Convenient Synthesis of Deuterosilanes by Direct H/D Exchange Mediated by Easily Accessible Pt(0) Complexes

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1. Experimental

Standard Schlenk techniques were used for all syntheses and all sample manipulations. Solvents were dried and kept over anhydrous CaCl₂, filtered, degassed, kept on t-BuLi in vacuum and distilled before use. All commercially available reagents were degassed from air and used without additional purification. (Ph₃P)₄Pt was purchased from Stream Chemicals.

NMR spectra were recorded at room temperature in hexane or benzene solutions in Young vacuum NMR tubes equipped with [D₆] DMSO capillars as external standard, using a Bruker EM-200, Bruker Avance 300 or Bruker Avance 500 instruments.

2. General procedure for the isotopic exchange of silanes

Neat silane (0.8 mmol) was added to a 100 mL Schlenk flask. The flask was cooled down in a liquid nitrogen bath until the silane was frozen and vacuum was applied to remove the air. To the degassed silane 1 mol % of the catalyst (0.008 mmol) dissolved in 1 mL of hexane was added. The flask was charged with 5 mol equivalents of D₂ relative to the silane (100 mL, 1 atm, 4 mmol) and the reaction was stirred at 60 °C for the time indicated in Table 1. To ensure full deuteration, after each 2 h, the reaction mixture was vacuumed and an additional 4 mmol portion of D₂ was added. The addition of D₂ was repeated two more times. The reaction yield was determined using ¹H and ²⁹Si NMR spectroscopies.

3. Synthesis of compounds 1, 2, 3 and 4

Pt(PEt₃)₃ (1)

1 was prepared according to a literature procedure.¹

(dmpe)Pt(PEt₃)₂ (2)

The synthesis of 2 was reported previously, however the NMR data was not provided.²

To a hexane solution of 1 (1.0 gr, 1.5 mmol) dmpe (1,2-Bis(dimethylphosphino)ethane) (0.22 gr, 1.5 mmol) dissolved in hexane was added at room temperature. The reaction mixture was then stirred for 10 minutes at r.t. to give (dmpe)Pt(PEt₃)₂ (2) in quantitative yield (determined by NMR spectroscopy) and free PEt₃. PEt₃ was removed under vacuum (10⁻³ torr) at r.t. and the residual 2 was dissolved in hexane.

NMR (in hexane with [D₆] DMSO capillary, 25°C), δ in ppm: ³¹P: δ = 1.51 (d, Jₚtₚ = 4005.96 Hz, t, Jₚtₚ = 56.43 Hz); δ = -18.43 (d, Jₚtₚ = 3445.09 Hz, t, Jₚtₚ = 56.43 Hz); ¹H: δ = 1.35 (PCH₂-CH₃); 1.03 (Me₂P); ¹³C: δ = 25.89 (PCH₂-CH₃); 23.82 (Me₂P); See Figure S1.
To a hexane solution of 1 (1.0 gr, 1.5 mmol) dtbpe (1,2-bis(di-tert-butylphosphino)ethane) (0.47 gr, 1.5 mmol) dissolved in hexane was added at room temperature. The reaction mixture was then stirred for 10 minutes at r.t. to give (dtbpe)Pt(PET₃) (3) in quantitative yield (determined by NMR spectroscopy) and free PET₃. PET₃ was removed under vacuum (10⁻³ torr) at r.t. and the residual 3 was dissolved in hexane.

NMR (in hexane with [D₆] DMSO capillary, 25°C), δ in ppm: ¹³¹P: δ = 126.15 (d, J_{Pt-P} = 3502.46 Hz, d, J_{P-P} = 164.09 Hz); δ = -39.59 (d, J_{P-P} = 5154.30 Hz, t, J_{P-P} = 164.09 Hz); ¹H: δ = 1.23 (tBu₂P); 1.13 (PCH₂-CH₃); 0.86 (PCH₂-CH₃); ¹³C: δ = 29.88 (tBu₂P). See Figure S2.
Synthesis of (dtbpe)PtD₂ (4)

4 or its H-analog (dtbpe)PtH₂ was previously synthesized using the less convenient reaction of (dtbpe)PtCl₂ with Hg/Na (1%) under atmosphere of H₂ or D₂. Here we report a much simpler synthesis. To a hexane solution of 3 (0.1 gr, 0.2 mmol), D₂ was added (1 atm) and immediately a quantitative precipitation of 4 as a white powder was observed. The powder was isolated from the reaction mixture in quantitative yield and dissolved in toluene.

NMR (in toluene with [D₆] DMSO capillary, 25°C), δ in ppm: $^{31}$P: δ = 106.76 (d, $J_{Pt-P}$ = 1839.30 Hz, t, $J_{P-D}$ (trans) = 26.46 Hz).

Compound 4 has a square planar geometry and although there are two different deuterium atoms on platinum we observe in the $^{31}$P NMR splitting only from the trans-deuterium. The coupling from the cis deuterium is not observed probably due to the fact that the width of the signal is larger than the coupling constant of the cis deuterium (which is expected to be small). See Figure S3.
4. Determination of $K_{eq}$ of reaction 2

To a toluene solution of 4 (0.1 gr, 0.2 mmol), PEt$_3$ was added (0.023 gr, 0.2 mmol) at r.t. and immediately the formation of 3 was observed. The equilibrium constant was determined using NMR spectroscopy to be $K_{eq}$=1 (Figure S4).

Figure S4. $^{31}$P NMR spectrum of reaction 2 (PEt$_3$ was added to (dtbpe)PtH$_2$).

5. DFT calculations for 1-3 and their corresponding platinum dihydrides complexes

DFT computations were carried out using the Gaussian 09 5 software at the B3LYP 6. D3 7/6-311+G(d,p) (for H, C, Si, P) level, Pt was described with LANL2DZ. 8

Optimized Cartesian coordinates for 1
| Element | X         | Y         | Z         |
|---------|-----------|-----------|-----------|
| Pt      | 0.016512000 | -0.006805000 | -0.017519000 |
| P       | 0.737083000  | 2.179628000  | -0.200915000 |
| C       | 1.508605000  | 2.662497000  | -1.823689000 |
| C       | 2.024474000  | 2.695310000  | 1.050034000  |
| C       | -0.536310000 | 3.534291000  | 0.038794000  |
| P       | 1.522584000  | -1.735053000 | 0.234021000  |
| C       | 1.642390000  | -2.921222000 | -1.192489000 |
| C       | 1.163280000  | -2.905491000 | 1.634031000  |
| C       | 3.310193000  | -1.279471000 | 0.539339000  |
| C       | -2.813829000 | -2.061973000 | -0.747479000 |
| C       | -3.348924000 | 0.810541000  | -0.850307000 |
| P       | 1.522584000  | -1.735053000 | 0.234021000  |
| H       | 0.716868000  | 2.543705000  | -2.569706000 |
| H       | 1.774372000  | 3.725032000  | -1.806541000 |
| H       | 2.871541000  | 2.025136000  | 0.875286000  |
| H       | 1.615902000  | 2.401984000  | 2.021679000  |
| H       | -0.082257000 | 4.518224000  | -0.200717000 |
| H       | -1.241496000 | 3.364314000  | -0.857979000 |
| H       | 2.368487000  | -3.710507000 | -0.972218000 |
| H       | 0.659325000  | -3.396980000 | -1.259271000 |
| H       | 1.940161000  | -3.674351000 | 1.702798000  |
| H       | 0.233546000  | -3.409929000 | 1.354767000  |
| H       | 3.284868000  | -0.609219000 | 1.403899000  |
| H       | 3.584832000  | -0.648620000 | -0.310490000 |
| H       | -3.905214000 | -2.143387000 | -0.746273000 |
| H       | -2.429609000 | -2.841311000 | -0.081494000 |
| H       | -3.423622000 | 1.642396000  | -0.141650000 |
| H       | -2.739205000 | 1.183637000  | -1.677133000 |
| H       | -2.539074000 | 0.306432000  | 2.259227000  |
| H       | -2.395924000 | -1.429646000 | 2.169395000  |
| C       | -4.735646000 | 0.406402000  | -1.368428000 |
| H       | -5.380084000 | 0.013898000  | -0.580789000 |
| H       | -5.242810000 | 1.270649000  | -1.810337000 |
| H       | -4.663405000 | -0.358146000 | -2.145824000 |
| C       | -2.255765000 | -2.257557000 | -2.161341000 |
| H       | -2.651158000 | -1.510653000 | -2.856163000 |
| H       | -1.167626000 | -2.158660000 | -2.156900000 |
| H       | -2.512977000 | -3.245213000 | -2.555501000 |
| C       | -4.435923000 | -0.703411000 | 1.954317000  |
| H       | -4.658736000 | -0.836837000 | 3.017733000  |
| C       | -4.965102000 | 0.192191000  | 1.620980000  |
| H       | -4.854930000 | -1.560776000 | 1.421285000  |
| C       | 1.975917000  | -2.219377000 | -2.512910000 |
| H       | 1.952728000  | -2.923191000 | -3.349988000 |
| H       | 1.257601000  | -1.419807000 | -2.713062000 |
| H       | 2.973210000  | -1.770770000 | -2.486822000 |
| C       | 0.986771000  | -2.178647000 | 2.971429000  |
| H       | 0.220782000  | -1.402715000 | 2.885920000  |
| H       | 0.690895000  | -2.874449000 | 3.762267000  |
Electronic energy: -1856.7397753 Hartree
Total thermal energy: -1856.102107 Hartree
Total enthalpy: -1856.101163 Hartree
Gibbs free enthalpy: -1856.206969 Hartree
Number of imaginary frequencies: 0

Optimized Cartesian coordinates for (Et₃P)₂PtH₂

Pt  0.139878000 -1.104999000 -0.314039000
P  1.836211000 0.432265000 0.236379000
P  -1.788551000 0.239563000 -0.131185000
C  1.960263000 0.877490000 2.031790000
C  3.540341000 -0.173795000 -0.154850000
C  -1.822093000 1.458213000 1.275437000
C  -3.334157000 -0.746409000 0.110027000
H  1.255764000 -2.225380000 -0.535384000
H  -0.805987000 -2.324462000 -0.731948000
H  2.872999000 1.456239000 2.205690000
H  1.112394000 1.534851000 2.246796000
H  4.283736000 0.533122000 0.228303000
H  3.649142000 -1.105611000 0.405401000
H  -0.967233000 2.119954000 1.106794000
H  -1.571039000 0.868730000 2.162451000
Electronic energy: -1278.7599259 Hartree
Total thermal energy: -1278.317572 Hartree
Total enthalpy: -1278.316628 Hartree
Gibbs free enthalpy: -1278.397132 Hartree
Number of imaginary frequencies: 0

Optimized Cartesian coordinates for 2

![Diagram of the optimized Cartesian coordinates for 2]
| Element | x       | y       | z       |
|---------|---------|---------|---------|
| Pt      | -0.0769 | -0.1356 | 0.0232  |
| P       | -0.3141 | -1.9843 | -1.4129 |
| P       | -0.5440 | -1.5779 | 1.8129  |
| C       | -1.0956 | -3.3296 | -0.3585 |
| C       | -0.5564 | -3.3110 | 1.0783  |
| C       | -1.4149 | -2.0573 | -2.9041 |
| C       | 1.1568  | -2.8961 | -2.0895 |
| C       | -2.1783 | -1.5505 | 2.6956  |
| C       | 0.5761  | -1.8651 | 3.2634  |
| P       | -1.7021 | 1.4987  | -0.3313 |
| C       | -3.1728 | 0.9618  | -1.3464 |
| C       | -1.2652 | 3.0584  | -1.2589 |
| C       | -2.5249 | 2.1678  | 1.2062  |
| C       | 2.7279  | 1.6744  | -1.3468 |
| C       | 3.4180  | -0.6626 | 0.2714  |
| C       | 2.5030  | 1.8037  | 1.5498  |
| P       | 2.1163  | 0.6813  | 0.1083  |
| H       | -2.1724 | -3.1318 | -0.3601 |
| H       | -0.9463 | -4.3120 | -0.8210 |
| H       | 0.4839  | -3.6531 | 1.0925  |
| H       | -1.1268 | -3.9907 | 1.7213  |
| H       | -1.5150 | -3.0758 | -3.2945 |
| H       | -2.4023 | -1.6743 | -2.6440 |
| H       | -0.9942 | -1.4181 | -3.6836 |
| H       | 1.7062  | -2.2436 | -2.7711 |
| H       | 0.8666  | -3.8084 | -2.6219 |
| H       | 1.8201  | -3.1627 | -1.2647 |
| H       | -2.9842 | -1.5516 | 1.9594  |
| H       | -2.3006 | -2.4053 | 3.3696  |
|   |    |    |                       |                       |
|---|----|----|----------------------|----------------------|
| H | -2.250010000 | -0.627334000 | 3.274342000         |                       |
| H | 0.268925000  | -2.730574000 | 3.860997000         |                       |
| H | 0.572986000  | -0.976236000 | 3.897806000         |                       |
| H | 1.593097000  | -2.021297000 | 2.897934000         |                       |
| H | -3.844852000 | 1.809509000  | -1.516623000        |                       |
| H | -2.763113000 | 0.676263000  | -2.319545000        |                       |
| H | -2.176935000 | 3.590050000  | -1.554228000        |                       |
| H | -0.779159000 | 2.711608000  | -2.175544000        |                       |
| H | -1.709207000 | 2.578070000  | 1.807225000         |                       |
| H | -2.870976000 | 1.283950000  | 1.748521000         |                       |
| H | 3.796236000  | 1.887516000  | -1.249645000        |                       |
| H | 2.204723000  | 2.633210000  | -1.299899000        |                       |
| H | 3.418009000  | -0.923516000 | 1.335700000         |                       |
| H | 2.994250000  | -1.524181000 | -0.245620000        |                       |
| H | 2.174572000  | 1.238781000  | 2.427350000         |                       |
| H | 1.793805000  | 2.630861000  | 1.456766000         |                       |
| C | 4.847905000  | -0.416784000 | -0.229609000        |                       |
| H | 5.318657000  | 0.446016000  | 0.243276000         |                       |
| H | 5.476574000  | -1.289673000 | -0.025602000        |                       |
| H | 4.866576000  | -0.249407000 | -1.309430000        |                       |
| C | 2.429862000  | 0.987407000  | -2.683547000        |                       |
| H | 2.963343000  | 0.036061000  | -2.772543000        |                       |
| H | 1.361021000  | 0.773346000  | -2.766810000        |                       |
| H | 2.733676000  | 1.617496000  | -3.525034000        |                       |
| C | 3.925763000  | 2.337082000  | 1.756729000         |                       |
| H | 3.950753000  | 3.041462000  | 2.594596000         |                       |
| H | 4.626633000  | 1.532276000  | 1.988777000         |                       |
| H | 4.298605000  | 2.865090000  | 0.875258000         |                       |
| C | -3.930809000 | -0.210911000 | -0.720278000        |                       |
H  -4.686737000  -0.608606000  -1.403904000
H  -3.237649000  -1.015021000  -0.608606000
H  -4.442812000   0.090934000   0.198007000
C   -0.333890000   3.992678000  -0.483205000
H   0.016171000  4.815207000  -1.113600000
H  -0.837489000  4.431061000   0.382580000
H   0.539649000  3.452281000  -0.116367000
C  -3.658668000  3.185746000   1.046647000
H  -4.029075000  3.510076000   2.024352000
H  -3.330750000  4.079550000   0.509374000
H  -4.507291000  2.764340000   0.501394000

Electronic energy: -2198.7386598 Hartree
Total thermal energy: -2198.090110 Hartree
Total enthalpy: -2198.089166 Hartree
Gibbs free enthalpy: -2198.195648 Hartree
Number of imaginary frequencies: 0

Optimized Cartesian coordinates for (dmpe)PtH₂

Pt   0.0000003000  -1.0681430000  -0.000015000
P    1.5980280000   0.6508420000   0.008564000
P   -1.5980330000   0.6508370000  -0.008578000
C    0.6910830000  2.2558730000   0.336986000
C   -0.6910910000  2.2559040000  -0.336832000
C    2.9783230000   0.7015600000  1.219494000
C    2.4468290000   0.9718400000  -1.593284000
C   -2.4468300000   0.9716570000  1.593307000
Electronic energy: -1041.5833093 Hartree
Total thermal energy: -1041.343479 Hartree
Total enthalpy: -1041.342535 Hartree
Gibbs free enthalpy: -1041.400619 Hartree

Number of imaginary frequencies: 0

Optimized Cartesian coordinates for 3
Pt  -0.113049000  0.425863000  -0.13006000
P   -1.243790000  -1.614909000  0.081034000
P   1.940087000   -0.689893000  -0.032094000
C   0.099165000  -2.884919000  0.479509000
C   1.504360000  -2.533464000  -0.058927000
C   1.940087000  -0.689893000  1.545869000
C   2.030295000  -2.257762000  0.032094000
C   1.940087000  -2.533464000  1.545869000
C   2.030295000  -2.257762000  0.032094000
C   3.798203000  -1.176401000  1.926810000
C   2.858993000  -0.466317000  1.636766000
C   3.195427000  -0.578395000  1.483331000
C   4.103993000  -1.748329000  0.748276000
C   3.967481000  -0.748276000  1.382512000
P   -0.949219000  2.549028000  -0.215374000
C   -1.516595000  3.166296000  1.450017000
C   1.493219000  4.023900000  -0.210451000
C   0.105383000  3.955993000  -0.854241000
C   -3.154801000  4.154941000  -1.291260000
C   -2.489602000  2.774201000  -1.245171000
H   0.129634000  -2.934621000  1.568478000
H   -0.191779000  -3.881423000  0.132786000
H   1.570017000  -2.822530000  -1.107859000
H   2.261383000  -3.120636000  0.469724000
H   -2.324942000  -0.212520000  -2.232802000
H   -3.775284000  -0.910303000  -1.513495000
H   -3.268795000  -1.430842000  -3.121612000
H   -2.270160000  -4.364539000  -0.979021000
H   -3.759489000  -3.415252000  -0.848856000
H   -3.148098000  -3.883175000  -2.431940000
H   -0.242159000  -3.338148000  -2.241160000
H   -0.251002000  -1.605561000  -2.631125000

S14
Electronic energy: -2091.4797042 Hartree
Total thermal energy: -2090.687394 Hartree
Total enthalpy: -2090.686449 Hartree
Gibbs free enthalpy: -2090.796696 Hartree
Number of imaginary frequencies: 0
Optimized Cartesian coordinates for (dtbpe)PtH₂
|    |    |    |    |
|----|----|----|----|
| H  | 1.283537000 | 0.204197000 | 2.848345000 |
| H  | -0.743701000 | 1.328147000 | 2.200464000 |
| H  | -1.283569000 | -0.204355000 | 2.848321000 |
| H  | 2.254454000 | 2.096091000 | -1.555525000 |
| H  | 3.855335000 | 1.459991000 | -1.189398000 |
| H  | 3.460103000 | 3.119219000 | -0.743862000 |
| H  | 3.376134000 | 1.33671000 | 2.575255000 |
| H  | 4.537468000 | 1.077048000 | 1.261820000 |
| H  | 4.054435000 | 2.710062000 | 1.705044000 |
| H  | 1.120749000 | 2.514356000 | 2.023509000 |
| H  | 0.628493000 | 2.686251000 | 0.324317000 |
| H  | 1.917823000 | 3.695353000 | 0.988263000 |
| H  | 2.901903000 | -1.900184000 | 2.522372000 |
| H  | 4.243418000 | -0.868075000 | 2.019295000 |
| H  | 4.244196000 | -2.579918000 | 1.610172000 |
| H  | 3.452949000 | -0.946265000 | -1.685926000 |
| H  | 4.621045000 | -0.379254000 | -0.475731000 |
| H  | 4.533201000 | -2.091605000 | -0.875133000 |
| H  | 1.541957000 | -2.566166000 | -0.935533000 |
| H  | 1.396205000 | -2.996443000 | 0.778600000 |
| H  | 2.796208000 | -3.538560000 | -0.138813000 |
| H  | -2.254376000 | -2.096049000 | -1.555655000 |
| H  | -3.855270000 | -1.459963000 | -1.189558000 |
| H  | -3.460052000 | -3.119207000 | -0.744072000 |
| H  | -3.376199000 | -1.333801000 | 2.575117000 |
| H  | -4.537496000 | -1.077144000 | 1.261655000 |
| H  | -4.054451000 | -2.710168000 | 1.704831000 |
| H  | -1.120790000 | -2.514449000 | 2.023402000 |
| H  | -0.628461000 | -2.686251000 | 0.324222000 |

S17
Electronic energy: -1513.5070394 Hartree
Total thermal energy: -1512.910213 Hartree
Total enthalpy: -1512.909269 Hartree
Gibbs free enthalpy: -1512.994735 Hartree
Number of imaginary frequencies: 0

6. DFT calculations for complexes in the proposed mechanism in Scheme 1

Optimized Cartesian coordinates for (Me₃P)₃Pt

```
PMe₃
  Me₃P - Pt
  \ PMe₃
Pt  -0.014520000  0.018892000  -0.010354000
P   0.555906000  -2.218360000  -0.009765000
C  -0.479653000  -3.388522000  -1.004624000
C   0.513477000  -3.042115000  1.645508000
C  2.244906000  -2.719733000  -0.588836000
P  -2.236291000  0.642324000  -0.010889000
```
|   |   |   |   |   |
|---|---|---|---|---|
| C | -3.444233000 | -0.420269000 | -0.929941000 |
| C | -2.709491000 | 2.307321000 | -0.673492000 |
| C | -3.033074000 | 0.705517000 | 1.656843000 |
| C | 1.307376000 | 3.383198000 | -0.213464000 |
| C | 2.998111000 | 1.380097000 | -1.298866000 |
| C | 2.712193000 | 1.635699000 | 1.531359000 |
| P | 1.687021000 | 1.579516000 | -0.007584000 |
| H | -0.482122000 | -3.063174000 | -2.046794000 |
| H | -0.112995000 | -4.419222000 | -0.947979000 |
| H | -0.494495000 | -2.963562000 | 2.056391000 |
| H | 1.196749000 | -2.524452000 | 2.320967000 |
| H | 2.399127000 | -3.803527000 | -0.541829000 |
| H | 2.382385000 | -2.380939000 | -1.617894000 |
| H | -4.466504000 | -0.029505000 | -0.881390000 |
| H | -3.133276000 | -0.488656000 | -1.974360000 |
| H | -3.786422000 | 2.494375000 | -0.599008000 |
| H | -2.404165000 | 2.373554000 | -1.719977000 |
| H | -2.493885000 | 1.417404000 | 2.284381000 |
| H | -2.962381000 | -0.278952000 | 2.122644000 |
| H | 2.209178000 | 4.005525000 | -0.199108000 |
| H | 0.640457000 | 3.694121000 | 0.593334000 |
| H | 3.456326000 | 0.396244000 | -1.185769000 |
| H | 2.534338000 | 1.425623000 | -2.286294000 |
| H | 3.153751000 | 0.651494000 | 1.696138000 |
| H | 2.066705000 | 1.863961000 | 2.381655000 |
| H | -3.417753000 | -1.425324000 | -0.504820000 |
| H | -4.084662000 | 1.003472000 | 1.591082000 |
| H | -1.506248000 | -3.345948000 | -0.636260000 |
| H | 0.799001000 | -4.097086000 | 1.579160000 |
Electronic energy: -1502.7994563 Hartree
Total thermal energy: -1502.433441 Hartree
Total enthalpy: -1502.432497 Hartree
Gibbs free enthalpy: -1502.515694 Hartree
Number of imaginary frequencies: 0

Optimized Cartesian coordinates for cis (Me₃P)₂PtH₂(5)

|        | x       | y       | z       |
|--------|---------|---------|---------|
| Pt     | -0.000025000 | -0.840081000 | 0.000017000 |
| H      | -1.050241000 | -2.047271000 | -0.000233000 |
| P      | -1.893272000 | 0.548210000 | -0.000073000 |
| C      | -3.004289000 | 0.242901000 | 1.434682000 |
| H      | -2.476560000 | 0.491764000 | 2.357181000 |
| H      | -3.921868000 | 0.834441000 | 1.367615000 |
| H      | -3.248150000 | -0.819721000 | 1.461787000 |
| C      | -3.004405000 | 0.244026000 | -1.434966000 |
| H      | -3.922117000 | 0.835260000 | -1.367058000 |
| H      | -2.476977000 | 0.494025000 | -2.357331000 |
| H      | -3.248027000 | -0.818626000 | -1.463126000 |
| C      | -1.785373000 | 2.391956000 | 0.000614000 |
| H      | -2.779118000 | 2.848840000 | 0.000345000 |
| H      | -1.240607000 | 2.725224000 | 0.885536000 |
| H      | -1.239785000 | 2.725835000 | -0.883566000 |
Optimized Cartesian coordinates for *trans* (Me₃P)₂PtH₂

![Structure of (Me₃P)₂PtH₂](image)

| Element | X          | Y          | Z          |
|---------|------------|------------|------------|
| Pt      | 0.000000000 | 0.046093000 | 0.000001000 |
| H       | 0.000000000 | 1.692445000 | -0.000003000 |
| P       | 2.286583000 | -0.009782000 | 0.000000000 |
| P       | -2.286583000 | -0.009782000 | 0.000000000 |
| C       | -3.016792000 | -0.887739000 | 1.439052000 |
| H       | -2.707736000 | -0.385290000 | 2.357092000 |

Electronic energy: -1042.8019513 Hartree
Total thermal energy: -1042.541143 Hartree
Total enthalpy: -1042.540199 Hartree
Gibbs free enthalpy: -1042.604365 Hartree
Number of imaginary frequencies: 0
Electronic energy: -1042.7994708 Hartree
Total thermal energy: -1042.539504 Hartree
Total enthalpy: -1042.538560 Hartree
Gibbs free enthalpy: -1042.603600 Hartree
Number of imaginary frequencies: 0

Optimized Cartesian coordinates for (Me₂P)₂Pt(SiMe₃)₅(H)₃ (SiMe₃ ligand is in the equatorial position)
Electronic energy: -1452.7481412 Hartree
Total thermal energy: -1452.358566 Hartree
Total enthalpy: -1452.357622 Hartree
Gibbs free enthalpy: -1452.437003 Hartree
Number of imaginary frequencies: 0

Optimized Cartesian coordinates for (Me₃P)₂Pt(SiMe₃)(H)₃ (the SiMe₃ ligand is in an axial position)

Pt  -0.034743000  -0.040596000  -0.808676000
P   1.542952000  -1.441432000  0.323585000
C   3.271978000  -0.837088000  0.188927000
H   3.373396000  0.089321000  0.754741000
H   3.979831000  -1.576491000  0.572716000
H   3.490331000  -0.622772000  -0.857709000
C   1.653777000  -3.127943000  -0.398088000
H   2.431355000  -3.728092000  0.083332000
H   0.686134000  -3.620923000  -0.291756000
H   1.860385000  -3.031722000  -1.464592000
C   1.414660000  -1.804061000  2.125932000
H   2.311718000  -2.322642000  2.475108000
H   1.296236000  -0.873337000  2.680107000
H   0.549218000  -2.437962000  2.316144000
P   -2.084217000  -0.513484000  0.336734000
C   -2.096739000  -1.670761000  1.769760000
H   -1.679549000  -2.633507000  1.469488000
H   -1.488501000  -1.257452000  2.575054000
H  -3.116256000  -1.824255000  2.133795000  
C  -3.029265000  0.907186000  1.018572000  
H  -3.208297000  1.630602000  0.222940000  
H  -3.985134000  0.577017000  1.434259000  
H  -2.442735000  1.394093000  1.798358000  
C  -3.309823000  -1.285764000  -0.792204000  
H  -4.266957000  -1.461013000  -0.292836000  
H  -3.453167000  -0.626761000  -1.649595000  
H  -2.898865000  -2.260080000  -1.161342000  
H  1.130593000  0.333880000  -1.804474000  
H  -0.880197000  0.893212000  -1.762397000  
H  -0.388314000  -1.289977000  -1.846891000  
Si  0.585495000  2.065772000  0.319489000  
C  0.840921000  1.937190000  2.213135000  
H  2.211645000  2.780640000  -0.368005000  
H  2.490124000  3.709502000  0.143904000  
H  3.047312000  2.081981000  -0.277661000  
H  2.093895000  3.004450000  -1.432807000  
C  -0.665387000  3.482930000  0.075006000  
H  -1.615970000  3.307324000  0.583232000  
H  -0.253497000  4.422595000  0.462160000  
H  -0.878821000  3.622159000  -0.988953000  

Electronic energy: -1452.7446593 Hartree  
Total thermal energy: -1452.354206 Hartree  
Total enthalpy: -1452.353262 Hartree  
Gibbs free enthalpy: -1452.432168 Hartree  
Number of imaginary frequencies: 0
Optimized Cartesian coordinates for *cis* \((\text{Me}_3\text{P})_2\text{Pt(\text{SiMe}_3)(H)}\) \((8)\)

![Optimized Cartesian coordinates](image)

| Atom | X         | Y         | Z         |
|------|-----------|-----------|-----------|
| Pt   | 0.06371   | -0.33901  | -0.02381  |
| P    | -0.34900  | 1.97703   | -0.00205  |
| C    | -1.56821  | 2.57177   | 1.24366   |
| H    | -1.19781  | 2.32919   | 2.24161   |
| H    | -1.71864  | 3.65216   | 1.16531   |
| H    | -2.51904  | 2.06079   | 1.10333   |
| C    | -0.98901  | 2.66832   | -1.58451  |
| H    | -1.17964  | 3.74192   | -1.49935  |
| H    | -0.24801  | 2.49419   | -2.36720  |
| H    | -1.90741  | 2.15526   | -1.86538  |
| C    | 1.05221   | 3.13190   | 0.33492   |
| H    | 0.71027   | 4.17061   | 0.35321   |
| H    | 1.50170   | 2.88711   | 1.29872   |
| H    | 1.81218   | 3.02077   | -0.43898  |
| P    | 2.45159   | -0.55099  | 0.00709   |
| C    | 3.69069   | 0.81856   | 0.13051   |
| H    | 3.60060   | 1.47477   | -0.73710  |
| H    | 3.50329   | 1.40903   | 1.02869   |
| H    | 4.71039   | 0.42366   | 0.16963   |
| C    | 2.99600   | -1.64633  | 1.38411   |
| H    | 2.43413   | -2.57907  | 1.32523   |
| H    | 4.06891   | -1.85418  | 1.33552   |
| H    | 2.76072   | -1.17038  | 2.33786   |
| C    | 3.06695   | -1.45158  | -1.47674  |
| Atom | X     | Y     | Z     |
|------|-------|-------|-------|
| H    | 4.133135 | -1.68273 | 1.39593 |
| H    | 2.494765 | -2.37393 | 1.583105 |
| H    | 2.894306 | -0.841535 | 2.365521 |
| Si   | -2.226820 | -1.024541 | 0.009888 |
| C    | -2.850818 | -1.070913 | 1.809601 |
| H    | -2.793655 | -0.087327 | 2.284933 |
| H    | -3.891712 | -1.412259 | 1.859286 |
| H    | -2.239756 | -1.756465 | 2.404027 |
| C    | -2.505413 | -2.765155 | -0.701084 |
| H    | -3.566866 | -3.039666 | -0.686401 |
| H    | -2.154128 | -2.821415 | -1.736042 |
| H    | -1.948008 | -3.509441 | -0.125233 |
| C    | -3.474231 | 0.053549 | -0.959946 |
| H    | -4.472307 | -0.395037 | -0.889754 |
| H    | -3.555179 | 1.080285 | -0.592427 |
| H    | -3.210152 | 0.096831 | -2.021609 |
| H    | 0.136141 | -1.93773 | -0.04287 |

Electronic energy: -1451.5697911 Hartree
Total thermal energy: -1451.196729 Hartree
Total enthalpy: -1451.195785 Hartree
Gibbs free enthalpy: -1451.276079 Hartree
Number of imaginary frequencies: 0

Optimized Cartesian coordinates for trans \((\text{Me}_3\text{P})_2\text{Pt}((\text{SiMe}_3)(\text{H}))\)
| Element | X         | Y         | Z         |
|---------|-----------|-----------|-----------|
| P       | 2.292868000 | 0.683142000 | -0.01276000 |
| P       | -2.292928000 | 0.683039000 | -0.01277100 |
| C       | -3.197077000 | 0.240330000 | 1.524626000 |
| H       | -2.815373000 | 0.858205000 | 2.339259000 |
| H       | -4.269758000 | 0.417828000 | 1.407470000 |
| H       | -3.023239000 | -0.805143000 | 1.772465000 |
| C       | -3.150617000 | -0.263097000 | -1.335992000 |
| H       | -4.227810000 | -0.076710000 | -1.312958000 |
| H       | -2.749050000 | 0.053421000 | -2.300331000 |
| H       | -2.960562000 | -1.328791000 | -1.221526000 |
| C       | -2.899005000 | 2.388382000 | -0.332893000 |
| H       | -3.991179000 | 2.421277000 | -0.386543000 |
| H       | -2.542411000 | 3.039654000 | 0.465554000 |
| H       | -2.469901000 | 2.742349000 | -1.271109000 |
| C       | 2.898890000 | 2.388476000 | -0.333036000 |
| H       | 3.991067000 | 2.421416000 | -0.386611000 |
| H       | 2.469855000 | 2.742292000 | -1.271343000 |
| H       | 2.542204000 | 3.039849000 | 0.465285000 |
| C       | 3.196919000 | 0.240631000 | 1.524741000 |
| H       | 3.022756000 | -0.804708000 | 1.772914000 |
| H       | 4.269655000 | 0.417759000 | 1.407531000 |
| H       | 2.815405000 | 0.858889000 | 2.339174000 |
| C       | 3.150623000 | -0.263038000 | -1.335903000 |
| H       | 4.227813000 | -0.076641000 | -1.312842000 |
| H       | 2.960573000 | -1.328731000 | -1.221438000 |
| H       | 2.749073000 | 0.053481200 | -2.300349000 |
| Si      | 0.000101000 | -1.969784000 | -0.005527000 |
| C      | 0.000109000 | -2.610436000 | -1.808737000 |
| H       | 0.879499000 | -2.256245000 | -2.355766000 |
Electronic energy: -1451.5635025 Hartree
Total thermal energy: -1451.190719 Hartree
Total enthalpy: -1451.189775 Hartree
Gibbs free enthalpy: -1451.268481 Hartree
Number of imaginary frequencies: 0

Optimized Cartesian coordinates for cis (Me₃P)₂Pt(SiMe₃)(H)₂ (9)
| Atom | X      | Y      | Z      |
|------|--------|--------|--------|
| H    | 0.545240000 | 4.374705000 | -0.363946000 |
| H    | 1.814066000 | 3.194839000 | 0.043658000 |
| H    | 1.120196000 | 3.208874000 | -1.583167000 |
| C    | -0.678110000 | 2.640017000 | 1.739305000 |
| H    | -0.924568000 | 3.704585000 | 1.801234000 |
| H    | -1.496176000 | 2.049248000 | 2.152330000 |
| H    | 0.214746000 | 2.439189000 | 2.334857000 |
| P    | 2.441149000 | -0.600565000 | 0.073123000 |
| C    | 3.586953000 | 0.830659000 | 0.320819000 |
| H    | 3.536876000 | 1.488650000 | -0.548650000 |
| H    | 3.268909000 | 1.396221000 | 1.199231000 |
| H    | 4.621291000 | 0.502785000 | 0.464083000 |
| C    | 2.886056000 | -1.664602000 | 1.507521000 |
| H    | 2.362160000 | -2.616076000 | 1.408093000 |
| H    | 3.964881000 | -1.836885000 | 1.570205000 |
| H    | 2.537160000 | -1.184788000 | 2.423631000 |
| C    | 3.264471000 | -1.478565000 | -1.324196000 |
| H    | 4.324799000 | -1.657682000 | -1.122326000 |
| H    | 2.759281000 | -2.432196000 | -1.485772000 |
| H    | 3.166549000 | -0.881273000 | -2.232965000 |
| Si   | -2.179910000 | -1.152778000 | 0.100186000 |
| C    | -3.194898000 | -0.254048000 | 1.436689000 |
| H    | -3.326022000 | 0.809006000 | 1.214655000 |
| H    | -4.194423000 | -0.696047000 | 1.521528000 |
| H    | -2.707837000 | -0.332414000 | 2.413083000 |
| C    | -2.248044000 | -2.996122000 | 0.541607000 |
| H    | -3.281513000 | -3.359717000 | 0.594105000 |
| H    | -1.713152000 | -3.590348000 | -0.204925000 |
| H    | -1.769699000 | -3.177487000 | 1.508422000 |
C  -3.146895000  -0.9549558000  -1.529841000
H  -4.184200000  -1.292102000  -1.417556000
H  -3.163952000  0.086344000  -1.864340000
H  -2.684916000  -1.548148000  -2.325157000
H  0.097385000  -0.290988000  -1.978673000
H  -0.124489000  -0.768334000  1.362021000
H  0.017675000  -1.129783000  -1.735596000

Electronic energy: -1452.7189388 Hartree
Total thermal energy: -1452.331585 Hartree
Total enthalpy: -1452.330814 Hartree
Gibbs free enthalpy: -1452.414906 Hartree
Number of imaginary frequencies: 0

6. DFT calculations for the transition states in Scheme 1 and Figure 1

Optimized Cartesian coordinates for the transition state in step b

Pt  0.000000000  -0.548313000  0.000084000
H  0.399506000  -2.507971000  -0.000372000
P  2.106886000  0.314672000  0.000018000
C  3.604885000  -0.774431000  0.001489000
H  3.577646000  -1.415863000  -0.881718000
H  4.535016000  -0.196475000  0.001109000
H  3.577256000  -1.414018000  0.886021000
C  2.484863000  1.419681000  1.429079000
H  3.494940000  1.835617000  1.358720000
H  1.754241000  2.229445000  1.449879000
H  2.390010000  0.852188000  2.356404000
C  2.485623000  1.417011000  -1.430898000

S31
H  3.495619000  1.833174000  -1.360722000
H  2.391373000  0.847786000  -2.357220000
H  1.754947000  2.226673000  -1.453651000
P  -2.106866000  0.314672000  0.000018000
C  -2.484868000  1.419673000  1.429084000
H  -2.390016000  0.852176000  2.356406000
H  -1.754247000  2.229438000  1.449890000
H  -3.494945000  1.835608000  1.358725000
C  -2.485619000  1.417019000  1.430893000
H  -2.391363000  0.847800000  2.357218000
H  -3.495616000  1.833179000  1.358725000
H  -1.754945000  2.226683000  1.449890000
C  -3.604884000  -0.774431000  0.001479000
H  -4.535015000  -0.196475000  0.001097000
H  -3.577642000  -1.415859000  0.881732000
H  -3.577259000  -1.414022000  0.886008000
H  -0.399507000  -2.507969000  0.000367000

Electronic energy:  -1042.7737236 Hartree
Total thermal energy:  -1042.515685 Hartree
Total enthalpy:  -1042.514741 Hartree
Gibbs free enthalpy:  -1042.578814 Hartree
Number of imaginary frequencies:  1

Optimized Cartesian coordinates for the transition state in step c

```
Pt  0.041485000  -0.197896000  -0.546130000
P  2.175266000  -0.962215000  0.274854000
C  3.561503000  -0.717571000  -0.914566000
H  3.684712000  0.351023000  -1.100409000
H  4.503047000  -1.136167000  -0.544631000
```
Electron energy: -1452.720612 Hartree
Total thermal energy: -1452.333390 Hartree
Total enthalpy: -1452.332446 Hartree
Gibbs free enthalpy: -1452.414042 Hartree
Number of imaginary frequencies: 1

Optimized Cartesian coordinates for the transition state in step f

S33
| Element | x1      | y1      | z1      |
|---------|---------|---------|---------|
| Si      | -1.888228000 | -1.848480000 | -0.013827000 |
| H       | -0.492975000 | -1.543625000 | -0.670987000 |
| C       | -3.363185000 | -1.018771000 | -0.852774000 |
| H       | -3.513853000 | 0.000424000 | -0.492709000 |
| H       | -3.212970000 | -0.971058000 | -1.935064000 |
| H       | -4.282934000 | -1.584805000 | -0.666805000 |
| C       | -1.960857000 | -1.672632000 | 1.864660000 |
| H       | -1.080853000 | -2.131198000 | 2.323609000 |
| H       | -1.987371000 | -0.627495000 | 2.176240000 |
| H       | -2.849681000 | -2.179513000 | 2.258499000 |
| C       | -1.991883000 | -3.702750000 | -0.405155000 |
| H       | -1.155767000 | -4.246158000 | 0.045443000 |
| H       | -2.921531000 | -4.132633000 | -0.015664000 |
| H       | -1.963694000 | -3.883594000 | -1.483909000 |

Electronic energy: -1451.5426535 Hartree
Total thermal energy: -1451.170812 Hartree
Total enthalpy: -1451.169868 Hartree
Gibbs free enthalpy: -1451.251494 Hartree
Number of imaginary frequencies: 1

Optimized Cartesian coordinates for the transition state in step g
Electronic energy: -1452.7189302 Hartree
Total thermal energy: -1452.332619 Hartree
Total enthalpy: -1452.331674 Hartree
Gibbs free enthalpy: -1452.413724 Hartree
Number of imaginary frequencies: 1

Optimized Cartesian coordinates for the transition state in step h

Pt  0.044560000  -0.328810000  -0.170461000
P  -0.341093000  2.073711000  0.013405000
C  -1.798330000  2.740048000  -0.900426000
H  -2.697507000  2.202745000  -0.599915000
|    |         |         |         |         |
|----|---------|---------|---------|---------|
| H  | -1.936423000 | 3.809363000 | -0.712463000 |
| H  | -1.648350000 | 2.575617000 | -1.969091000 |
| C  | 0.962379000  | 3.266512000 | -0.531867000 |
| H  | 0.625001000  | 4.303153000 | -0.431575000 |
| H  | 1.860540000  | 3.126914000 | 0.070794000  |
| H  | 1.214154000  | 3.068816000 | -1.575532000 |
| C  | -0.660474000 | 2.661548000 | 1.730468000  |
| H  | -0.876693000 | 3.733790000 | 1.763335000  |
| H  | -1.500316000 | 2.104757000 | 2.146962000  |
| H  | 0.218897000  | 2.448882000 | 2.341696000  |
| P  | 2.443588000  | -0.599514000 | 0.082388000  |
| C  | 3.598705000  | 0.820913000 | 0.339285000  |
| H  | 3.562268000  | 1.480907000 | -0.529055000 |
| H  | 3.283340000  | 1.386837000 | 1.218308000  |
| H  | 4.627482000  | 0.478596000 | 0.487201000  |
| C  | 2.872746000  | -1.672850000 | 1.514035000  |
| H  | 2.335621000  | -2.616413000 | 1.409661000  |
| H  | 3.949011000  | -1.860076000 | 1.578652000  |
| H  | 2.526809000  | -1.191547000 | 2.430368000  |
| C  | 3.263480000  | -1.479019000 | -1.315217000 |
| H  | 4.322944000  | -1.663340000 | -1.113819000 |
| H  | 2.753625000  | -2.430196000 | -1.476592000 |
| H  | 3.166247000  | -0.881214000 | -2.223598000 |
| Si | -2.208150000 | -1.101558000 | 0.108133000  |
| C  | -3.206302000 | -0.153787000 | 1.421783000  |
| H  | -3.336324000 | 0.903362000  | 1.173593000  |
| H  | -4.206974000 | -0.589805000 | 1.522658000  |
| H  | -2.713668000 | -0.210724000 | 2.396591000  |
| C  | -2.299266000 | -2.929444000 | 0.601997000  |
7. Calculated Pt-H Bond Dissociation Energies

Pt-H bond dissociation energies of several Pt(II) complexes (Table 1S) were calculated using the Gaussian 09 software at the B3LYP-D3/6-311+G(d,p) (for H, C, Si, P) level. Pt was described with LANL2DZ. These values are in the range of other experimentally known Pt-H bonds (78-84 kcal mol\(^{-1}\)) which were reported previously.

Table 1S

| Complex                      | BDE (Pt-H) (kcal mol\(^{-1}\)) |
|------------------------------|-------------------------------|
| cis \((\text{Me}_3\text{P})_2\text{PtH}_2\) \((5)\) | 80.39                         |
| trans \((\text{Me}_3\text{P})_2\text{PtH}_2\) | 79.63                         |
| cis \((\text{Me}_3\text{P})_2\text{Pt(SiMe}_3\text{)}\text{(H)} \((8)\) | 75.04                         |
| trans \((\text{Me}_3\text{P})_2\text{Pt(SiMe}_3\text{)}\text{(H)} | 68.71                         |
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