| H | 9.737463 | -1.479911 | -3.47969 |
| H | 9.957745 | -2.733096 | -2.25376 |
| C | -5.425199 | 3.248239 | -1.35390 |
| C | -5.526564 | 3.209159 | 1.03382 |
| C | -6.601430 | -2.789803 | -1.81273 |
| C | -5.840533 | 3.829138 | -0.16462 |
| B | -3.485699 | 0.003646 | -0.23757 |
| C | 1.462232 | -3.137149 | 4.37902 |
| H | 1.950023 | -4.088567 | 4.60676 |
| H | 1.422355 | -2.536104 | 5.29203 |
| H | 0.426241 | -3.344114 | 4.09035 |

SUPPORTING INFORMATION

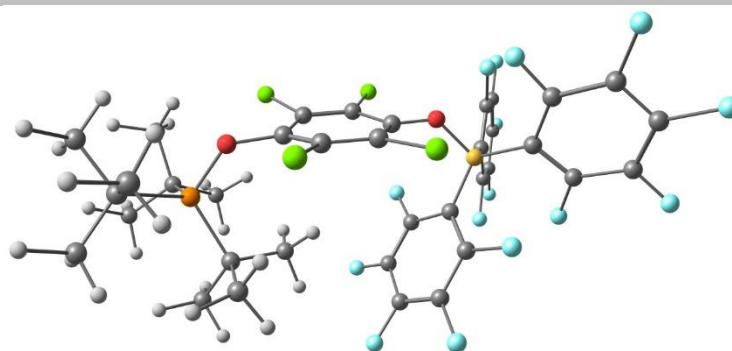
tBu₃P-TCQ-B(C₆F₅)₃

E: -5243.09778967 a.u.

G: -5242.601066 a.u.

Cartesian coordinates:

| | | | |
|----|-----------|-----------|----------|
| Cl | 2.661570 | -2.714316 | -1.46791 |
| P | 5.168964 | 0.001847 | -0.17936 |
| Cl | -0.410683 | -2.569697 | -1.15224 |
| Cl | 2.836514 | 2.635618 | -2.10372 |
| Cl | -0.254692 | 2.746988 | -1.78938 |
| F | -2.158426 | -2.675897 | 1.48657 |
| F | -0.667144 | 1.820938 | 1.26948 |
| F | -4.463965 | -1.045362 | 1.69840 |
| F | -3.596657 | 1.480430 | -2.22833 |
| O | 4.062563 | -0.054145 | -1.37988 |
| F | -2.886316 | -1.387209 | -2.75597 |
| F | 0.927834 | 1.374805 | 3.34529 |
| F | 1.092066 | -1.103510 | 4.44821 |
| F | -3.269816 | 1.457892 | 2.50272 |
| F | -0.502756 | -3.108972 | 3.49668 |
| F | -6.457481 | -2.732571 | 1.10555 |
| O | -1.476224 | 0.222103 | -1.20227 |
| F | -5.019055 | 3.725910 | -2.10292 |
| F | -4.861645 | -3.050227 | -3.31553 |
| F | -4.712248 | 3.675274 | 2.59710 |
| F | -5.604556 | 4.855595 | 0.30797 |
| F | -6.678039 | -3.756604 | -1.41483 |
| C | 2.662171 | 0.006298 | -1.39406 |
| C | -4.524972 | -1.530650 | 0.44688 |
| C | 1.898321 | -1.165597 | -1.32616 |
| C | 1.980939 | 1.212834 | -1.60976 |
| C | -3.554540 | -1.152555 | -0.47760 |
| C | 0.506352 | -1.114862 | -1.23262 |
| C | -0.189826 | 0.117037 | -1.26749 |
| C | -1.438632 | -1.628058 | 1.89818 |
| C | -3.308089 | 1.372501 | 0.12362 |
| C | 0.590067 | 1.269624 | -1.52947 |
| C | -1.533019 | -0.388407 | 1.27241 |
| C | 0.143719 | 0.388246 | 2.88689 |
| C | -0.697497 | 0.592079 | 1.80635 |
| C | -3.814793 | 2.000343 | -1.01390 |
| C | -3.660576 | 1.974907 | 1.32695 |
| C | -3.720952 | -1.683971 | -1.75294 |
| C | -5.568602 | -2.398358 | 0.16673 |
| C | 0.219580 | -0.871425 | 3.45989 |
| C | -0.577954 | -1.887635 | 2.96384 |
| C | -4.755758 | -2.558671 | -2.07754 |
| C | -4.572716 | 3.163999 | -0.97621 |
| C | -4.420567 | 3.136549 | 1.40978 |
| C | -5.684302 | -2.919362 | -1.11505 |
| C | -4.877151 | 3.739570 | 0.24866 |
| B | -2.452058 | -0.024693 | -0.04498 |
| C | 5.798113 | 1.787369 | -0.08454 |
| C | 5.996671 | 2.351397 | -1.51861 |
| C | 4.790978 | 2.672117 | 0.68305 |
| C | 7.156410 | 1.900964 | 0.64140 |
| H | 7.028932 | 2.234837 | -1.85018 |
| H | 5.341565 | 1.904880 | -2.26434 |
| H | 5.779402 | 3.423023 | -1.50130 |
| H | 4.741138 | 2.430354 | 1.74540 |
| H | 5.137437 | 3.707788 | 0.60643 |
| H | 3.785022 | 2.642527 | 0.26688 |
| H | 7.409264 | 2.966555 | 0.67118 |
| H | 7.141162 | 1.543832 | 1.67169 |
| H | 7.965185 | 1.400618 | 0.10598 |
| C | 6.520005 | -1.128634 | -0.84997 |



SUPPORTING INFORMATION

| | | | |
|---|----------|-----------|----------|
| C | 7.560039 | -1.466655 | 0.23720 |
| C | 5.924330 | -2.442932 | -1.38394 |
| C | 7.235377 | -0.461391 | -2.04167 |
| H | 8.007639 | -0.590241 | 0.70846 |
| H | 7.152443 | -2.111159 | 1.01829 |
| H | 8.370329 | -2.022522 | -0.24679 |
| H | 5.262293 | -2.266679 | -2.23208 |
| H | 6.760989 | -3.061010 | -1.72776 |
| H | 5.384529 | -3.013225 | -0.62988 |
| H | 7.872437 | -1.220175 | -2.50790 |
| H | 6.535054 | -0.108748 | -2.80296 |
| H | 7.885232 | 0.361471 | -1.74254 |
| C | 4.472175 | -0.582184 | 1.47689 |
| C | 3.075929 | 0.021167 | 1.73557 |
| C | 4.319986 | -2.113008 | 1.55569 |
| C | 5.416745 | -0.159586 | 2.62451 |
| H | 2.999029 | 1.094154 | 1.56868 |
| H | 2.301301 | -0.472357 | 1.14707 |
| H | 2.846318 | -0.153656 | 2.79029 |
| H | 5.276979 | -2.638448 | 1.57759 |
| H | 3.807032 | -2.331694 | 2.49853 |
| H | 3.703714 | -2.519362 | 0.75580 |
| H | 5.035071 | -0.629612 | 3.53667 |
| H | 6.444849 | -0.503863 | 2.49079 |
| H | 5.420782 | 0.915933 | 2.80260 |

MECP: $t\text{Bu}_3\text{P--TCQ-B}(\text{C}_6\text{F}_5)_3$

Singlet:

E: -5243.02778325 a.u

G: -5242.546850 a.u

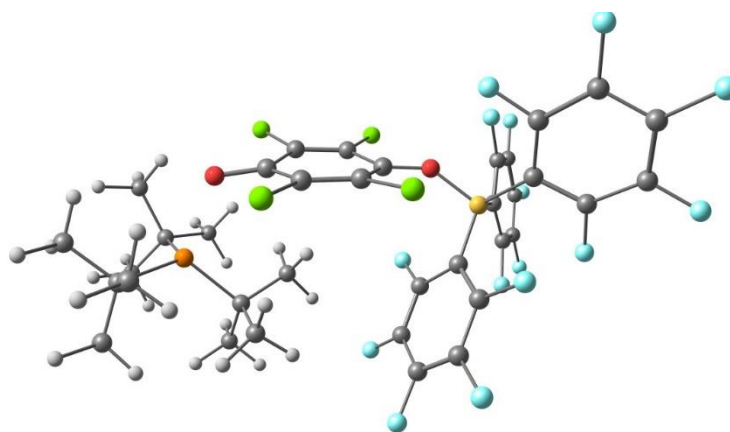
Triplet:

E: -5243.02834157 a.u

G: -5242.546371 a.u

Cartesian coordinates:

| | | | |
|----|-----------|-----------|----------|
| Cl | 2.500934 | -2.801061 | -1.80881 |
| P | 5.302211 | 0.101858 | -0.01892 |
| Cl | -0.574632 | -2.503451 | -1.32823 |
| Cl | 2.911443 | 2.508299 | -2.58128 |
| Cl | -0.136591 | 2.851796 | -1.79251 |
| F | -2.615255 | -2.898159 | 1.05303 |
| F | -0.322492 | 1.217429 | 1.59198 |
| F | -4.661575 | -1.014727 | 1.43974 |
| F | -3.440296 | 1.965084 | -1.79011 |
| O | 3.899966 | -0.209454 | -2.00018 |
| F | -2.771968 | -0.846794 | -2.90066 |
| F | 1.039796 | 0.149811 | 3.64603 |
| F | 0.675426 | -2.441253 | 4.32646 |
| F | -3.008119 | 1.038714 | 2.84356 |
| F | -1.196194 | -3.937726 | 3.01374 |
| F | -6.807113 | -2.267050 | 0.44303 |
| O | -1.383508 | 0.428012 | -1.04065 |
| F | -4.590472 | 4.287259 | -1.20092 |
| F | -4.898976 | -2.094349 | -3.86153 |
| F | -4.178495 | 3.343385 | 3.39537 |
| F | -4.984842 | 5.013178 | 1.39827 |
| F | -6.949876 | -2.823946 | -2.22484 |
| C | 2.640092 | -0.103408 | -1.92751 |
| C | -4.683636 | -1.269917 | 0.12023 |
| C | 1.777968 | -1.243290 | -1.70482 |
| C | 1.965187 | 1.168959 | -2.06085 |
| C | -3.598768 | -0.889980 | -0.66540 |
| C | 0.430579 | -1.110344 | -1.45364 |
| C | -0.171368 | 0.188769 | -1.36344 |



SUPPORTING INFORMATION

| | | | |
|---|-----------|-----------|----------|
| C | -1.738646 | -2.080969 | 1.65018 |
| C | -3.101405 | 1.397501 | 0.49041 |
| C | 0.636636 | 1.313535 | -1.75628 |
| C | -1.569300 | -0.764895 | 1.22959 |
| C | 0.141916 | -0.587114 | 2.97699 |
| C | -0.588500 | -0.058275 | 1.92417 |
| C | -3.563406 | 2.274704 | -0.49092 |
| C | -3.353718 | 1.804106 | 1.79643 |
| C | -3.725133 | -1.180866 | -2.01869 |
| C | -5.805696 | -1.918396 | -0.36897 |
| C | -0.052146 | -1.908847 | 3.34628 |
| C | -1.001269 | -2.661483 | 2.67737 |
| C | -4.834567 | -1.831118 | -2.55308 |
| C | -4.182139 | 3.485875 | -0.21296 |
| C | -3.974985 | 3.005942 | 2.11865 |
| C | -5.881526 | -2.201944 | -1.72584 |
| C | -4.388896 | 3.856999 | 1.10720 |
| B | -2.403018 | -0.021903 | 0.02937 |
| C | 6.183050 | 1.770133 | -0.22018 |
| C | 6.528637 | 1.963339 | -1.71270 |
| C | 5.278085 | 2.946424 | 0.18776 |
| C | 7.463420 | 1.835484 | 0.63683 |
| H | 7.343743 | 1.323604 | -2.04827 |
| H | 5.660062 | 1.788139 | -2.35157 |
| H | 6.851138 | 3.001205 | -1.85061 |
| H | 4.991219 | 2.933696 | 1.23996 |
| H | 5.850444 | 3.865350 | 0.02208 |
| H | 4.381082 | 3.010375 | -0.42972 |
| H | 7.911645 | 2.824780 | 0.48732 |
| H | 7.258557 | 1.723607 | 1.70481 |
| H | 8.211941 | 1.097937 | 0.34485 |
| C | 6.486979 | -1.364130 | -0.16505 |
| C | 7.231806 | -1.608549 | 1.16236 |
| C | 5.705301 | -2.629011 | -0.56131 |
| C | 7.505987 | -1.120950 | -1.29280 |
| H | 7.783582 | -0.733013 | 1.51156 |
| H | 6.562745 | -1.940275 | 1.95937 |
| H | 7.958733 | -2.411800 | 0.99375 |
| H | 5.229568 | -2.501375 | -1.53448 |
| H | 6.423947 | -3.453238 | -0.63231 |
| H | 4.945827 | -2.919278 | 0.16321 |
| H | 8.074834 | -2.047560 | -1.42487 |
| H | 7.015359 | -0.897277 | -2.24418 |
| H | 8.226133 | -0.334541 | -1.06368 |
| C | 4.173803 | 0.033980 | 1.49290 |
| C | 2.919996 | 0.892293 | 1.21699 |
| C | 3.673172 | -1.394901 | 1.76644 |
| C | 4.907575 | 0.540452 | 2.75182 |
| H | 3.119174 | 1.857154 | 0.75477 |
| H | 2.211829 | 0.349511 | 0.58733 |
| H | 2.420714 | 1.081796 | 2.16856 |
| H | 4.462492 | -2.068848 | 2.10515 |
| H | 2.935562 | -1.329109 | 2.57334 |
| H | 3.173896 | -1.834153 | 0.89840 |
| H | 4.226950 | 0.418380 | 3.60259 |
| H | 5.812753 | -0.032992 | 2.96624 |
| H | 5.170274 | 1.597827 | 2.69714 |

SUPPORTING INFORMATION

MECP: Mes₃P-TCQ-B(C₆F₅)₃

Singlet

E: -5818.20180583 a.u.

G: -5817.582222 a.u.

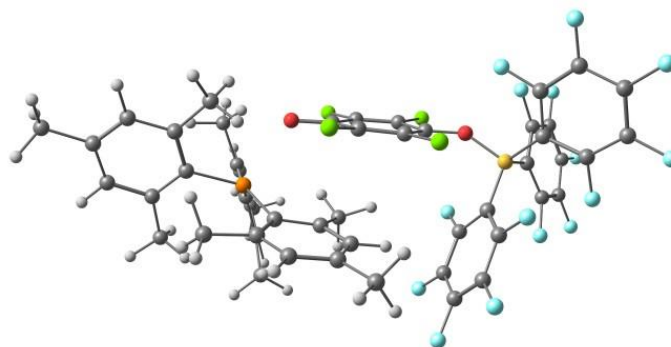
Triplet:

E: -5818.20238061 a.u.

G: -5817.581759 a.u.

Cartesian coordinates:

| | | | |
|----|-----------|-----------|----------|
| Cl | 1.660019 | -2.733433 | -1.42836 |
| P | 4.598125 | -0.085219 | -0.02469 |
| Cl | -1.386817 | -2.504170 | -0.80213 |
| Cl | 1.953418 | 2.594136 | -2.24624 |
| Cl | -1.182136 | 2.806940 | -1.82388 |
| F | -3.641834 | -2.623897 | 1.47962 |
| F | -1.736948 | 1.713776 | 1.36026 |
| F | -5.840642 | -0.983424 | 1.18511 |
| F | -4.396894 | 1.517536 | -2.40083 |
| O | 2.956416 | -0.127557 | -1.89770 |
| F | -3.427507 | -1.316492 | -2.87802 |
| F | -0.592140 | 1.259445 | 3.72108 |
| F | -0.969760 | -1.130954 | 4.99447 |
| F | -4.633784 | 1.456056 | 2.33889 |
| F | -2.506194 | -3.040440 | 3.82753 |
| F | -7.734599 | -2.578064 | 0.17742 |
| O | -2.385409 | 0.359509 | -1.09975 |
| F | -5.828236 | 3.755473 | -2.42686 |
| F | -5.318606 | -2.885541 | -3.85779 |
| F | -6.076677 | 3.670306 | 2.27703 |
| F | -6.696084 | 4.867414 | -0.09125 |
| F | -7.499189 | -3.548935 | -2.36299 |
| C | 3.587658 | -1.095100 | 1.05467 |
| C | 6.189552 | -0.758346 | -0.59169 |
| C | 5.303999 | 3.853050 | -0.55211 |
| H | 5.561225 | 4.481169 | -1.40120 |
| C | 5.117277 | 4.443634 | 0.69692 |
| C | 6.257654 | -1.565008 | -1.74855 |
| C | 7.379171 | -0.405077 | 0.09529 |
| C | 5.164839 | 2.484809 | -0.75339 |
| C | 4.686228 | 2.233003 | 1.64376 |
| C | 4.820089 | 1.663844 | 0.35419 |
| C | 1.706311 | -0.045950 | -1.73096 |
| C | -5.666537 | -1.450987 | -0.06298 |
| C | 0.889399 | -1.196872 | -1.42339 |
| C | 3.966566 | -2.420478 | 1.41839 |
| C | 1.002994 | 1.211544 | -1.86292 |
| C | -4.521065 | -1.097692 | -0.77119 |
| C | -0.463999 | -1.093811 | -1.17234 |
| C | 7.508392 | -1.962560 | -2.21762 |
| H | 7.552642 | -2.589314 | -3.10486 |
| C | 8.599005 | -0.830641 | -0.42339 |
| H | 9.508665 | -0.572686 | 0.11333 |
| C | 2.273151 | -0.634267 | 1.36349 |
| C | 4.826542 | 3.613255 | 1.77508 |
| H | 4.722107 | 4.047674 | 2.76666 |
| C | -1.132853 | 0.165104 | -1.26873 |
| C | 5.426779 | 1.944248 | -2.13937 |
| H | 4.674213 | 1.214182 | -2.44618 |
| H | 5.413269 | 2.759644 | -2.86680 |
| H | 6.412591 | 1.468091 | -2.19066 |
| C | -2.939257 | -1.606703 | 1.99307 |
| C | -4.384053 | 1.390775 | -0.02937 |
| C | -0.348051 | 1.306637 | -1.66319 |
| C | -2.798098 | -0.403162 | 1.30935 |
| C | 1.788262 | 0.788626 | 1.22169 |



SUPPORTING INFORMATION

| | | | |
|---|-----------|-----------|----------|
| H | 2.311399 | 1.379417 | 0.47186 |
| H | 0.722310 | 0.803845 | 0.98378 |
| H | 1.901899 | 1.307771 | 2.17903 |
| C | 8.691444 | -1.593949 | -1.58610 |
| C | 3.016081 | -3.243398 | 2.01396 |
| H | 3.312504 | -4.247027 | 2.30588 |
| C | -1.377113 | 0.324633 | 3.17849 |
| C | 5.047698 | -2.051274 | -2.49822 |
| H | 4.262594 | -2.399770 | -1.82560 |
| H | 4.607021 | -1.259482 | -3.10865 |
| H | 5.324383 | -2.879044 | -3.15601 |
| C | -1.980318 | 0.528520 | 1.94624 |
| C | -4.755429 | 2.027889 | -1.21354 |
| C | -4.875570 | 1.983937 | 1.12817 |
| C | 4.507329 | 1.468808 | 2.93548 |
| H | 4.270833 | 0.414040 | 2.81005 |
| H | 5.433734 | 1.533992 | 3.51753 |
| H | 3.718835 | 1.923262 | 3.54223 |
| C | -4.454770 | -1.602188 | -2.06506 |
| C | 7.413434 | 0.348656 | 1.40276 |
| H | 6.609878 | 0.041041 | 2.07796 |
| H | 8.358557 | 0.154437 | 1.91569 |
| H | 7.329769 | 1.429493 | 1.25431 |
| C | 5.350303 | -3.003228 | 1.24989 |
| H | 5.575510 | -3.253542 | 0.20939 |
| H | 6.131609 | -2.326205 | 1.60230 |
| H | 5.426558 | -3.924879 | 1.83114 |
| C | -6.666236 | -2.269339 | -0.56269 |
| C | 1.367309 | -1.526266 | 1.92264 |
| H | 0.354432 | -1.182568 | 2.10209 |
| C | -1.570163 | -0.884524 | 3.83045 |
| C | 5.220102 | 5.934605 | 0.86933 |
| H | 5.945213 | 6.366120 | 0.17327 |
| H | 4.250096 | 6.405615 | 0.67028 |
| H | 5.514982 | 6.200580 | 1.88849 |
| C | -2.351097 | -1.856900 | 3.22883 |
| C | 1.703205 | -2.835718 | 2.24359 |
| C | -5.437723 | -2.424998 | -2.60878 |
| C | 10.031023 | -2.013392 | -2.12932 |
| H | 9.930259 | -2.819137 | -2.86168 |
| H | 10.523611 | -1.168665 | -2.62498 |
| H | 10.694380 | -2.354207 | -1.32805 |
| C | -5.514664 | 3.189001 | -1.25808 |
| C | -5.642584 | 3.143986 | 1.12794 |
| C | -6.550043 | -2.762223 | -1.85519 |
| C | -5.961740 | 3.754937 | -0.07339 |
| B | -3.503270 | -0.000147 | -0.11547 |
| C | 0.675680 | -3.757348 | 2.83771 |
| H | 1.110740 | -4.719709 | 3.11920 |
| H | 0.220038 | -3.310901 | 3.72753 |
| H | -0.130469 | -3.941812 | 2.11845 |

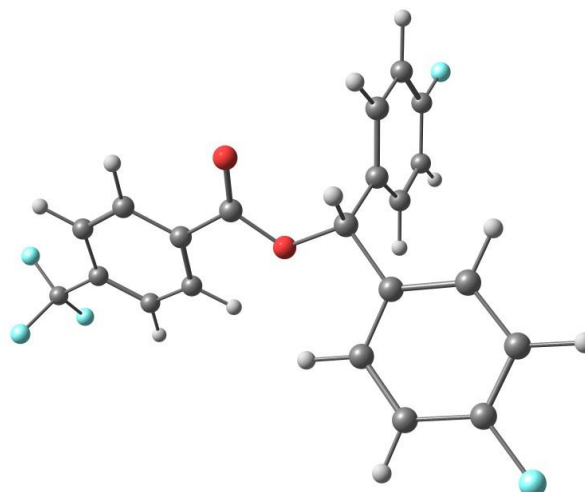
SUPPORTING INFORMATION

9

E: -1457.69732749 a.u

Cartesian coordinates:

| | | | |
|---|-----------|-----------|----------|
| C | -4.452268 | -0.118826 | -0.12203 |
| C | -3.401028 | -0.638283 | -0.87403 |
| C | -2.092791 | -0.474967 | -0.43646 |
| C | -1.837774 | 0.207383 | 0.75421 |
| C | -2.894196 | 0.729276 | 1.50194 |
| C | -4.201374 | 0.565558 | 1.06615 |
| H | -3.603995 | -1.161387 | -1.80190 |
| H | -1.268013 | -0.867505 | -1.02002 |
| H | -2.673780 | 1.262388 | 2.42034 |
| H | -5.024583 | 0.973787 | 1.64216 |
| C | -0.452360 | 0.412619 | 1.26891 |
| O | 0.462002 | -0.198908 | 0.50005 |
| O | -0.187226 | 1.045780 | 2.26548 |
| C | -5.874877 | -0.344254 | -0.56378 |
| F | -6.385483 | -1.456378 | -0.00741 |
| F | -5.968313 | -0.489259 | -1.89511 |
| F | -6.672734 | 0.675729 | -0.20959 |
| C | 1.845731 | -0.028848 | 0.86979 |
| H | 1.881463 | 0.052221 | 1.96057 |
| C | 2.592085 | -1.273764 | 0.42874 |
| C | 3.989322 | -1.257442 | 0.39410 |
| C | 1.923537 | -2.455147 | 0.10893 |
| C | 4.709434 | -2.393512 | 0.04660 |
| H | 4.523634 | -0.342690 | 0.63382 |
| C | 2.630391 | -3.600439 | -0.24744 |
| H | 0.840338 | -2.484216 | 0.13651 |
| C | 4.014435 | -3.551262 | -0.27220 |
| H | 5.793288 | -2.390179 | 0.01510 |
| H | 2.120581 | -4.522839 | -0.50284 |
| C | 2.364116 | 1.257578 | 0.26431 |
| C | 2.570611 | 2.379463 | 1.06579 |
| C | 2.595877 | 1.348684 | -1.11096 |
| C | 3.016257 | 3.576890 | 0.51329 |
| H | 2.364702 | 2.322296 | 2.13025 |
| C | 3.033706 | 2.536912 | -1.68016 |
| H | 2.439135 | 0.477140 | -1.74005 |
| C | 3.239530 | 3.633677 | -0.85310 |
| H | 3.183839 | 4.457457 | 1.12328 |
| H | 3.219905 | 2.624779 | -2.74478 |
| F | 4.702230 | -4.650454 | -0.61571 |
| F | 3.668200 | 4.782140 | -1.39586 |



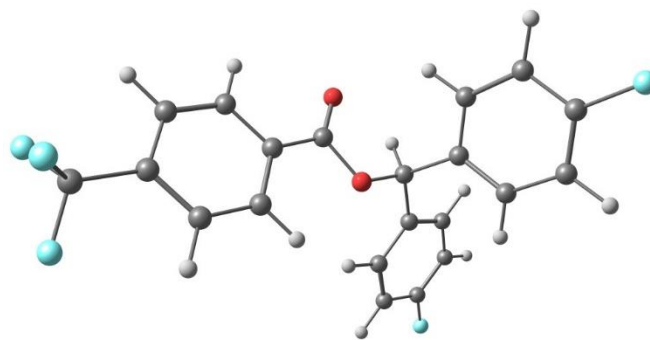
SUPPORTING INFORMATION

9⁻

E: -1457.77944049 a.u

Cartesian coordinates:

| | | | |
|---|-----------|-----------|----------|
| C | -4.522855 | 0.134889 | -0.08813 |
| C | -3.442752 | 0.500776 | -0.92812 |
| C | -2.141023 | 0.344685 | -0.52446 |
| C | -1.823921 | -0.205975 | 0.76344 |
| C | -2.929100 | -0.589476 | 1.59464 |
| C | -4.224492 | -0.426934 | 1.18034 |
| H | -3.652563 | 0.920823 | -1.90877 |
| H | -1.332271 | 0.629831 | -1.18959 |
| H | -2.708731 | -1.008164 | 2.57181 |
| H | -5.040455 | -0.722076 | 1.83546 |
| C | -0.504365 | -0.373207 | 1.24712 |
| O | 0.466778 | 0.066555 | 0.32118 |
| O | -0.142616 | -0.839947 | 2.34021 |
| C | -5.912906 | 0.226940 | -0.56302 |
| F | -6.369633 | -0.893141 | -1.20593 |
| F | -6.104092 | 1.232594 | -1.45552 |
| F | -6.804969 | 0.428055 | 0.44126 |
| C | 1.803505 | 0.004180 | 0.75725 |
| H | 1.791143 | -0.089128 | 1.84988 |
| C | 2.464296 | -1.253021 | 0.19988 |
| C | 3.264242 | -1.250696 | -0.94234 |
| C | 2.196778 | -2.472070 | 0.83237 |
| C | 3.807956 | -2.432760 | -1.44107 |
| H | 3.472602 | -0.314570 | -1.45186 |
| C | 2.730897 | -3.660959 | 0.34870 |
| H | 1.537299 | -2.469209 | 1.69658 |
| C | 3.533297 | -3.619119 | -0.78185 |
| H | 4.432836 | -2.441762 | -2.32806 |
| H | 2.528828 | -4.611914 | 0.83043 |
| C | 2.514845 | 1.292364 | 0.38571 |
| C | 3.856008 | 1.476513 | 0.73550 |
| C | 1.848937 | 2.322314 | -0.27686 |
| C | 4.525826 | 2.655705 | 0.42893 |
| H | 4.387321 | 0.679590 | 1.24993 |
| C | 2.503807 | 3.511457 | -0.59201 |
| H | 0.804493 | 2.184319 | -0.53268 |
| C | 3.833150 | 3.657699 | -0.23485 |
| H | 5.566266 | 2.806448 | 0.69720 |
| H | 1.992734 | 4.318930 | -1.10580 |
| F | 4.061928 | -4.768060 | -1.25444 |
| F | 4.476147 | 4.805460 | -0.53789 |



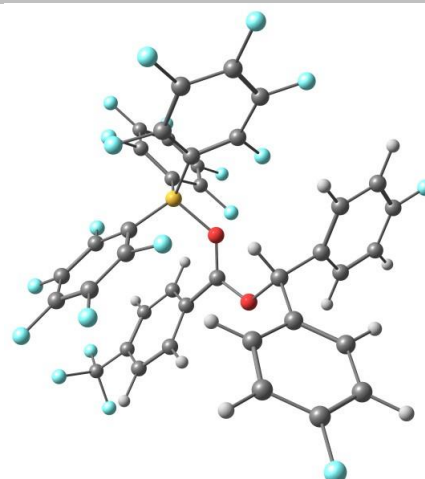
SUPPORTING INFORMATION

9-B(C₆F₅)₃

E: -3666.00137179 a.u

Cartesian coordinates:

| | | | |
|---|-----------|-----------|----------|
| C | 4.106211 | 1.806687 | -1.55374 |
| C | 3.258180 | 2.789078 | -1.04062 |
| C | 1.902786 | 2.531683 | -0.91787 |
| C | 1.405288 | 1.275316 | -1.28393 |
| C | 2.249350 | 0.305406 | -1.82259 |
| C | 3.603833 | 0.577320 | -1.96504 |
| H | 3.661759 | 3.745979 | -0.72713 |
| H | 1.233923 | 3.281147 | -0.50839 |
| H | 1.847882 | -0.650074 | -2.13035 |
| H | 4.267805 | -0.175912 | -2.37110 |
| C | -0.009084 | 0.972011 | -0.99658 |
| O | -0.818383 | 1.972273 | -1.18297 |
| O | -0.447946 | -0.108487 | -0.55952 |
| C | 5.582010 | 2.110029 | -1.63153 |
| F | 6.073687 | 2.384757 | -0.41461 |
| F | 5.809432 | 3.185596 | -2.40294 |
| F | 6.283065 | 1.088658 | -2.13777 |
| C | -2.179443 | 1.897103 | -0.60800 |
| H | -2.082495 | 1.311932 | 0.30899 |
| C | -2.522162 | 3.326643 | -0.26206 |
| C | -3.431720 | 4.077576 | -1.00471 |
| C | -1.880339 | 3.915111 | 0.83389 |
| C | -3.697684 | 5.401416 | -0.66910 |
| H | -3.946949 | 3.627855 | -1.84708 |
| C | -2.131321 | 5.236120 | 1.17782 |
| H | -1.182887 | 3.333762 | 1.43064 |
| C | -3.039335 | 5.959621 | 0.41539 |
| H | -4.405619 | 5.998163 | -1.23313 |
| H | -1.645758 | 5.705015 | 2.02624 |
| C | -3.101240 | 1.182131 | -1.55840 |
| C | -4.117959 | 0.384615 | -1.03478 |
| C | -2.973319 | 1.309407 | -2.94183 |
| C | -4.999059 | -0.286766 | -1.87190 |
| H | -4.217354 | 0.273151 | 0.04145 |
| C | -3.845879 | 0.642602 | -3.79453 |
| H | -2.181716 | 1.924279 | -3.35950 |
| C | -4.845785 | -0.145542 | -3.24302 |
| H | -5.775475 | -0.929936 | -1.47540 |
| H | -3.756974 | 0.720850 | -4.87220 |
| F | -3.290477 | 7.232475 | 0.74341 |
| F | -5.683977 | -0.793768 | -4.06094 |
| C | -1.187666 | -1.594446 | 1.32748 |
| C | -2.328601 | -1.980476 | 0.62452 |
| C | -1.297139 | -1.649662 | 2.71356 |
| C | -3.522442 | -2.331685 | 1.23964 |
| C | -2.469344 | -2.013301 | 3.36795 |
| C | -3.592778 | -2.348560 | 2.62596 |
| C | 1.259616 | -0.307211 | 1.31131 |
| C | 0.856637 | 0.835318 | 1.99925 |
| C | 2.638598 | -0.473090 | 1.23187 |
| C | 1.722764 | 1.762341 | 2.55239 |
| C | 3.550011 | 0.430202 | 1.77240 |
| C | 3.091454 | 1.555603 | 2.43920 |
| C | 0.672049 | -2.505579 | -0.28174 |
| C | 1.188902 | -3.543837 | 0.48990 |
| C | 0.525375 | -2.791427 | -1.63219 |
| C | 1.567263 | -4.771996 | -0.02856 |
| C | 0.894114 | -4.007739 | -2.19811 |
| C | 1.415285 | -5.006292 | -1.39021 |
| B | 0.153778 | -1.187054 | 0.50209 |
| F | -2.310461 | -2.021753 | -0.71370 |



SUPPORTING INFORMATION

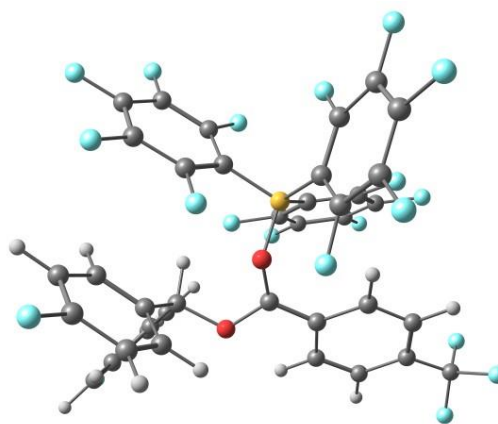
| | | | |
|---|-----------|-----------|----------|
| F | -4.595606 | -2.652577 | 0.51297 |
| F | -4.724984 | -2.685302 | 3.23539 |
| F | -2.523677 | -2.035607 | 4.69830 |
| F | -0.258262 | -1.339173 | 3.49663 |
| F | 0.037711 | -1.871272 | -2.48626 |
| F | 0.746667 | -4.216626 | -3.50578 |
| F | 1.771874 | -6.175264 | -1.91270 |
| F | 2.065652 | -5.723020 | 0.75790 |
| F | 1.340585 | -3.359794 | 1.80880 |
| F | -0.457706 | 1.135587 | 2.08811 |
| F | 3.174896 | -1.492046 | 0.55204 |
| F | 4.857124 | 0.234314 | 1.62385 |
| F | 3.947275 | 2.437993 | 2.94045 |
| F | 1.252852 | 2.856202 | 3.15414 |

9-B(C₆F₅)₃⁻

E: -3666.12671452 a.u

Cartesian coordinates:

| | | | |
|---|-----------|-----------|----------|
| C | 4.608279 | 1.321777 | -1.60419 |
| C | 3.806806 | 2.469310 | -1.49032 |
| C | 2.442945 | 2.365381 | -1.33341 |
| C | 1.810771 | 1.087164 | -1.26084 |
| C | 2.637648 | -0.064595 | -1.40909 |
| C | 3.999641 | 0.057293 | -1.56603 |
| H | 4.268846 | 3.451170 | -1.52644 |
| H | 1.834367 | 3.257536 | -1.23887 |
| H | 2.185893 | -1.047924 | -1.40891 |
| H | 4.606751 | -0.836576 | -1.66934 |
| C | 0.429793 | 0.976731 | -1.02828 |
| O | -0.295519 | 2.118159 | -1.19438 |
| O | -0.249904 | -0.106865 | -0.75726 |
| C | 6.089886 | 1.441743 | -1.69104 |
| F | 6.690840 | 1.433131 | -0.47779 |
| F | 6.479428 | 2.590244 | -2.28738 |
| F | 6.649180 | 0.429203 | -2.38762 |
| C | -1.590469 | 2.193039 | -0.59903 |
| H | -1.585714 | 1.605915 | 0.32200 |
| C | -1.784351 | 3.657977 | -0.24151 |
| C | -2.578677 | 4.513520 | -1.00250 |
| C | -1.094231 | 4.176387 | 0.85938 |
| C | -2.697344 | 5.862076 | -0.67415 |
| H | -3.116224 | 4.124292 | -1.86134 |
| C | -1.200506 | 5.518794 | 1.20088 |
| H | -0.465115 | 3.521506 | 1.45374 |
| C | -2.004987 | 6.341085 | 0.42495 |
| H | -3.314189 | 6.536637 | -1.25814 |
| H | -0.672604 | 5.930236 | 2.05434 |
| C | -2.664444 | 1.625999 | -1.50368 |
| C | -3.943939 | 1.419935 | -0.98493 |
| C | -2.408698 | 1.292713 | -2.83010 |
| C | -4.956423 | 0.883113 | -1.76993 |
| H | -4.148948 | 1.671237 | 0.05293 |
| C | -3.411508 | 0.755445 | -3.63228 |
| H | -1.411552 | 1.434683 | -3.23156 |
| C | -4.668477 | 0.557698 | -3.08669 |
| H | -5.946438 | 0.695154 | -1.37112 |
| H | -3.222511 | 0.476050 | -4.66305 |
| F | -2.117083 | 7.642641 | 0.75236 |
| F | -5.641968 | 0.033436 | -3.85608 |
| C | -1.570129 | -1.202055 | 1.07940 |
| C | -2.690110 | -1.397297 | 0.26882 |
| C | -1.839083 | -1.163321 | 2.44377 |
| C | -3.985685 | -1.502799 | 0.76044 |



SUPPORTING INFORMATION

| | | | |
|---|-----------|-----------|----------|
| C | -3.121496 | -1.254216 | 2.97554 |
| C | -4.204332 | -1.419256 | 2.12718 |
| C | 1.127276 | -0.587650 | 1.34728 |
| C | 0.995631 | 0.626606 | 2.01268 |
| C | 2.391631 | -1.155674 | 1.46168 |
| C | 2.010338 | 1.262688 | 2.70599 |
| C | 3.442238 | -0.565869 | 2.15881 |
| C | 3.255575 | 0.656250 | 2.78142 |
| C | 0.165972 | -2.611111 | -0.26701 |
| C | 0.223987 | -3.699997 | 0.59921 |
| C | 0.203752 | -2.935715 | -1.61860 |
| C | 0.324263 | -5.017976 | 0.18340 |
| C | 0.303484 | -4.246854 | -2.08061 |
| C | 0.361714 | -5.294061 | -1.17674 |
| B | -0.081277 | -1.112326 | 0.36129 |
| F | -2.555564 | -1.519612 | -1.05620 |
| F | -5.022217 | -1.693214 | -0.06323 |
| F | -5.442946 | -1.511020 | 2.62026 |
| F | -3.318911 | -1.191674 | 4.29735 |
| F | -0.853782 | -1.038237 | 3.34397 |
| F | 0.162614 | -1.994563 | -2.56998 |
| F | 0.341376 | -4.503663 | -3.39288 |
| F | 0.457112 | -6.555752 | -1.60639 |
| F | 0.383038 | -6.019805 | 1.06798 |
| F | 0.193516 | -3.489068 | 1.92571 |
| F | -0.185769 | 1.281007 | 1.99141 |
| F | 2.698922 | -2.309687 | 0.85037 |
| F | 4.636431 | -1.160906 | 2.21107 |
| F | 4.253284 | 1.240461 | 3.44561 |
| F | 1.798806 | 2.446601 | 3.29293 |

SUPPORTING INFORMATION

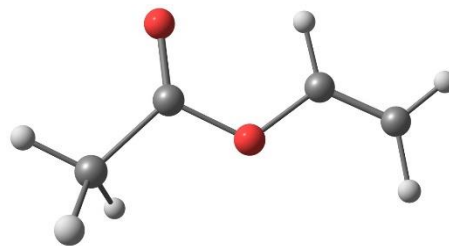
MVK

E: -306.462052415 a.u

G: -306.3974584 a.u

Cartesian coordinates:

| | | | |
|---|-----------|-----------|----------|
| C | 0.938843 | 0.169349 | -0.00000 |
| O | -0.256114 | -0.481220 | 0.00023 |
| O | 1.048737 | 1.367981 | -0.00002 |
| C | 2.068259 | -0.823679 | -0.00010 |
| H | 1.998483 | -1.467125 | -0.88212 |
| H | 3.018744 | -0.290755 | -0.00056 |
| H | 1.999108 | -1.466554 | 0.88237 |
| C | -1.405614 | 0.279770 | 0.00002 |
| C | -2.591208 | -0.311881 | -0.00011 |
| H | -1.238398 | 1.350425 | 0.00004 |
| H | -3.491346 | 0.290716 | -0.00029 |
| H | -2.689256 | -1.392149 | -0.00009 |

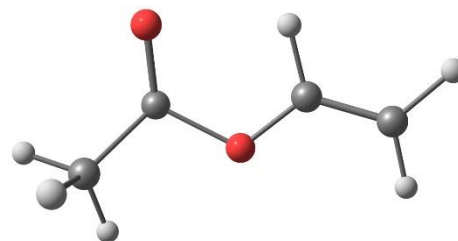
MVK⁻

E: -306.501258065 a.u

G: -306.4411338 a.u

Cartesian coordinates:

| | | | |
|---|-----------|-----------|----------|
| C | -1.050944 | 0.195938 | -0.35217 |
| O | 0.320697 | -0.553280 | -0.24051 |
| O | -1.069647 | 1.387937 | 0.05174 |
| C | -2.032983 | -0.832151 | 0.19754 |
| H | -1.953137 | -0.937341 | 1.29754 |
| H | -3.056097 | -0.504576 | -0.02711 |
| H | -1.874009 | -1.821965 | -0.24725 |
| C | 1.355524 | 0.206258 | 0.04772 |
| C | 2.636100 | -0.218330 | 0.10339 |
| H | 1.092361 | 1.249296 | 0.24673 |
| H | 3.429918 | 0.480837 | 0.35119 |
| H | 2.906381 | -1.253804 | -0.08976 |

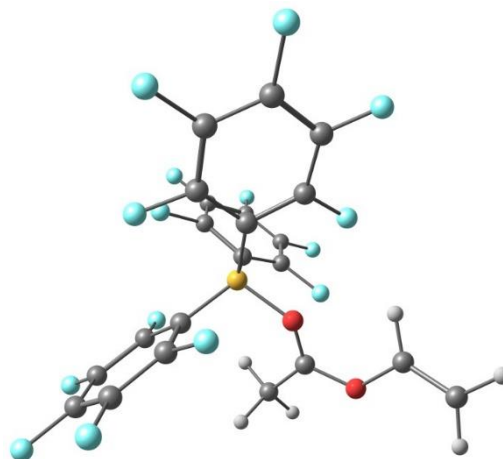
MVK-B(C₆F₅)₃

E: -2514.76160625 a.u

G: -2514.573696 a.u

Cartesian coordinates:

| | | | |
|---|-----------|-----------|----------|
| C | -0.325347 | -0.629280 | 2.74664 |
| O | -0.063748 | -0.318838 | 3.98784 |
| O | -0.010587 | 0.166929 | 1.84753 |
| C | 0.498166 | 1.401805 | -0.28857 |
| C | 1.663507 | 1.939768 | 0.25302 |
| C | -0.039378 | 2.118539 | -1.35420 |
| C | 2.246161 | 3.119991 | -0.18602 |
| C | 0.515627 | 3.301031 | -1.83137 |
| C | 1.664095 | 3.808058 | -1.24159 |
| C | -1.651953 | -0.299143 | -0.03901 |
| C | -2.589875 | 0.682758 | 0.28112 |
| C | -2.188093 | -1.473045 | -0.55897 |
| C | -3.954369 | 0.541078 | 0.07584 |
| C | -3.548402 | -1.658674 | -0.78323 |
| C | -4.437430 | -0.641895 | -0.46902 |
| C | 0.983030 | -1.176180 | -0.17832 |
| C | 1.107368 | -1.435330 | -1.54301 |
| C | 1.888352 | -1.855925 | 0.62660 |
| C | 2.035731 | -2.311896 | -2.08088 |
| C | 2.837078 | -2.746373 | 0.13347 |
| C | 2.912998 | -2.975179 | -1.23077 |
| B | -0.077633 | -0.017790 | 0.26144 |



SUPPORTING INFORMATION

| | | | |
|---|-----------|-----------|----------|
| F | 2.298990 | 1.303924 | 1.25819 |
| F | 3.355443 | 3.587077 | 0.38643 |
| F | 2.204617 | 4.938810 | -1.68398 |
| F | -0.046824 | 3.949046 | -2.84933 |
| F | -1.139936 | 1.693110 | -1.98386 |
| F | 1.891341 | -1.698631 | 1.97002 |
| F | 3.668514 | -3.373595 | 0.96391 |
| F | 3.812114 | -3.821256 | -1.72151 |
| F | 2.097595 | -2.520825 | -3.39315 |
| F | 0.286600 | -0.815118 | -2.40038 |
| F | -2.181601 | 1.837496 | 0.82525 |
| F | -1.405822 | -2.529399 | -0.82810 |
| F | -4.001815 | -2.808971 | -1.27733 |
| F | -5.740193 | -0.803839 | -0.66969 |
| F | -4.798949 | 1.518090 | 0.39871 |
| C | -1.035349 | -1.926911 | 2.57360 |
| H | -2.109725 | -1.724579 | 2.50374 |
| H | -0.726108 | -2.416012 | 1.64946 |
| H | -0.845635 | -2.569098 | 3.43328 |
| C | 0.685935 | 0.833839 | 4.26923 |
| C | 0.638394 | 1.322560 | 5.49516 |
| H | 1.272706 | 1.203483 | 3.43887 |
| H | 1.237226 | 2.189847 | 5.74431 |
| H | 0.016249 | 0.879750 | 6.26511 |

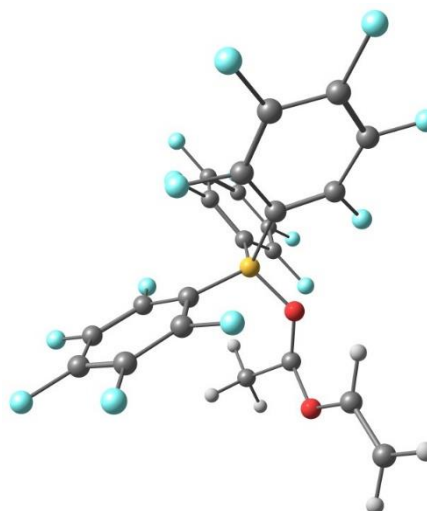
MVK-B(C₆F₅)₃⁻

E: -2514.85601450 a.u

G: -2514.673878 a.u

Cartesian coordinates:

| | | | |
|---|-----------|-----------|----------|
| C | -0.997638 | -0.511385 | 2.72787 |
| O | -2.048672 | 0.144407 | 3.38368 |
| O | -0.338489 | 0.242858 | 1.84919 |
| C | 0.503797 | 1.412490 | -0.17486 |
| C | 1.466330 | 2.129450 | 0.53618 |
| C | 0.120728 | 1.994829 | -1.37886 |
| C | 1.985045 | 3.348907 | 0.11642 |
| C | 0.616028 | 3.211960 | -1.83608 |
| C | 1.553008 | 3.897873 | -1.08102 |
| C | -1.402231 | -0.581018 | -0.29137 |
| C | -2.526304 | 0.243395 | -0.27412 |
| C | -1.624549 | -1.847462 | -0.81825 |
| C | -3.771994 | -0.135228 | -0.75356 |
| C | -2.854618 | -2.270422 | -1.31305 |
| C | -3.937302 | -1.407846 | -1.28097 |
| C | 1.282204 | -1.042525 | 0.23173 |
| C | 1.746401 | -1.311451 | -1.05423 |
| C | 2.075563 | -1.555500 | 1.25200 |
| C | 2.889522 | -2.044124 | -1.33279 |
| C | 3.232566 | -2.297496 | 1.01871 |
| C | 3.643915 | -2.543180 | -0.27981 |
| B | -0.020063 | -0.037970 | 0.43015 |
| F | 1.969779 | 1.647754 | 1.67994 |
| F | 2.905034 | 3.992100 | 0.84664 |
| F | 2.040661 | 5.068988 | -1.50495 |
| F | 0.198936 | 3.725996 | -3.00015 |
| F | -0.768327 | 1.401410 | -2.18950 |
| F | 1.765717 | -1.375352 | 2.54193 |
| F | 3.953365 | -2.774433 | 2.04171 |
| F | 4.752017 | -3.253341 | -0.51876 |
| F | 3.275326 | -2.273358 | -2.59431 |
| F | 1.061653 | -0.852165 | -2.11524 |
| F | -2.439645 | 1.487725 | 0.21660 |
| F | -0.653016 | -2.775887 | -0.84139 |



SUPPORTING INFORMATION

| | | | |
|---|-----------|-----------|----------|
| F | -3.005415 | -3.506672 | -1.80539 |
| F | -5.127567 | -1.796600 | -1.74947 |
| F | -4.810290 | 0.707184 | -0.71911 |
| C | -1.360769 | -1.944925 | 2.49517 |
| H | -2.297800 | -2.055688 | 1.92711 |
| H | -0.566476 | -2.458838 | 1.94996 |
| H | -1.501864 | -2.448980 | 3.45790 |
| C | -2.078582 | 1.492962 | 3.41040 |
| C | -2.972762 | 2.157590 | 4.14521 |
| H | -1.338947 | 1.982663 | 2.78589 |
| H | -2.983660 | 3.241014 | 4.12692 |
| H | -3.707819 | 1.640064 | 4.75335 |

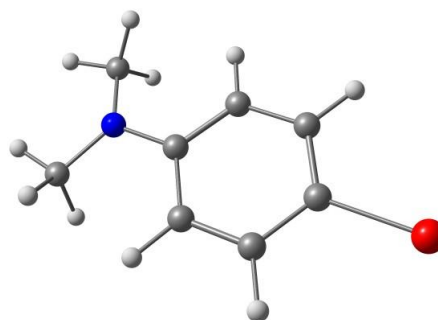
Me₂N-Ph-Br

E: -2939.76139352 a.u

G: -2939.592074 a.u

Cartesian coordinates:

| | | | |
|----|-----------|-----------|----------|
| C | -0.387797 | 1.201586 | -0.02607 |
| C | -1.083574 | 0.000010 | -0.01555 |
| C | -0.387793 | -1.201581 | -0.02600 |
| C | 1.000301 | -1.203584 | -0.05092 |
| C | 1.732691 | 0.000013 | -0.07413 |
| C | 1.000311 | 1.203596 | -0.05099 |
| H | -0.926265 | 2.143075 | -0.01072 |
| H | -0.926276 | -2.143059 | -0.01060 |
| H | 1.509033 | -2.159894 | -0.05197 |
| H | 1.509017 | 2.159918 | -0.05213 |
| N | 3.116625 | 0.000000 | -0.12397 |
| C | 3.827048 | -1.244454 | 0.07781 |
| H | 4.900862 | -1.057368 | 0.02333 |
| H | 3.606868 | -1.706073 | 1.05298 |
| H | 3.581778 | -1.969405 | -0.70734 |
| C | 3.827061 | 1.244439 | 0.07794 |
| H | 4.900875 | 1.057317 | 0.02365 |
| H | 3.581909 | 1.969418 | -0.70722 |
| H | 3.606734 | 1.706035 | 1.05308 |
| Br | -2.980869 | -0.000003 | 0.02236 |

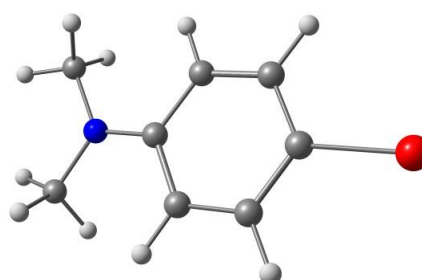
**Me₂N-Ph-Br⁺**

E: -2939.55403083 a.u

G: -2939.387203 a.u

Cartesian coordinates:

| | | | |
|----|-----------|-----------|----------|
| C | -0.393273 | 1.222002 | 0.04677 |
| C | -1.094403 | 0.000003 | -0.00004 |
| C | -0.393274 | -1.221996 | -0.04688 |
| C | 0.977008 | -1.228938 | -0.04331 |
| C | 1.711421 | -0.000001 | -0.00005 |
| C | 0.977007 | 1.228944 | 0.04319 |
| H | -0.942953 | 2.155185 | 0.09048 |
| H | -0.942955 | -2.155177 | -0.09060 |
| H | 1.493733 | -2.178643 | -0.09764 |
| H | 1.493738 | 2.178648 | 0.09747 |
| N | 3.057720 | -0.000004 | 0.00000 |
| C | 3.818622 | -1.249904 | 0.08545 |
| H | 4.859834 | -1.015678 | 0.29853 |
| H | 3.434362 | -1.875371 | 0.89336 |
| H | 3.764682 | -1.792546 | -0.86399 |
| C | 3.818633 | 1.249901 | -0.08533 |
| H | 4.859897 | 1.015665 | -0.29815 |
| H | 3.434574 | 1.875311 | -0.89339 |
| H | 3.764456 | 1.792594 | 0.86406 |
| Br | -2.947253 | -0.000001 | 0.00003 |



SUPPORTING INFORMATION

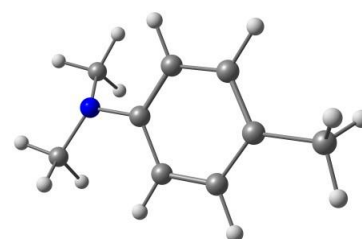
Me₂N-Ph-Me

E: -405.501234272 a.u

G: -405.5012343 a.u

Cartesian coordinates:

| | | | |
|---|-----------|-----------|----------|
| C | 1.498066 | -1.168160 | -0.21867 |
| C | 2.186969 | 0.025666 | 0.02669 |
| C | 1.424985 | 1.178393 | 0.18180 |
| C | 0.032100 | 1.153840 | 0.11234 |
| C | -0.652907 | -0.040970 | -0.13343 |
| C | 0.116548 | -1.205274 | -0.30506 |
| H | 2.059728 | -2.088972 | -0.36153 |
| H | 1.922159 | 2.126819 | 0.37298 |
| H | -0.511211 | 2.080072 | 0.26242 |
| H | -0.373759 | -2.145120 | -0.53920 |
| N | -2.056856 | -0.102551 | -0.25654 |
| C | -2.770751 | 1.155677 | -0.27715 |
| H | -3.812636 | 0.963835 | -0.55180 |
| H | -2.768195 | 1.679577 | 0.69608 |
| H | -2.340717 | 1.820326 | -1.03165 |
| C | -2.738273 | -1.104386 | 0.54789 |
| H | -3.755563 | -1.243017 | 0.16720 |
| H | -2.227872 | -2.066387 | 0.49048 |
| H | -2.802463 | -0.814186 | 1.61119 |
| C | 3.692639 | 0.047352 | 0.11179 |
| H | 4.054964 | -0.578222 | 0.93618 |
| H | 4.150187 | -0.332282 | -0.80934 |
| H | 4.067102 | 1.062585 | 0.27554 |

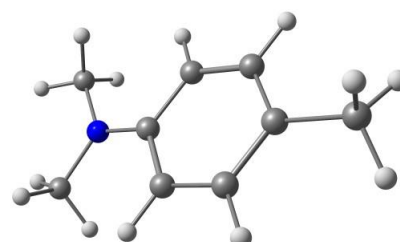
**Me₂N-Ph-Me⁺**

E: -405.304739020 a.u

G: -405.1379112 a.u

Cartesian coordinates:

| | | | |
|---|-----------|-----------|----------|
| C | -1.453496 | 1.211685 | 0.04265 |
| C | -2.180103 | 0.000408 | -0.01286 |
| C | -1.453498 | -1.210948 | -0.06468 |
| C | -0.082618 | -1.227050 | -0.05459 |
| C | 0.652848 | 0.000005 | -0.00138 |
| C | -0.082641 | 1.227336 | 0.04528 |
| H | -1.994677 | 2.151518 | 0.08862 |
| H | -1.994387 | -2.150408 | -0.12013 |
| H | 0.434733 | -2.176133 | -0.11741 |
| H | 0.434493 | 2.176520 | 0.10822 |
| N | 2.000555 | -0.000144 | 0.00278 |
| C | 2.763359 | -1.247028 | 0.10334 |
| H | 3.795415 | -1.009380 | 0.35528 |
| H | 2.354617 | -1.881895 | 0.89108 |
| H | 2.745201 | -1.781137 | -0.85239 |
| C | 2.764174 | 1.246600 | -0.09329 |
| H | 3.798322 | 1.008611 | -0.33613 |
| H | 2.361942 | 1.880187 | -0.88542 |
| H | 2.737984 | 1.782239 | 0.86140 |
| C | -3.674730 | -0.000315 | 0.01382 |
| H | -4.023747 | -0.040049 | 1.05464 |
| H | -4.086460 | 0.907818 | -0.43415 |
| H | -4.087092 | -0.871035 | -0.50248 |



SUPPORTING INFORMATION

References

- [1] S. Stoll, A. J. Schweiger, *Magn. Reson.* **2006**, *178*, 42–55. EasySpin is available free of charge at <http://easyspin.org>
- [2] L. Liu, L. L. Cao, Y. Shao, G. Ménard, D. W. Stephan, *Chem* **2017**, *3*, 259–267
- [3] Def2-svp and def2-tzvp basissets: a) A. Schäfer, H. Horn, R. Ahlrichs, *J. Chem. Phys.* **1992**, *97*, 2571; b) Ansgar Schäfer, C. Huber, R. Ahlrichs, *J. Chem. Phys.* **1994**, *100*, 5829; c) F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys.*, **2005**, *7*, 3297–3305; d) F. Weigend, *Phys. Chem. Chem. Phys.*, **2006**, *8*, 1057–1065
- [4] ω B97X-D: J. –Da. Chai, M. Head-Gordon, *Phys. Chem. Chem. Phys.* **2008**, *10*, 6615–6620
- [5] Gaussian 09, Revision D.01, M.J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian, Inc., Wallingford CT, 2013.
- [6] a) A. D. McLean, G. S. Chandler *J. Chem. Phys.* **1980**, *72*, 5639–5648; b) K. Raghavachari, J. S. Binkley, R. Seeger, J. A. Pople *J. Chem. Phys.* **1980**, *72*, 650–654; c) J.-P. Blaudeau, M. P. McGrath, L. A. Curtiss, L. Radom *J. Chem. Phys.* **1997**, *107*, 5016–5021; d) A. J. H. Wachters *J. Chem. Phys.*, **1970**, *52*, 1033; e) P. J. Hay *J. Chem. Phys.* **1977**, *66*, 4377–4384; f) K. Raghavachari, G. W. Trucks *J. Chem. Phys.* **1989**, *91*, 1062–1065; g) R. C. Binning Jr., L. A. Curtiss *J. Comp. Chem.* **1990**, *11*, 1206–1216; h) M. P. McGrath, L. Radom *J. Chem. Phys.* **1991**, *94*, 511–516; i) L. A. Curtiss, M. P. McGrath, J.-P. Blaudeau, N. E. Davis, R. C. Binning Jr., L. Radom *J. Chem. Phys.* **1995**, *103*, 6104–6113; j) T. Clark, J. Chandrasekhar, G. W. Spitznagel, P. V. R. Schleyer, *J. Comp. Chem.* **1983**, *4*, 294–301.
- [7] J. N. Harvey, M. Aschi, H. Schwarz, W. Koch, *Theor. Chem. Acc.* **1998**, *99*, 95–99
- [8] K. L. Gannon, M. A. Blitz, C.-H. Liang, M. J. Pilling, P. W. Seakins, D. R. Glowacki, J. N. Harvey, *Faraday Discuss.*, **2010**, *147*, 173–188