Electronic Supporting Information for:

E-H (E = B, Si, Ge) Bond Activation of Pinacolborane, Silanes, and Germanes by Nucleophilic Palladium Carbene Complex

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1 Experimental **S6**
1.1 General remarks S6
1.2 References S6
1.3 Synthesis of [PC(SiH_2Ph)P]PdH (**3**) S7
1.4 Synthesis of [PC($SiHPh_2$)P]PdH (**4**) S8
1.5 Synthesis of [PC($SiPh_3$)P]PdH (**5**) S9
1.6 Reaction of of [PC(sp^2)P]Pd(PMe_3) (**1**) with $PhSiH_3$ S10
1.7 Reaction of of [PC(sp^2)P]Pd(PMe_3) (**1**) with Ph_2SiH_2 ..... S10
1.8 Reaction of of [PC(sp^2)P]Pd(PMe_3) (**1**) with Ph_3SiH S11
1.9 Thermolysis of the hydrides **3**-**5** S12
1.10 Synthesis of [PC(Bpin)P]PdH (**9**) S12
1.11 Synthesis of [PC(H)P]Pd(GeH_2Ph) (**10**) S13
1.12 Synthesis of [PC(H)P]Pd($GeHPh_2$) (**11**) S14
1.13 Synthesis of [PC(H)P]Pd($GePh_3$) (**12**) S15
1.14 Reaction of [PC(sp^2)P]Pd(PPh_3) (**2**) with $PhGeH_3$ S15
1.15 Reaction of [PC(sp^2)P]Pd(PPh_3) (**2**) with Ph_2GeH_2 ..... S16
1.16 Reaction of [PC(sp^2)P]Pd(PPh_3) (**2**) with Ph_3GeH S16
1.17 X-ray data for compounds **3**-**5**, **8**-**13** S17

2 DFT results **S19**
Figure S1. Calculated mechanism and reaction profile for the formation of the hydride products from [PC(sp^2)P]Pd(PMe_3) (**1**) S19
Figure S2. Calculated mechanism and reaction profile for the formation of the hydride products from [PC(sp^2)P]Pd(PPh_3) (**2**) S20
Figure S3. Calculated mechanism and reaction profile for the formation of the silyl products from [PC(sp^2)P]Pd(PMe_3) (**1**) S21
Figure S4. Calculated mechanism and reaction profile for the formation of the silyl products from [PC(sp^2)P]Pd(PPh_3) (**2**) S22

Figure S5. Calculated mechanism and reaction profile for the formation of the silyls from [PC(sp^2)P]Pd(PMe_3) (**1**) by a deprotonation mechanism..... S23
Figure S6. Calculated mechanism and reaction profile for the formation of the silyls from [PC(sp^2)P]Pd(PPh_3) (**2**) by a deprotonation mechanism S24

3 NMR Spectra **S25**
3.1 NMR Spectra for [PC(SiH_2Ph)P]PdH (**3**) S25
Figure S7. ^{1}H NMR spectrum for [PC(SiH_2Ph)P]PdH (**3**) S25
Figure S8. ^{31}P{^{1}H} NMR spectrum for [PC(SiH_2Ph)P]PdH (**3**)..... S26
Figure S9. ^{13}C{^{1}H} NMR spectrum for [PC(SiH_2Ph)P]PdH (**3**) S27
Figure S10. ^{29}Si{^{1}H} NMR spectrum for [PC(SiH_2Ph)P]PdH (**3**)..... S28
Figure S11. ^{1}H-^{13}C HSQC NMR spectrum for [PC(SiH_2Ph)P]PdH (**3**)..... S29
3.2 NMR Spectra for [PC($SiHPh_2$)P]PdH (**4**) S30
Figure S12. ^{1}H NMR spectrum for [PC($SiHPh_2$)P]PdH (**4**)..... S30
Figure S13. ^{31}P{^{1}H} NMR spectrum for [PC($SiHPh_2$)P]PdH (**4**) S31
Figure S14. ^{13}C{^{1}H} NMR spectrum for [PC($SiHPh_2$)P]PdH (**4**) S32
Figure S15. ^{29}Si{^{1}H} NMR spectrum for [PC($SiHPh_2$)P]PdH (**4**)..... S33
3.3 NMR Spectra for [PC($SiPh_3$)P]PdH (**5**) S34
Figure S16. ^{1}H NMR spectrum for [PC($SiPh_3$)P]PdH (**5**)..... S34
Figure S17. ^{31}P{^{1}H} NMR spectrum for [PC($SiPh_3$)P]PdH (**5**) S35
Figure S18. ^{13}C{^{1}H} NMR spectrum for [PC($SiPh_3$)P]PdH (**5**) S36
Figure S19. ^{29}Si{^{1}H} NMR spectrum for [PC($SiPh_3$)P]PdH (**5**)..... S37
Figure S20. ^{1}H-^{13}C HSQC NMR spectrum for [PC($SiPh_3$)P]PdH (**5**)..... S38
Figure S21. ^{1}H-^{1}H COSY NMR spectrum for [PC($SiPh_3$)P]PdH (**5**)..... S39
3.4 NMR Spectra for [PC(H)P]Pd($SiHPh_2$) (**7**) S40
Figure S22. ^{1}H NMR spectrum for [PC(H)P]Pd($SiHPh_2$) (**7**)..... S40
Figure S23. ^{31}P{^{1}H} NMR spectrum for [PC(H)P]Pd($SiHPh_2$) (**7**) S41
Figure S24. ^{13}C{^{1}H} NMR spectrum for [PC(H)P]Pd($SiHPh_2$) (**7**) S42
Figure S25. ^{29}Si{^{1}H} NMR spectrum for [PC(H)P]Pd($SiHPh_2$) (**7**)..... S43
3.5 NMR Spectra for [PC(H)P]Pd($SiPh_3$) (**8**) S44
Figure S26. ^{1}H NMR spectrum for [PC(H)P]Pd($SiPh_3$) (**8**)..... S44
Figure S27. ^{31}P{^{1}H} NMR spectrum for [PC(H)P]Pd($SiPh_3$) (**8**) S45
Figure S28. ^{13}C{^{1}H} NMR spectrum for [PC(H)P]Pd($SiPh_3$) (**8**) S46
Figure S29. ^{29}Si{^{1}H} NMR spectrum for [PC(H)P]Pd($SiPh_3$) (**8**)..... S47
Figure S30. ^{1}H-^{13}C HSQC NMR spectrum for [PC(H)P]Pd($SiPh_3$) (**8**) S48
Figure S31. ^{31}P{^{1}H} NMR spectrum for [PC(H)P]Pd(PMe_3)($SiPh_3$) (**14**) S49
3.6 NMR Spectra for [PC(Bpin)P]PdH (**9**) S50
Figure S32. ^{1}H NMR spectrum for [PC(Bpin)P]PdH (**9**)..... S50
Figure S33. ^{31}P{^{1}H} NMR spectrum for [PC(Bpin)P]PdH (**9**) S51
Figure S34. ^{13}C{^{1}H} NMR spectrum for [PC(Bpin)P]PdH (**9**)..... S52
Figure S35. ^{11}B NMR spectrum for [PC(Bpin)P]PdH (**9**)..... S53
Figure S36. ^{1}H-^{13}C HSQC NMR spectrum for [PC(Bpin)P]PdH (**9**)..... S54
Figure S37. ^{1}H-^{1}H COSY NMR spectrum for [PC(Bpin)P]PdH (**9**) S55
3.7 NMR Spectra for [PC(H)P]Pd(GeH_2Ph) (**10**) S56
Figure S38. ^{1}H NMR spectrum for [PC(H)P]Pd(GeH_2Ph) (**10**) S56

Figure S39. $^{31}P\{^{1}H\}$ NMR spectrum for [PC(H)P]Pd(GeH_2Ph) (**10**) S57
Figure S40. $^{13}C\{^{1}H\}$ NMR spectrum for [PC(H)P]Pd(GeH_2Ph) (**10**) S58
Figure S41. ^{1}H-^{13}C HSQC NMR spectrum for [PC(H)P]Pd(GeH_2Ph) (**10**) S59
Figure S42. ^{1}H-^{1}H COSY NMR spectrum for [PC(H)P]Pd(GeH_2Ph) (**10**) S60
3.8 NMR Spectra for [PC(H)P]Pd($GeHPh_2$) (**11**) S61
Figure S43. ^{1}H NMR spectrum for [PC(H)P]Pd($GeHPh_2$) (**11**) S61
Figure S44. $^{31}P\{^{1}H\}$ NMR spectrum for [PC(H)P]Pd($GeHPh_2$) (**11**) S62
Figure S45. $^{13}C\{^{1}H\}$ NMR spectrum for [PC(H)P]Pd($GeHPh_2$) (**11**) S63
Figure S46. ^{1}H-^{13}C HSQC NMR spectrum for [PC(H)P]Pd($GeHPh_2$) (**11**) S64
3.9 NMR Spectra for [PC(H)P]Pd($GePh_3$) (**12**) S65
Figure S47. ^{1}H NMR spectrum for [PC(H)P]Pd($GePh_3$) (**12**) S65
Figure S48. $^{31}P\{^{1}H\}$ NMR spectrum for [PC(H)P]Pd($GePh_3$) (**12**) S66
Figure S49. $^{13}C\{^{1}H\}$ NMR spectrum for [PC(H)P]Pd($GePh_3$) (**12**) S67
Figure S50. ^{1}H-^{13}C HSQC NMR spectrum for [PC(H)P]Pd($GePh_3$) (**12**) S68
Figure S51. ^{1}H-^{1}H COSY NMR spectrum for [PC(H)P]Pd($GePh_3$) (**12**) S69
3.10 NMR Spectra for [PC(H)P]Pd(PMe_3)(GeH_2Ph) (**15**) S70
Figure S52. $^{31}P\{^{1}H\}$ NMR spectrum for [PC(H)P]Pd(PMe_3)(GeH_2Ph) (**15**) S70
3.11 NMR Spectra for [PC(H)P]Pd(PMe_3)($GeHPh_2$) (**13**) S71
Figure S53. ^{1}H NMR spectrum for [PC(H)P]Pd(PMe_3)($GeHPh_2$) (**13**) S71
Figure S54. $^{31}P\{^{1}H\}$ NMR spectrum for [PC(H)P]Pd(PMe_3)($GeHPh_2$) (**13**) S72

4 Crystallographic Tables **S73**
4.1 Crystal data for [PC(SiH_2Ph)P]PdH (**3**) S73
Figure S55. Thermal-ellipsoid representation of **3** S73
Table S1. Crystal data and structure refinement for **3** S74
Table S2. Atomic coordinates and equivalent isotropic displacement parameters ($Å^2$) for **3** S75
Table S3. Anisotropic displacement parameters ($Å^2$) for **3** S77
Table S4. Distances [Å] for **3** S78
Table S5. Angles [°] for **3** S79
4.2 Crystal data for [PC($SiHPh_2$)P]PdH (**4**) S81
Figure S56. Thermal-ellipsoid representation of **4** S81
Table S6. Crystal data and structure refinement for **4** S82
Table S7. Atomic coordinates and equivalent isotropic displacement parameters ($Å^2$) for **4** S83
Table S8. Anisotropic displacement parameters ($Å^2$) for **4** S86
Table S9. Distances [Å] for **4** S88
Table S10. Angles [°] for **4** S90
4.3 Crystal data for [PC($SiPh_3$)P]PdH (**5**) S93
Figure S57. Thermal-ellipsoid representation of **5** S93
Table S11. Crystal data and structure refinement for **5** S94
Table S12. Atomic coordinates and equivalent isotropic displacement parameters ($Å^2$) for **5** S95
Table S13. Anisotropic displacement parameters ($Å^2$) for **5** S98
Table S14. Distances [Å] for **5** S100

Table S15. Angles [°] for **5** S102
4.4 Crystal data for [PC(H)P]Pd($SiPh_3$)·C_5H_{12} (**8·C_5H_{12}**) S105
Figure S58. Thermal-ellipsoid representation of **8·C_5H_{12}** S105
Table S16. Crystal data and structure refinement for **8·C_5H_{12}** S106
Table S17. Atomic coordinates and equivalent isotropic displacement parameters ($Å^2$) for **8·C_5H_{12}** S107
Table S18. Anisotropic displacement parameters ($Å^2$) for **8·C_5H_{12}** S111
Table S19. Distances [Å] for **8·C_5H_{12}** S113
Table S20. Angles [°] for **8·C_5H_{12}** S115
4.5 Crystal data for [PC(Bpin)P]PdH (**9**) S118
Figure S59. Thermal-ellipsoid representation of **9** S118
Table S21. Crystal data and structure refinement for **9** S119
Table S22. Atomic coordinates and equivalent isotropic displacement parameters ($Å^2$) for **9** S120
Table S23. Anisotropic displacement parameters ($Å^2$) for **9** S123
Table S24. Distances [Å] for **9** S124
Table S25. Angles [°] for **9** S126
4.6 Crystal data for [PC(H)P]Pd(GeH_2Ph) (**10**) S129
Figure S60. Thermal-ellipsoid representation of **10** S129
Table S26. Crystal data and structure refinement for **10** S130
Table S27. Atomic coordinates and equivalent isotropic displacement parameters ($Å^2$) for **10** S131
Table S28. Anisotropic displacement parameters ($Å^2$) for **10** S133
Table S29. Distances [Å] for **10** S134
Table S30. Angles [°] for **10** S135
4.7 Crystal data for [PC(H)P]Pd($GeHPh_2$) (**11**) S137
Figure S61. Thermal-ellipsoid representation of **11** S137
Table S31. Crystal data and structure refinement for **11** S138
Table S32. Atomic coordinates and equivalent isotropic displacement parameters ($Å^2$) for **11** S139
Table S33. Anisotropic displacement parameters ($Å^2$) for **11** S142
Table S34. Distances [Å] for **11** S144
Table S35. Angles [°] for **11** S146
4.8 Crystal data for [PC(H)P]Pd($GePh_3$) (**12**) S149
Figure S62. Thermal-ellipsoid representation of **12** S149
Table S36. Crystal data and structure refinement for **12** S150
Table S37. Atomic coordinates and equivalent isotropic displacement parameters ($Å^2$) for **12** S151
Table S38. Anisotropic displacement parameters ($Å^2$) for **12** S154
Table S39. Distances [Å] for **12** S156
Table S40. Angles [°] for **12** S158
4.9 Crystal data for [PC(H)P]Pd(PMe_3)($GeHPh_2$)·0.5C_5H_{12} (**13·0.5C_5H_{12}**) S161
Figure S63. Thermal-ellipsoid representation of **13·C_5H_{12}** S161
Table S41. Crystal data and structure refinement for **13·C_5H_{12}** S162

Table S42. Atomic coordinates and equivalent isotropic displacement parameters ($Å^2$) for **13**·C_5H_{12} S163
Table S43. Anisotropic displacement parameters ($Å^2$) for **13**·C_5H_{12} S166
Table S44. Distances [Å] for **13**·C_5H_{12} S168
Table S45. Angles [°] for **13**·C_5H_{12} S170

1 Experimental

1.1 General remarks

All experiments are performed under an inert atmosphere of N_2 using standard glovebox techniques. Hexanes, *n*-pentane and diethylether were dried by passing through a column of activated alumina and stored in the glovebox. THF was dried over $LiAlH_4$ followed by vacuum transfer and stored in the glovebox. C_6D_6 was dried over CaH_2 followed by vacuum transfer, and stored in the glovebox. [PC(sp^2)P]Pd(PMe_3) (**1**) and [PC(sp^2)P]Pd(PPh_3) (**2**) were prepared according to literature procedures.[1] All other materials were used as received. ^{1}H, $^{13}C\{^{1}H\}$, $^{31}P\{^{1}H\}$ and $^{29}Si\{^{1}H\}$NMR spectra were recorded on Bruker DRX 400 or 500 spectrometer. All chemical shifts were reported in δ units with references to the residual solvent resonance of the deuterated solvents for proton and carbon chemical shifts or to external H_3PO_4 for $^{31}P\{^{1}H\}$ NMR. CHN analyses were performed on a CE-440 Elemental Analyzer or by Midwest Microlab. Gaussian 03 (revision D.02) was used for all reported calculations.[2] The B3LYP (DFT) method was used to carry out the geometry optimizations on model compounds specified in text using the LANL2DZ basis set. The validity of the true minima was checked by the absence of negative frequencies in the energy Hessian.

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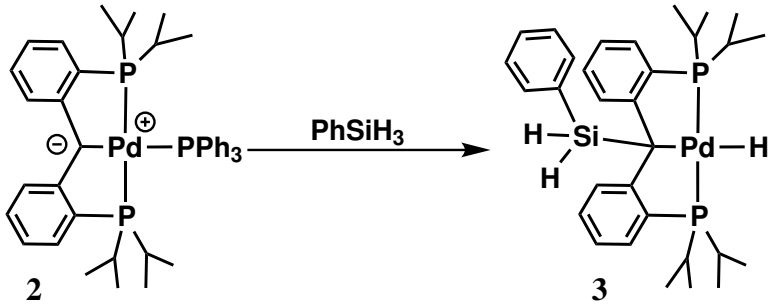
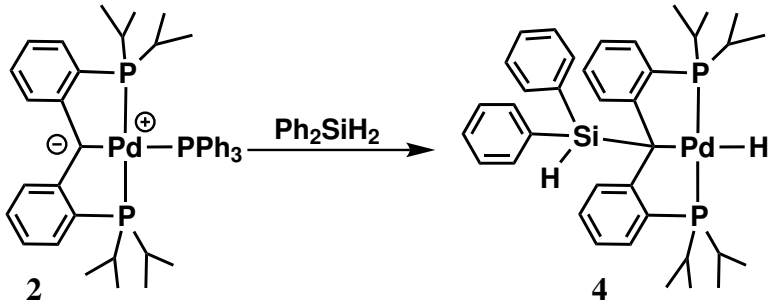
1.3 Synthesis of [PC(SiH$_2$Ph)P]PdH (3)



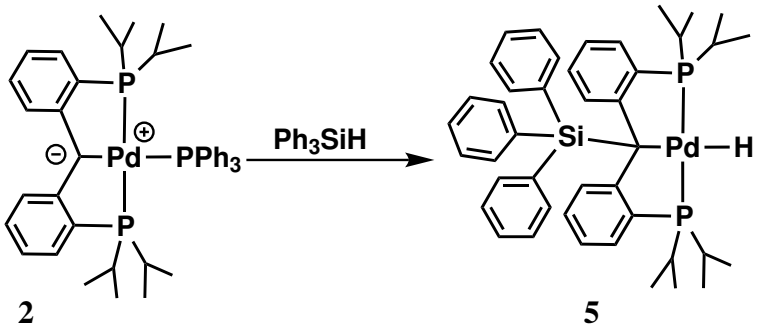
In a 20 mL scintillation vial, 76.7 mg of [PC(sp^2)P]Pd(PPh$_3$) (**2**, 0.1 mmol) was stirred in 5 mL of THF prior to the addition of a 1 mL solution of PhSiH$_3$ (0.1 M in THF) at room temperature. The color became off-white within 3 min. The ^{1}H and ^{31}P{^{1}H} NMR spectra of the crude mixture showed the formation of the product, [PC(SiH$_2$Ph)P]PdH (**3**), and PPh$_3$. The volatiles were removed under reduced pressure and the resulted solid was extracted with *n*-pentane and filtered. After removing the volatiles under reduced pressure again, the product was obtained as an off-white solid. Recrystallization was performed at -35 °C from a concentrated Et$_2$O solution, in order to remove PPh$_3$, yielding after 3 recrystallizations an analytically pure product in moderate yield (60%, 36.8 mg). **For 3**: ^{1}H NMR (500 MHz, C$_6$D$_6$, 298 K) δ 7.76 (dd, *J* = 8.1, 1.0 Hz, 2H, Ar*H*), 7.24 (dtd, *J* = 5.4, 4.1, 1.4 Hz, 2H, Ar*H*), 7.22 – 7.19 (m, 2H, Ar*H*), 7.14 – 7.02 (m, 5H, Ar*H*), 6.94 (t, *J* = 7.3 Hz, 2H, Ar*H*), 5.19 (td, *J* = 2.6, 0.6 Hz, 2H, C–SiPh*H*$_2$), 2.45 (dqd, *J* = 10.4, 7.1, 3.4 Hz, 2H, –C*H*(CH$_3$)$_2$), 2.06 (ddq, *J* = 10.7, 6.7, 4.0 Hz, 2H, –C*H*(CH$_3$)$_2$), 1.33 (q, *J* = 7.2 Hz, 6H, –CH(C*H*$_3$)$_2$), 1.25 – 1.16 (m, 6H, –CH(C*H*$_3$)$_2$), 1.20 – 1.11 (m, 6H, –CH(C*H*$_3$)$_2$), 0.68 (dt, *J* = 7.8, 7.0 Hz, 6H, –CH(C*H*$_3$)$_2$), −5.32 (t, $^2J_{HP}$ = 11.9 Hz, 1H, Pd–*H*). ^{31}P{^{1}H} NMR (202 MHz, C$_6$D$_6$, 298 K) δ 61.12 (s). ^{13}C{^{1}H} NMR (126 MHz, C$_6$D$_6$, 298 K) δ 159.48 (t, *J* = 13.5 Hz, Ar*C*), 137.51 (t, *J* = 17.1 Hz, Ar*C*), 136.80 (s, Ar*C*), 135.90 (s, Ar*C*), 132.71 (s, Ar*C*), 129.65 (s, Ar*C*), 128.95 (t, *J* = 7.5 Hz, Ar*C*), 128.78 (s, Ar*C*), 127.57 (s, Ar*C*), 123.16 (t, *J* = 3.3 Hz, Ar*C*), 60.40 (s, Ar$_2$*C*–SiPhH$_2$), 26.41 (t, *J* = 11.6 Hz, –*C*H(CH$_3$)$_2$), 26.26 (t, *J* = 13.1 Hz, –*C*H(CH$_3$)$_2$), 21.97 (t, *J* = 4.0 Hz, –CH(*C*H$_3$)$_2$), 19.38 (t, *J* = 3.8 Hz, –CH(*C*H$_3$)$_2$), 19.31 (t, *J* = 1.8 Hz, –CH(*C*H$_3$)$_2$), 19.10 (t, *J* = 1.5 Hz, –CH(*C*H$_3$)$_2$). ^{29}Si{^{1}H} NMR (79 MHz, C$_6$D$_6$, 298 K) δ −31.20 (s). Anal. Calcd. for C$_{31}$H$_{44}$P$_2$PdSi: C, 60.73; H, 7.23. Found: C, 60.91; H, 7.05.

1.4 Synthesis of [PC(SiHPh$_2$)P]PdH (4)



76.7 mg of [PC(sp^2)P]Pd(PPh$_3$) (**2**, 0.1 mmol) was dissolved in 5 mL of THF in a 20 mL scintillation vial. To this mixture, 1 mL of Ph_2SiH_2 (0.1 M solution in THF) was added at room temperature. After 30 minutes, the volatiles were removed under reduced pressure to generate a cream powder. The ^{1}H and ^{31}P{^{1}H} NMR spectra of the crude mixture showed the formation of the product, [PC(SiHPh$_2$)P]PdH (**4**), and PPh_3. Analytically pure [PC(SiHPh$_2$)P]PdH (**4**) was isolated after several recrystallizations from a concentrated Et_2O solution at −35 °C in 67% yield, (46.2 mg). **For 4**: ^{1}H NMR (500 MHz, C_6D_6, 298 K) δ 7.72 (dd, *J* = 8.1, 1.4 Hz, 2H, Ar*H*), 7.23 (dtd, *J* = 7.8, 4.0, 1.5 Hz, 2H, Ar*H*), 7.13 (d, *J* = 1.7 Hz, 2H, Ar*H*), 7.12 (d, *J* = 1.9 Hz, 2H, Ar*H*), 7.11 – 7.07 (m, 2H, Ar*H*), 7.06 – 7.01 (m, 6H, Ar*H*), 6.96 (t, *J* = 7.5 Hz, 2H, Ar*H*), 6.00 (t, *J* = 4.29 Hz, 1H, C–Si*H*Ph$_2$), 2.13 (ddh, *J* = 10.7, 7.2, 3.5 Hz, 2H, –C*H*(CH$_3$)$_2$), 1.99 (ttd, *J* = 9.6, 5.5, 4.8, 2.9 Hz, 2H, –C*H*(CH$_3$)$_2$), 1.21 (q, *J* = 6.9 Hz, 6H, –CH(C*H*$_3$)$_2$), 1.10 (td, *J* = 8.3, 6.7 Hz, 6H, –CH(C*H*$_3$)$_2$), 1.03 (td, *J* = 9.0, 7.4 Hz, 6H, –CH(C*H*$_3$)$_2$), 0.59 (td, *J* = 7.7, 6.9 Hz, 6H, –CH(C*H*$_3$)$_2$), −5.71 (t, $^2J_{HP}$ = 11.7 Hz, 1H, Pd–*H*). ^{31}P{^{1}H} NMR (202 MHz, C_6D_6, 298 K) δ 60.32(s). ^{13}C{^{1}H} NMR (126 MHz, C_6D_6, 298 K) δ 158.87 (t, *J* = 13.5 Hz, Ar*C*), 139.00 (t, *J* = 16.8 Hz, Ar*C*), 138.16 (s, Ar*C*), 136.21(s, Ar*C*) , 132.94 (s, Ar*C*), 129.83 (s, Ar*C*), 129.59 (t, *J* = 7.4 Hz, Ar*C*), 128.87 (s, Ar*C*), 127.80 (s, Ar*C*), 123.48 (t, *J* = 3.2 Hz, Ar*C*), 62.22 (s, Ar$_2$*C*–SiHPh$_2$), 26.21 (t, *J* = 11.1 Hz, –*C*H(CH$_3$)$_2$), 25.98 (t, *J* = 12.8 Hz, –*C*H(CH$_3$)$_2$), 22.76 (t, *J* = 4.9 Hz, –CH(*C*H$_3$)$_2$), 19.60 (t, *J* = 4.0 Hz, –CH(*C*H$_3$)$_2$), 19.31 (s, –CH(*C*H$_3$)$_2$), 18.79 (s, –CH(*C*H$_3$)$_2$). ^{29}Si{^{1}H} NMR (79 MHz, C_6D_6, 298 K) δ −20.72 (s). Anal. Calcd. for $C_{37}H_{48}P_2PdSi$: C, 64.48; H, 7.02. Found: C, 64.19; H, 6.72.

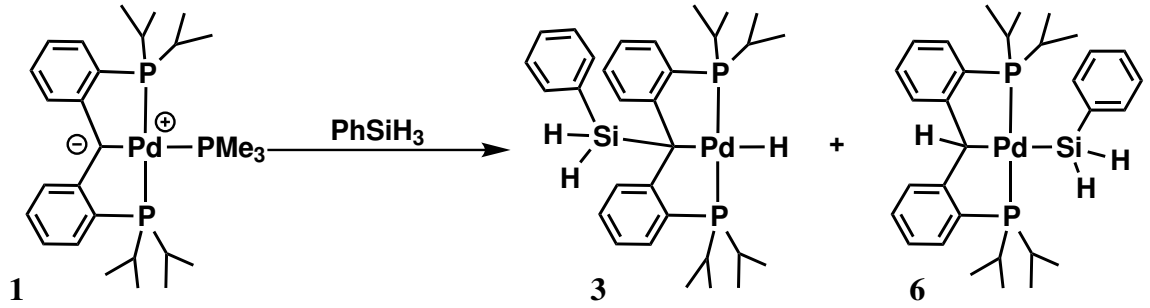
1.5 Synthesis of [PC(SiPh$_3$)P]PdH (5)



2 **5**

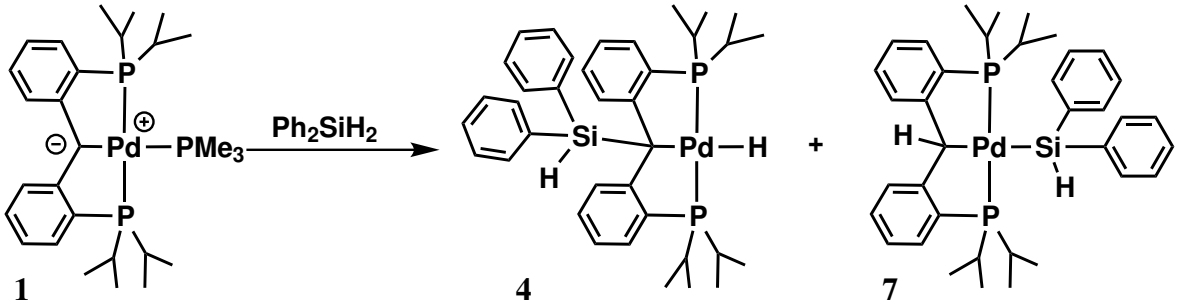
61.4 mg of [PC(sp^2)P]Pd(PPh$_3$) (**2**, 0.08 mmol) was dissolved in 5 mL of THF and then 0.8 mL of Ph$_3$SiH (0.1 M solution in Et$_2$O) was added. The reaction mixture was stirred at room temperature. The reaction mixture remained brown for 36 hours but became progressively lighter afterwards and, after 72 hours, the solution was light yellow. In a separate experiment heating the reaction mixture to 70 °C did not lead to an increase in yield and produced side-products. After 72 hours, the volatiles were removed under reduced pressure and the residue was triturated 3 times with 5 mL of *n*-pentane. ^{1}H and ^{31}P{^{1}H} NMR spectra of this residue showed the reaction to be complete, and to contain the product, [PC(SiPh$_3$)P]PdH (**5**) and PPh$_3$. Successive recrystallizations from a concentrated *n*-pentane solution afforded **5**, as a light yellow solid, in good yield (38.5 mg, 63%). **For 5**: ^{1}H NMR (400 MHz, C$_6$D$_6$, 298 K) δ 7.87 (d, *J* = 8.1 Hz, 2H, Ar*H*), 7.41 – 7.35 (m, 6H, Ar*H*), 7.22 – 7.17 (m, 2H, Ar*H*), 7.09 – 7.04 (m, 9H, Ar*H*), 6.97 (m, 4H, Ar*H*), 2.09 – 1.94 (m, 2H, –C*H*(CH$_3$)$_2$), 1.36 (dd, *J* = 7.0, 3.4 Hz, 2H, –C*H*(CH$_3$)$_2$), 1.29 – 1.19 (m, 6H, –CH(C*H*$_3$)$_2$), 1.16 – 1.08 (m, 6H, –CH(C*H*$_3$)$_2$), 1.05 (q, *J* = 6.8 Hz, 6H, –CH(C*H*$_3$)$_2$), 0.60 – 0.45 (m, 6H, –CH(C*H*$_3$)$_2$), −5.84 (t, $^2J_{HP}$ = 9.1 Hz, 1H, Pd–*H*). ^{31}P{^{1}H} NMR (162 MHz, C$_6$D$_6$, 298 K) δ 58.61(s). ^{13}C{^{1}H} NMR (101 MHz, C$_6$D$_6$, 298 K) δ 160.52 (t, *J* = 14.2 Hz, Ar*C*), 140.25 (t, *J* = 17.1 Hz, Ar*C*), 139.36 (s, Ar*C*), 138.30 (s, Ar*C*) , 134.29 (d, *J* = 18.1 Hz, Ar*C*), 132.97 (s, Ar*C*), 132.48 (t, *J* = 7.6 Hz, Ar*C*), 129.12 (s, Ar*C*), 128.48 (s, Ar*C*), 127.27 (s, Ar*C*), 123.67 (t, *J* = 3.2 Hz, Ar*C*), 65.45 (s, Ar$_2$*C*–SiPh$_3$), 26.88 (t, *J* = 10.9 Hz, –*C*H(CH$_3$)$_2$), 25.88 (t, *J* = 13.3 Hz, –*C*H(CH$_3$)$_2$), 23.33 (t, *J* = 4.1 Hz, –CH(*C*H$_3$)$_2$), 20.25 (t, *J* = 4.0 Hz, –CH(*C*H$_3$)$_2$), 19.96 (t, *J* = 2.0 Hz, –CH(*C*H$_3$)$_2$), 18.42 (s, –CH(*C*H$_3$)$_2$). ^{29}Si{^{1}H} NMR (79 MHz, C$_6$D$_6$, 298 K) δ −9.01 (s). Anal. Calcd. For C$_{43}$H$_{52}$P$_2$PdSi C, 67.48; H, 6.85; Found: C, 67.41; H, 6.98.

1.6 Reaction of of [PC(sp^2)P]Pd(PMe$_3$) (1) with PhSiH$_3$



Starting from 58.1 mg of [PC(sp^2)P]Pd(PMe$_3$) (**1**, 0.1 mmol) and following the procedure used for the reaction of [PC(sp^2)P]Pd(PPh$_3$) (**2**) with PhSiH$_3$, [PC(SiH$_2$Ph)P]PdH (**3**) was obtained in 90% yield (as assessed by ^{1}H and ^{31}P{^{1}H} NMR spectroscopy), and small traces (less than 5%) of the other isomer, [PC(H)P]Pd(SiH$_2$Ph) (**6**) could be detected in the crude mixture. Crystallization from a concentrated *n*-pentane solution yielded an analytically pure sample of [PC(SiH$_2$Ph)P]PdH (**3**), isolated in 82% yield (50.3 mg). **For 6**: ^{1}H NMR (500 MHz, C_6D_6, 298 K) δ 6.18 (s, Ar_2C*H*-Pd). ^{31}P{^{1}H} NMR (202 MHz, C_6D_6, 298 K) δ 53.51 (s).

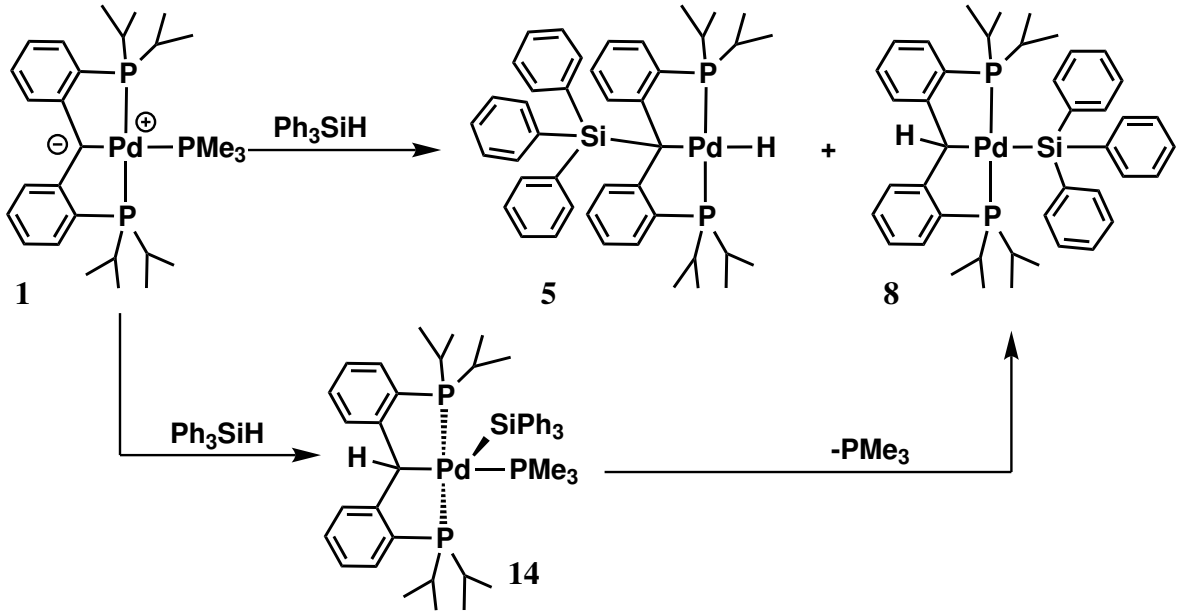
1.7 Reaction of of [PC(sp^2)P]Pd(PMe$_3$) (1) with Ph$_2$SiH$_2$



In a 20 mL scintillation vial, 58.1 mg of [PC(sp^2)P]Pd(PMe$_3$) (**1**, 0.1 mmol) was dissolved in 5 mL of THF and cooled to −78 °C. To this solution, 1 mL of Ph$_2$SiH$_2$ (0.1 M solution in THF) was added at −78 °C and the reaction mixture was stirred for 2 hours at this temperature. The mixture turned light orange. The volatiles were removed under reduced pressure, and a 2:1 molar ratio formed as indicated by ^{1}H and ^{31}P{^{1}H} NMR spectroscopy, the major component being [PC(SiHPh$_2$)P]PdH (**4**), while the minor product was its isomer, [PC(H)P]Pd(SiHPh$_2$) (**7**). Running the reaction at room temperature for 2 hours resulted in a [PC(SiHPh$_2$)P]PdH (**4**) to [PC(H)P]Pd(SiHPh$_2$) (**7**) molar ratio of 1:2. No other intermediates were identified in the crude reaction mixture. Recrystallization at −35 °C from a concentrated Et$_2$O solution of either reaction mixture only afforded the [PC(SiHPh$_2$)P]PdH (**4**) isomer, as an off-white solid, in 53% (from the reaction ran at room temperature, 36.5 mg), and 26.2% (from the reaction ran at −78 °C, 18.1 mg) yield, respectively. After successive crystallizations, the major component of the mother liquor by ^{1}H and ^{31}P{^{1}H} NMR spectroscopy was [PC(H)P]Pd(SiHPh$_2$) (**7**) but it still contained the hydride isomer [PC(SiHPh$_2$)P]PdH (**4**) as an impurity. Isolated yield for **7**: 15% (−78 °C reaction, 10.3 mg) and 32% (room temperature reaction, 22.1 mg). **For 7**: ^{1}H NMR (500 MHz, C_6D_6, 298 K) δ 7.93 (dd,

J = 7.9, 1.3 Hz, 4H, ArH), 7.53 (d, J = 7.9 Hz, 2H, ArH), 7.22 (t, J = 7.3 Hz, 4H, ArH), 7.20 – 7.16 (m, 2H, ArH), 7.14 – 7.12 (m, 2H, ArH), 7.04 – 7.00 (m, 2H, ArH), 6.88 (t, J = 7.4 Hz, 2H, ArH), 5.86 (s, 1H, Ar_2CH–Pd), 5.71 (t, $^3J_{HP}$= 9.1 Hz, 1H, Pd–SiHPh$_2$), 2.27 – 2.18 (m, 2H, –CH(CH$_3$)$_2$), 2.18 – 2.13 (m, 2H, –CH(CH$_3$)$_2$), 1.01 (dd, J = 16.0, 7.8 Hz, 12H, –CH(CH_3)$_2$), 0.88 (dd, J = 14.3, 7.1 Hz, 9H, –CH(CH_3)$_2$), 0.84 (dd, J = 13.2, 6.5 Hz, 3H, –CH(CH_3)$_2$). ^{31}P{^{1}H} NMR (202 MHz, C_6D_6, 298 K) δ 54.78 (s). ^{13}C{^{1}H} NMR (126 MHz, C_6D_6, 298 K) δ 159.09 (t, J = 13.9 Hz, ArC), 146.64 (s, ArC), 137.37 (s, ArC), 136.98 (s, ArC), 132.33 (s, ArC), 130.11 (s, ArC), 127.98 (s, ArC), 127.35 (s, ArC), 127.30 (s, ArC), 123.92 (t, J = 3.2 Hz, ArC), 67.33 (s, Ar_2CH–Pd), 26.41 (t, J = 11.2 Hz, –CH(CH$_3$)$_2$), 25.98 (t, J = 13.1 Hz, –CH(CH$_3$)$_2$), 19.86 (t, J = 2.9 Hz, –CH(CH$_3$)$_2$), 19.64 (t, J = 2.4 Hz, –CH(CH$_3$)$_2$), 18.32 (s, –CH(CH$_3$)$_2$), 18.17(s, –CH(CH$_3$)$_2$). ^{29}Si{^{1}H} NMR (99 MHz, C_6D_6, 298 K) δ −10.06 (t, $^2J_{SiP}$ = 45.0, 21.7 Hz).

1.8 Reaction of of [PC(sp^2)P]Pd(PMe$_3$) (1) with Ph$_3$SiH



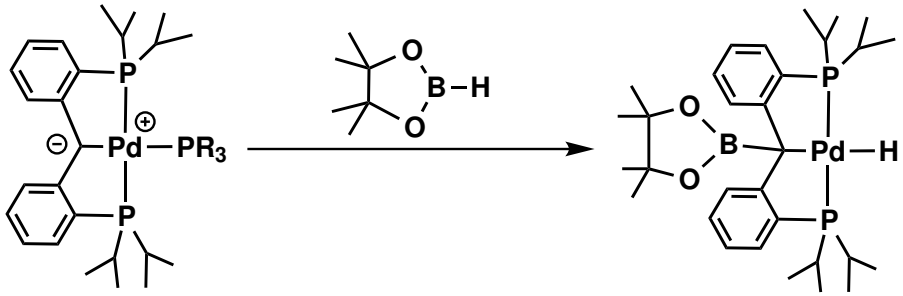
In a 20 mL scintillation vial, 58.1 mg of [PC(sp^2)P]Pd(PMe$_3$) (**1**, 0.1 mmol) was stirred in 5 mL of toluene with 26.8 mg of Ph$_3$SiH. Aliquots taken from the reaction mixture (after 1, 3, and 6 hours) showed that no reaction occurred at room temperature. The mixture was then transferred to a Schlenk flask, brought outside of the box, heated at 72 °C and the aliquots of the reaction mixture were checked by ^{1}H and ^{31}P{^{1}H} NMR spectroscopy every 12 hours. The intermediate [PC(H)P]Pd(PMe$_3$)(SiPh$_3$) (**14**) was also observed in the ^{31}P{^{1}H} NMR spectrum. Complete conversion occurred after 6 days at 72 °C. ^{1}H and ^{31}P{^{1}H} NMR data showed that all carbene converted to the product, along with PMe$_3$ and small amounts of the isomer [PC(SiPh$_3$)P]PdH (**5**). Multiple recrystallizations from a concentrated *n*-pentane solution at -35 °C were necessary to isolate analytically pure **8** as a yellow solid. Yield: 47% yield (36.0 mg). **For 8**: ^{1}H NMR (400 MHz, C_6D_6, 298 K) δ 7.99 (dd, J = 8.0, 1.4 Hz, 6H, ArH), 7.43 (d, J = 7.9 Hz, 2H, ArH), 7.23 – 7.07 (m, 13H, ArH), 6.85 (t, J = 7.4 Hz, 2H, ArH), 6.04 (s, 1H, Ar_2CH–Pd), 2.00 – 1.85 (m, 2H, –CH(CH$_3$)$_2$), 1.68 (m, –CH(CH$_3$)$_2$), 1.02 – 0.95 (m, 6H, –CH(CH_3)$_2$), 0.95 – 0.86 (m, 12H, –CH(CH_3)$_2$), 0.83

(q, J = 6.9 Hz, 6H, –CH(CH_3)$_2$). ^{31}P{^{1}H} NMR (162 MHz, C_6D_6, 298 K) δ 53.11 (s). ^{13}C{^{1}H} NMR (101 MHz, C_6D_6, 298 K) δ 158.82 (t, J = 13.7 Hz, Ar*C*), 148.40 (s, Ar*C*), 138.03 (s, Ar*C*), 136.93 (t, J = 17.4 Hz, Ar*C*), 132.90 (s, Ar*C*), 130.03 (s, Ar*C*), 127.85 (t, J = 8.2 Hz, Ar*C*), 127.31 (s, Ar*C*), 127.12 (s, Ar*C*), 123.69 (t, J = 3.2 Hz, Ar*C*), 67.22 (s, Ar$_2$*C*H–Pd), 26.04 (t, J = 12.3 Hz, –*C*H(CH$_3$)$_2$), 26.05 – 25.80 (m, –*C*H(CH$_3$)$_2$), 21.37 (t, J = 3.6 Hz, –CH(*C*H$_3$)$_2$), 20.22 (t, J = 2.5 Hz, –CH(*C*H$_3$)$_2$), 18.50 (s, –CH(*C*H$_3$)$_2$), 18.21 (s, –CH(*C*H$_3$)$_2$). ^{29}Si{^{1}H} NMR (79 MHz, C_6D_6, 298 K) δ 2.20 (t, $^2J_{SiP}$ = 20.7 Hz). Anal. Calcd. for $C_{43}H_{52}P_2PdSi$: C, 67.48; H, 6.85. Found: 67.12; H, 7.16. **For 14**: ^{31}P{^{1}H} NMR (162 MHz, C_6D_6) δ 25.93 (d, $^2J_{PP}$ = 97.2 Hz, Pd–*P*^{i}Pr$_2$), −38.58 (t, $^2J_{PP}$ = 97.2 Hz, Pd–*P*(CH$_3$)$_3$).

1.9 Thermolysis of the hydrides 3-5

A solution of the corresponding hydride (**3**: 6.1 mg, **4**: 6.9 mg, **5**: 7.6 mg) in 0.7 mL of C_6D_6 was monitored at room temperature for 5 days. No decomposition was observed. At 72 °C, the hydrides decomposed into several unidentified products over the course of 48 hours. No silyl isomers were observed. The experiment was repeated in the presence of one equivalent of PMe_3 or PPh_3. In all cases no reaction was observed at room temperature. At 72 °C, in the presence of phosphines the hydrides decompose. No isomerisation to the corresponding silyl isomers was observed.

1.10 Synthesis of [PC(Bpin)P]PdH (9)



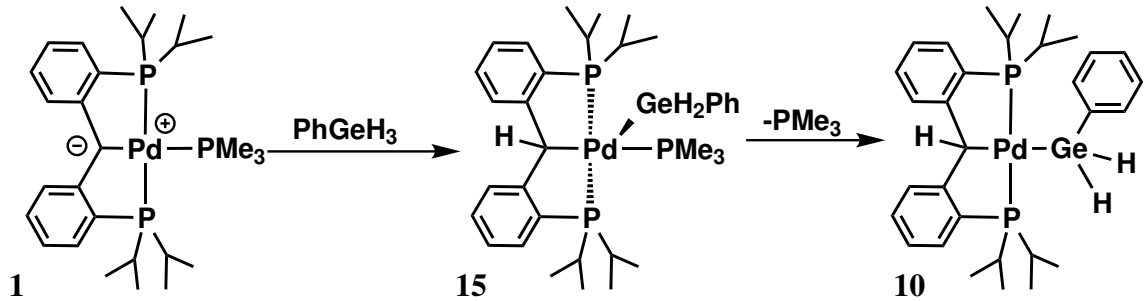
1: R = Me
2: R = Ph

9

In a 20 mL scintillation vial, 58.1 mg of [PC(sp^2)P]Pd(PMe$_3$) (**1**, 0.1 mmol) was dissolved in 5 mL of THF prior to the addition of a 1 mL solution of 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (pinacolborane, 0.1 M in THF). The solution turned immediately lighter in color (from dark brown to yellow). After 5 additional minutes, the reaction mixture was light yellow. The volatiles were removed under reduced pressure and the solids were triturated 3 times with *n*-pentane, yielding 58.9 mg of a cream powder of [PC(Bpin)P]PdH (**9**) in 93% yield (0.093 mmol). The ^{1}H and ^{31}P{^{1}H} NMR spectra showed this product to be pure. An analytically pure sample was obtained by crystallization from a saturated *n*-pentane solution at −35 °C. Alternatively, starting from 76.7 mg of [PC(sp^2)P]Pd(PPh$_3$) (**2**, 0.1 mmol) and following the same procedure, the same product [PC(Bpin)P]PdH (**9**) was obtained within 1 min, and was isolated in moderate yield (51%, 32.3 mg)

by repeated recrystallizations from a concentrated Et_2O solution. **For 9**: ^{1}H NMR (400 MHz, C_6D_6, 298 K) δ 7.88 (d, *J* = 8.1 Hz, 2H, Ar*H*), 7.28 (dtd, *J* = 5.2, 4.1, 1.2 Hz, 2H, Ar*H*), 7.22 (t, *J* = 7.5 Hz, 2H, Ar*H*), 6.91 (t, *J* = 7.3 Hz, 2H, Ar*H*), 3.08 – 2.89 (m, 2H, –C*H*$(CH_3)_2$), 2.25 – 2.04 (m, 2H, –C*H*$(CH_3)_2$), 1.43 – 1.33 (m, 12H, –CH(C*H*$_3)_2$), 1.19 (dt, *J* = 8.0, 6.9 Hz, 6H, –CH(C*H*$_3)_2$), 0.98 (s, 12H, B–OC(C*H*$_3)_2$), 0.72 (dd, *J* = 15.1, 7.1 Hz, 6H, –CH(C*H*$_3)_2$), -5.71 (t, $^2J_{HP}$ = 10.8 Hz, 1H, Pd–*H*). ^{31}P{^{1}H} NMR (162 MHz, C_6D_6, 298 K) δ 60.11 (s). ^{13}C{^{1}H} NMR (101 MHz, C_6D_6, 298 K) δ 160.18 (t, $^1J_{CP}$ = 14.2 Hz, Ar*C*), 138.45 (t, $^2J_{CP}$ = 17.9 Hz, Ar*C*), 131.98 (s, Ar*C*), 129.53 (s, Ar*C*), 128.75 (t, $^2J_{CP}$ = 7.6 Hz, Ar*C*), 122.84 (t, $^3J_{CP}$ = 3.3 Hz, Ar*C*), 81.72 (s, –O*C*$(CH_3)_2$), 26.07 (t, $^1J_{CP}$ = 11.2 Hz, –*C*H$(CH_3)_2$), 25.29 (t, $^1J_{CP}$ = 13.0 Hz, –*C*H$(CH_3)_2$), 25.01 (s, –OC(*C*H$_3)_2$), 22.58 (t, $^2J_{CP}$ = 4.6 Hz, –CH(*C*H$_3)_2$), 19.60 (t, $^2J_{CP}$ = 1.5 Hz, –CH(*C*H$_3)_2$), 19.51 (t, $^2J_{CP}$ = 3.8 Hz, –CH(*C*H$_3)_2$), 18.69 (s, –CH(*C*H$_3)_2$). ^{11}B NMR (128 MHz, C_6D_6, 298 K) δ 30.89 (s). Anal. Calcd. for $C_{31}H_{49}BO_2P_2Pd$: C, 58.83; H, 7.80. Found: C, 58.61; H, 7.55.

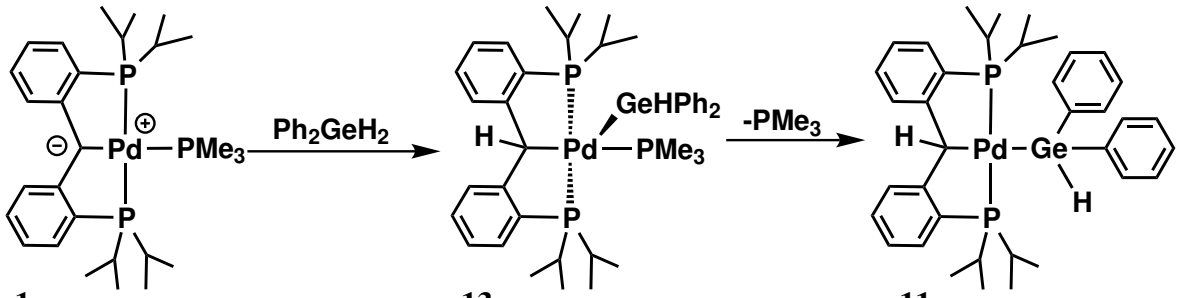
1.11 Synthesis of [PC(H)P]Pd(GeH$_2$Ph) (10)



58.1 mg of [PC(sp^2)P]Pd(PMe$_3$) (**1**, 0.1 mmol) was dissolved in 5 mL of THF in a scintillation vial. To this mixture, a solution of PhGeH$_3$ (1 mL, 0.1 M in Et_2O) was added dropwise. After 10 minutes of stirring at room temperature, a slight color change was observed. After 30 min this deep red reaction mixture turned yellow. The volatiles were removed under reduced pressure and the residue was triturated 3 times with 5 mL of *n*-pentane. 55.2 mg (0.084 mmol) of [PC(H)P]Pd(GeH$_2$Ph) (**10**) was obtained as a cream powder in 84% yield. The ^{1}H and ^{31}P{^{1}H} NMR showed the product to be pure. An analytically pure sample was obtained by recrystallization at −35 °C from a concentrated Et_2O solution. The ^{31}P{^{1}H} NMR of the aliquot of the reaction mixture taken after 10 minutes showed the presence of [PC(H)P]Pd(PMe$_3$)(GeH$_2$Ph) (**15**). This intermediate was not observed in the final crude reaction mixture. **For 10**: ^{1}H NMR (400 MHz, C_6D_6, 298 K) δ 8.01 (ddd, *J* = 7.4, 2.6, 1.4 Hz, 2H, Ar*H*), 7.49 7.45 (m, 2H, Ar*H*), 7.24 (t, *J* = 7.3 Hz, 2H, Ar*H*), 7.16 (dtd, *J* = 9.0, 3.9, 1.5 Hz, 2H, Ar*H*,), 7.13 – 7.08 (m, 3H, Ar*H*), 6.88 (tdt, *J* = 7.3, 1.9, 1.1 Hz, 2H, Ar*H*), 6.04 (s, 1H, Ar$_2$C*H*–Pd), 4.66 (t, *J* = 5.4 Hz, 2H, Pd–Ge*H*$_2$Ph), 2.54 2.26 (m, 4H, –C*H*$(CH_3)_2$), 1.12 (dq, *J* = 8.1, 7.2 Hz, 12H, –CH(C*H*$_3)_2$), 0.97 (dd, *J* = 14.0, 7.0 Hz, 6H, –CH(C*H*$_3)_2$), 0.89 (dd, *J* = 15.5, 7.1 Hz, 6H, –CH(C*H*$_3)_2$). ^{31}P{^{1}H} NMR (202 MHz, C_6D_6, 298 K) δ 57.07 (s). ^{13}C{^{1}H} NMR (101 MHz, C_6D_6, 298 K) δ 159.13 (t, *J* = 14.3 Hz, Ar*C*), 147.66 (s, Ar*C*), 137.36 (s, Ar*C*), 137.07 (t, *J* = 16.9 Hz, Ar*C*), 132.38 (s, Ar*C*), 130.22 (s, Ar*C*), 128.00 – 127.77 (m, Ar*C*), 127.51 (s, Ar*C*), 126.55 (s, Ar*C*), 124.28 (s, Ar*C*), 64.74 (s, Ar$_2$*C*H–Pd), 26.74 – 26.44 (m, –*C*H$(CH_3)_2$), 26.47 – 26.15 (m, –*C*H$(CH_3)_2$), 19.94 (s, –CH(*C*H$_3)_2$), 19.06 (s, –CH(*C*H$_3)_2$), 18.70 (s, –CH(*C*H$_3)_2$), 18.05 (s, –CH(*C*H$_3)_2$). Anal. Calcd. for $C_{31}H_{44}GeP_2Pd$:

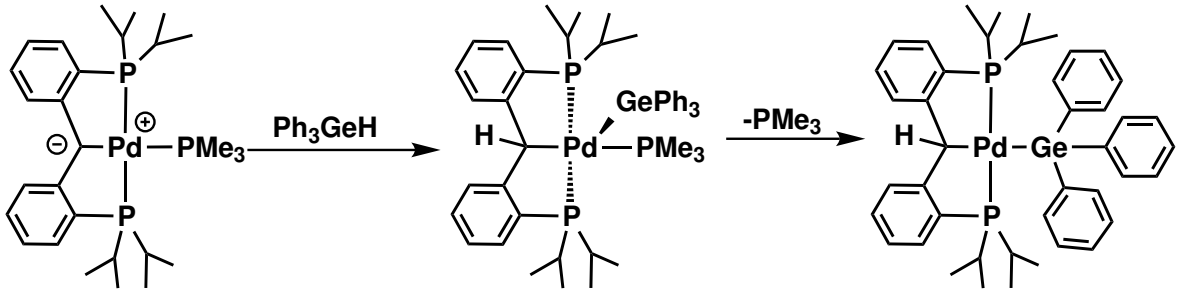
C, 56.61; H, 6.74. Found: C, 56.33; H, 6.52. **For 15**: $^{31}P\{^{1}H\}$ NMR (202 MHz, C_6D_6, 298 K) δ 32.09 (d, $^{2}J_{PP}$ = 32.0 Hz, Pd–$P^{i}Pr_2$), −21.13 (t, $^{2}J_{PP}$ = 32.0 Hz, Pd–$P(CH_3)_3$).

1.12 Synthesis of [PC(H)P]Pd(GeHPh$_2$) (11)



58.1 mg of [PC(sp^2)P]Pd(PMe_3) (**1**, 0.1 mmol) was added to a scintillation vial and dissolved in 5 mL of THF. To this mixture, 1 mL of a 0.1 M solution of Ph_2GeH_2 in THF was added afterwards and the reaction mixture was stirred at room temperature for 2 hours, during which time the color changed to light orange. The volatiles were removed under reduced pressure and the oily residue was triturated three times with *n*-pentane, yielding [PC(H)P]Pd(GeHPh$_2$) (**11**) as a waxy solid in 71% yield (53.6 mg). An analytically pure sample was obtained by cooling a concentrated Et_2O solution at -35 °C. The $^{31}P\{^{1}H\}$ NMR of an aliquot of the reaction mixture confirmed the presence of the intermediate [PC(H)P]Pd(PMe_3)(GeHPh$_2$) (**13**). This intermediate (**13**) undergoes a rapid conversion to the final product, **11**, in solution, but is stable at −35 °C in the solid state. **For 11**: ^{1}H NMR (500 MHz, C_6D_6, 298 K) δ 7.94 (dd, *J* = 7.9, 1.4 Hz, 4H, Ar*H*), 7.49 (d, *J* = 7.8 Hz, 2H, Ar*H*), 7.25 – 7.21 (m, 4H, Ar*H*), 7.19 – 7.16 (m, 1H, Ar*H*), 7.15 – 7.09 (m, 5H, Ar*H*), 6.88 (t, *J* = 7.4 Hz, 2H, Ar*H*), 6.03 (s, 1H, Ar_2CH–Pd), 5.59 (t, *J* = 7.2 Hz, 1H, Pd–Ge*H*Ph_2), 2.27 (dqd, *J* = 11.6, 4.6, 2.5 Hz, 2H, –C*H*$(CH_3)_2$), 2.18 (dddd, *J* = 14.0, 9.2, 4.7, 2.2 Hz, 2H, –C*H*$(CH_3)_2$), 1.03 (dtd, *J* = 13.0, 8.3, 7.3 Hz, 12H, –CH(C*H*$_3)_2$), 0.96 (dd, *J* = 14.2, 7.1 Hz, 6H, –CH(C*H*$_3)_2$), 0.87 (dd, *J* = 14.5, 7.1 Hz, 6H, –CH(C*H*$_3)_2$). $^{31}P\{^{1}H\}$ NMR (202 MHz, C_6D_6, 298 K) δ 55.93 (s). $^{13}C\{^{1}H\}$ NMR (126 MHz, C_6D_6, 298 K) δ 158.91 (t, *J* = 14.1 Hz, Ar*C*), 149.90 (s, Ar*C*), 137.18 (s, Ar*C*), 137.00 (t, *J* = 17.2 Hz, Ar*C*), 132.36 (s, Ar*C*), 130.18 (s, Ar*C*), 127.84 127.67 (m, Ar*C*), 127.50 (s, Ar*C*), 126.78 (s, Ar*C*), 124.29 (t, *J* = 3.2 Hz, Ar*C*), 65.64 (t, $^{2}J_{CP}$ = 1.7 Hz, Ar_2CH–Pd), 26.33 (t, $^{1}J_{CP}$ = 11.1 Hz, –*C*H$(CH_3)_2$), 26.08 (t, $^{1}J_{CP}$ = 13.2 Hz, –*C*H$(CH_3)_2$), 19.87 (t, $^{2}J_{CP}$ = 3.0 Hz, –CH(*C*H$_3)_2$), 19.55 (t, $^{2}J_{CP}$ = 2.4 Hz, –CH(*C*H$_3)_2$), 18.39 (s, –CH(*C*H$_3)_2$), 18.14 (s, –CH(*C*H$_3)_2$). Anal. Calcd. for $C_{37}H_{48}GeP_2Pd$: C, 60.56; H, 6.59. Found: C, 60.44; H, 6.21. **For 13**: ^{1}H NMR (400 MHz, C_6D_6) 7.77 – 7.70 (m, 4H, Ar*H*), 7.17 – 7.14 (m, 7H, Ar*H*), 7.12 – 7.08 (m, 2H, Ar*H*), 6.95-6.88 (m, 1H, Ar*H*), 6.88-6.84 (m, 2H, Ar*H*), 6.80 – 6.75 (m, 2H, Ar*H*), 5.33 (dt, *J* = 18.9, 14.8 Hz, 1H, Ar_2CH–Pd), 4.92 (dt, *J* = 10.2, 4.2 Hz, 1H, Pd–Ge*H*Ph_2), 2.11 – 2.01 (m, 2H, –C*H*$(CH_3)_2$), 1.96 (m, 2H, –C*H*$(CH_3)_2$), 1.29 (d, *J* = 7.9 Hz, 9H, Pd–P(C*H*$_3)_3$), 1.27 – 1.19 (m, 3H, –CH(C*H*$_3)_2$), 1.15 1.09 (m, 6H, –CH(C*H*$_3)_2$), 1.09 – 1.01 (m, 3H, –CH(C*H*$_3)_2$), 0.93 – 0.86 (m, 6H, –CH(C*H*$_3)_2$), 0.82 – 0.77 (m, 6H, –CH(C*H*$_3)_2$). $^{31}P\{^{1}H\}$ NMR (162 MHz, C_6D_6, 298 K) δ 30.50 (d, *J* = 31.2 Hz, Pd–*P*($^{i}Pr_2$)), −21.73 (t, *J* = 31.1 Hz, Pd–*P*$(CH_3)_3$).

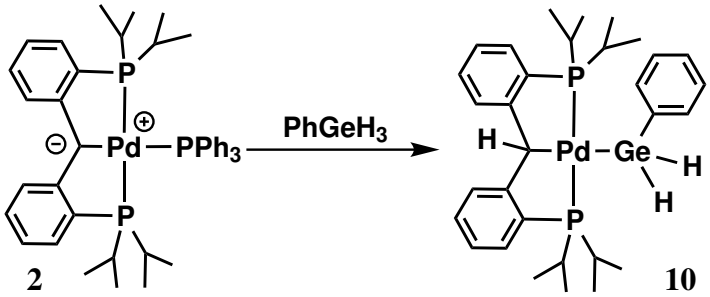
1.13 Synthesis of [PC(H)P]Pd($GePh_3$) (12)



1 **16**(not observed) **12**

In a 20 mL scintillation vial, 58.1 mg of [PC(sp^2)P]Pd(PMe_3) (**1**, 0.1 mmol) and 30.5 mg of Ph_3GeH (0.1 mmol) were stirred in 5 mL of THF for 3 days at room temperature. The color became lighter brown and finally light yellow. The ^1H and $^{31}P\{^1H\}$ NMR spectra of an aliquot taken after 1 and 2 days showed the reaction to be incomplete. After three days, the volatiles were removed under reduced pressure and the residue was triturated 3 times with 5 mL of *n*-pentane. The solid product [PC(H)P]Pd($GePh_3$) (**12**) was obtained in high yield (87%, 70.4 mg) as an off-white powder. An analytically pure sample was obtained by crystallization at -35 °C from a concentrated Et_2O solution. The [PC(H)P]Pd(PMe_3)($GePh_3$) (**16**) intermediate was not observed in aliquots of the reaction mixture. **For 12**: ^1H NMR (500 MHz, C_6D_6, 298 K) δ 7.97 (dd, *J* = 8.0, 1.4 Hz, 6H, Ar*H*), 7.41 (d, *J* = 7.9 Hz, 2H, Ar*H*), 7.24 – 7.17 (m, 6H, Ar*H*), 7.16 – 7.08 (m, 7H, Ar*H*), 6.86 (t, *J* = 7.4 Hz, 2H, Ar*H*), 6.16 (s, 1H, Ar_2CH–Pd), 2.03 (m, 2H, –C*H*(CH_3)$_2$), 1.72 (m, 2H, –C*H*(CH_3)$_2$), 0.96 (dd, *J* = 15.8, 8.6 Hz, 12H, –CH(C*H*$_3$)$_2$), 0.88 (dd, *J* = 13.5, 6.7 Hz, 6H, –CH(C*H*$_3$)$_2$), 0.84 (m, 6H, –CH(C*H*$_3$)$_2$). $^{31}P\{^1H\}$ NMR (202 MHz, C_6D_6, 298 K) δ 55.00 (s). $^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6, 298 K) δ 158.62 (t, *J* = 13.9 Hz, Ar*C*), 152.15 (s, Ar*C*), 137.21 (s, Ar*C*), 136.68 (t, *J* = 17.3 Hz, Ar*C*), 132.67 (s, Ar*C*), 130.12 (s, Ar*C*), 127.66 (t, *J* = 8.5 Hz, Ar*C*), 127.33 (s, Ar*C*), 126.85 (s, Ar*C*), 124.16 (t, *J* = 3.1 Hz, Ar*C*), 65.95 (s, Ar_2CH–Pd), 26.22 (t, *J* = 12.7 Hz, –*C*H(CH_3)$_2$), 25.94 (t, *J* = 10.5 Hz, –*C*H(CH_3)$_2$), 20.96 (t, *J* = 3.5 Hz, –CH(*C*H$_3$)$_2$), 20.01 (t, *J* = 2.5 Hz, –CH(*C*H$_3$)$_2$), 18.52 (s, –CH(*C*H$_3$)$_2$), 17.94 (s, –CH(*C*H$_3$)$_2$). Anal. Calcd. for $C_{43}H_{52}GeP_2Pd$: C, 63.77; H, 6.47. Found: C, 64.18; H, 6.51.

1.14 Reaction of [PC(sp^2)P]Pd(PPh_3) (2) with $PhGeH_3$

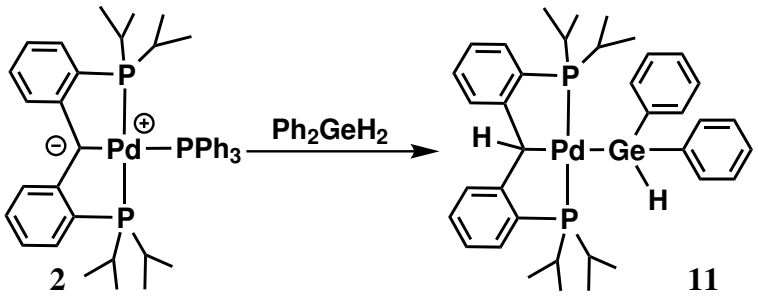


2 **10**

Starting from 76.7 mg of [PC(sp^2)P]Pd(PPh_3) (**2**, 0.1 mmol) and following the same procedure as that described above for the reaction of [PC(sp^2)P]Pd(PMe_3) (**1**) with $PhGeH_3$ above, the product

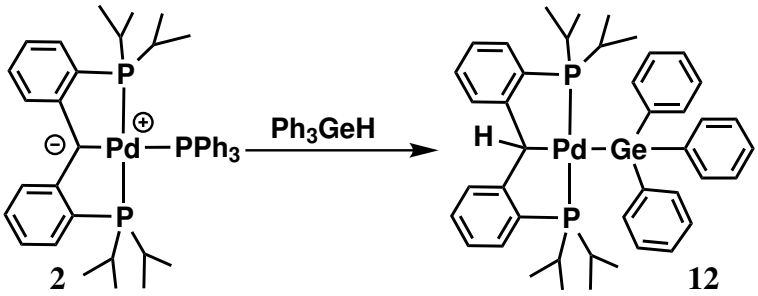
[PC(H)P]Pd(GeH_2Ph) (**10**) was obtained after 1 min. It was isolated in moderate yield (53%, 34.8 mg) due to multiple recrystallizations needed to remove the byproduct (PPh_3).

1.15 Reaction of [PC(sp^2)P]Pd(PPh_3) (2) with Ph_2GeH_2



Starting from 76.7 mg of [PC(sp^2)P]Pd(PPh_3) (**2**, 0.1 mmol) and following the same procedure as that described above for the reaction of [PC(sp^2)P]Pd(PMe_3) (**1**) with Ph_2GeH_2, the product [PC(H)P]Pd($GeHPh_2$) (**11**) was obtained after 30 min. It was isolated in moderate yield (57%, 41.8 mg) due to multiple recrystallizations needed to remove the byproduct (PPh_3).

1.16 Reaction of [PC(sp^2)P]Pd(PPh_3) (2) with Ph_3GeH



Starting from 76.7 mg of [PC(sp^2)P]Pd(PPh_3) (**2**, 0.1 mmol) and following the same procedure as that described above for the reaction of [PC(sp^2)P]Pd(PMe_3) (**1**) with Ph_3GeH, the product [PC(H)P]Pd($GePh_3$) (**12**) was obtained after 1 day. It was isolated in moderate yield (48%, 38.9 mg) due to multiple recrystallizations needed to remove the byproduct (PPh_3).

1.17 X-ray data for compounds 3-5, 8-13

X−Ray crystal structure of [PC(SiH$_2$Ph)P]PdH (3). Single crystals were obtained from a concentrated solution of diethyl ether at −35 °C in the glovebox. Crystal and refinement data for **3**: $C_{31}H_{44}P_2PdSi$; M_r =613.09; Orthorhombic; space group *Pbca*; *a* = 17.0258(7) Å; *b* = 18.6108(8) Å; *c* = 19.0877(8) Å; α = 90°; β = 90°; γ = 90°; V = 6048.2(4) Å^3; Z = 8; T = 120(2) K; λ = 0.71073 Å; μ = 0.777 mm^{-1}; d_{calc} = 1.347 g·cm^{-3}; 135804 reflections collected; 5331 unique (R_{int} = 0.0258); giving R_1 = 0.0235, wR_2 = 0.0574 for 5118 data with [I>2σ(I)] and R_1 = 0.0249, wR_2 = 0.0580 for all 5331 data. Residual electron density (e$^-$·Å^{-3}) max/min: 0.449/−0.442.

X−Ray crystal structure of [PC(SiHPh$_2$)P]PdH (4). Single crystals were obtained from a concentrated solution of diethyl ether layered with *n*-pentane at −35 °C in the glovebox. Crystal and refinement data for **4**: $C_{37}H_{48}P_2PdSi$; M_r =689.18; Monoclinic; space group $P2_1/n$; *a* = 9.402(3) Å; *b* = 19.186(5) Å; *c* = 19.053(5) Å; α = 90°; β = 93.284(5)°; γ = 90°; V = 3431.3(16) Å^3; Z = 4; T = 120(2) K; λ = 0.71073 Å; μ = 0.693 mm^{-1}; d_{calc} = 1.334 g·cm^{-3}; 37894 reflections collected; 6047 unique (R_{int} = 0.0665); giving R_1 = 0.0316, wR_2 = 0.0656 for 4806 data with [I>2σ(I)] and R_1 = 0.0495, wR_2 = 0.0694 for all 6047 data. Residual electron density (e$^-$·Å^{-3}) max/min: 0.411/−0.400.

X−Ray crystal structure of [PC(SiPh$_3$)P]PdH (5). Single crystals were obtained from a concentrated solution of diethyl ether at −35 °C in the glovebox. Crystal and refinement data for **5**: $C_{43}H_{52}P_2PdSi$; M_r =765.28; Triclinic; space group $P\bar{1}$; *a* = 9.5894(6) Å; *b* = 10.6642(7) Å; *c* = 19.5486(13) Å; α = 78.851(3)°; β = 76.192(3)°; γ = 76.697(2)°; V = 1868.9(2) Å^3; Z = 2; T = 120(2) K; λ = 0.71073 Å; μ = 0.644 mm^{-1}; d_{calc} = 1.360 g·cm^{-3}; 56344 reflections collected; 9370 unique (R_{int} = 0.0469); giving R_1 = 0.0333, wR_2 = 0.0732 for 7945 data with [I>2σ(I)] and R_1 = 0.0443, wR_2 = 0.0772 for all 9370 data. Residual electron density (e$^-$·Å^{-3}) max/min: 1.946/−1.739.

X−Ray crystal structure of [PC(H)P]Pd(SiPh$_3$)·C$_5$H$_{12}$ (8·C$_5$H$_{12}$). Single crystals were obtained from a concentrated solution of diethyl ether layered with *n*-pentane at −35 °C in the glovebox. Crystal and refinement data for **8·C$_5$H$_{12}$**: $C_{48}H_{64}P_2PdSi$; M_r =837.42; Monoclinic; space group $P2_1/c$; *a* = 11.401(2) Å; *b* = 12.592(2) Å; *c* = 30.423(5) Å; α = 90°; β = 97.666(3)°; γ = 90°; V = 4328.5(13) Å^3; Z = 4; T = 120(2) K; λ = 0.71073 Å; μ = 0.562 mm^{-1}; d_{calc} = 1.285 g·cm^{-3}; 126183 reflections collected; 10820 unique (R_{int} = 0.0937); giving R_1 = 0.0412, wR_2 = 0.0852 for 8147 data with [I>2σ(I)] and R_1 = 0.0684, wR_2 = 0.0983 for all 10820 data. Residual electron density (e$^-$·Å^{-3}) max/min: 1.455/−0.960.

X−Ray crystal structure of [PC(Bpin)P]PdH (9). Single crystals were obtained from a concentrated solution of diethyl ether at −35 °C in the glovebox. Crystal and refinement data for **9**: $C_{31}H_{49}BO_2P_2Pd$; M_r =632.85; Monoclinic; space group $P2_1/c$; *a* = 17.3966(10) Å; *b* = 10.0819(6) Å; *c* = 19.8141(11) Å; α = 90°; β = 115.8960(18)°; γ = 90°; V = 3126.3(3) Å^3; Z = 4; T = 120(2) K; λ = 0.71073 Å; μ = 0.721 mm^{-1}; d_{calc} = 1.345 g·cm^{-3}; 71734 reflections collected; 5509 unique (R_{int} = 0.0279); giving R_1 = 0.0203, wR_2 = 0.0513 for 4985 data with [I>2σ(I)] and R_1 = 0.0237, wR_2 = 0.0528 for all 5509 data. Residual electron density (e$^-$·Å^{-3}) max/min: 0.781/−0.667.

X−Ray crystal structure of [PC(H)P]Pd(GeH$_2$Ph) (10). Single crystals were obtained from a concentrated solution of diethyl ether at −35 °C in the glovebox. Crystal and refinement data for **10**: $C_{31}H_{44}GeP_2Pd$; M_r =657.59; Triclinic; space group $P\bar{1}$; *a* = 8.3636(3) Å; *b* = 10.0092(4) Å;

c = 18.4078(7) Å; α = 94.2185(11)°; β = 93.3363(11)°; γ = 100.7761(11)°; V = 1505.62(10) Å^3; Z = 2; T = 120(2) K; λ = 0.71073 Å; μ = 1.719 mm^{-1}; d_{calc} = 1.451 g·cm^{-3}; 32263 reflections collected; 5270 unique (R_{int} = 0.0429); giving R_1 = 0.0340, wR_2 = 0.0693 for 4607 data with [I>2σ(I)] and R_1 = 0.0412, wR_2 = 0.0725 for all 5270 data. Residual electron density (e$^-$·Å^{-3}) max/min: 1.013/−1.472.

X−Ray crystal structure of [PC(H)P]Pd(GeHPh$_2$) (11). Single crystals were obtained from a concentrated solution of diethyl ether at −35 °C in the glovebox. Crystal and refinement data for **11**: $C_{37}H_{48}GeP_2Pd$; M_r =733.68; Monoclinic; space group $I2/a$; a = 22.9918(15) Å; b = 12.0605(7) Å; c = 25.6249(17) Å; α = 90°; β = 105.728(4)°; γ = 90°; V = 6839.6(7) Å^3; Z = 8; T = 120(2) K; λ = 0.71073 Å; μ = 1.522 mm^{-1}; d_{calc} = 1.425 g·cm^{-3}; 48072 reflections collected; 6020 unique (R_{int} = 0.0538); giving R_1 = 0.0337, wR_2 = 0.0735 for 4867 data with [I>2σ(I)] and R_1 = 0.0495, wR_2 = 0.0776 for all 6020 data. Residual electron density (e$^-$·Å^{-3}) max/min: 0.744/−0.722.

X−Ray crystal structure of [PC(H)P]Pd(GePh$_3$) (12). Single crystals were obtained from a concentrated solution of diethyl ether layered at −35 °C in the glovebox. Crystal and refinement data for **12**: $C_{43}H_{52}GeP_2Pd$; M_r =809.78; Monoclinic; space group $P2_1/c$; a = 11.6399(15) Å; b = 19.396(3) Å; c = 17.6306(18) Å; α = 90°; β = 105.713(2)°; γ = 90°; V = 3831.6(8) Å^3; Z = 4; T = 120(2) K; λ = 0.71073 Å; μ = 1.366 mm^{-1}; d_{calc} = 1.404 g·cm^{-3}; 28856 reflections collected; 6706 unique (R_{int} = 0.1035); giving R_1 = 0.0499, wR_2 = 0.0946 for 4441 data with [I>2σ(I)] and R_1 = 0.0976, wR_2 = 0.1041 for all 6706 data. Residual electron density (e$^-$·Å^{-3}) max/min: 1.045/−1.175.

X−Ray crystal structure of [PC(H)P]Pd(PMe$_3$)(GeHPh$_2$)·0.5C$_5$H$_{12}$ (13·0.5C$_5$H$_{12}$). Single crystals were obtained from a concentrated solution of diethyl ether of the crude reaction mixture layered with *n*-pentane at −35 °C in the glovebox. Crystal and refinement data for **13·C$_5$H$_{12}$**: $C_{85}H_{114}Ge_2P_6Pd_2$; M_r =1679.56; Monoclinic; space group $P2_1/c$; a = 9.5430(4) Å; b = 20.3870(10) Å; c = 21.3674(11) Å; α = 90°; β = 99.3602(14)°; γ = 90°; V = 4101.7(3) Å^3; Z = 2; T = 120(2) K; λ = 0.71073 Å; μ = 1.316 mm^{-1}; d_{calc} = 1.360 g·cm^{-3}; 98578 reflections collected; 7227 unique (R_{int} = 0.0462); giving R_1 = 0.0296, wR_2 = 0.0661 for 6323 data with [I>2σ(I)] and R_1 = 0.0369, wR_2 = 0.0681 for all 7227 data. Residual electron density (e$^-$·Å^{-3}) max/min: 0.761/−0.551.

2 DFT results

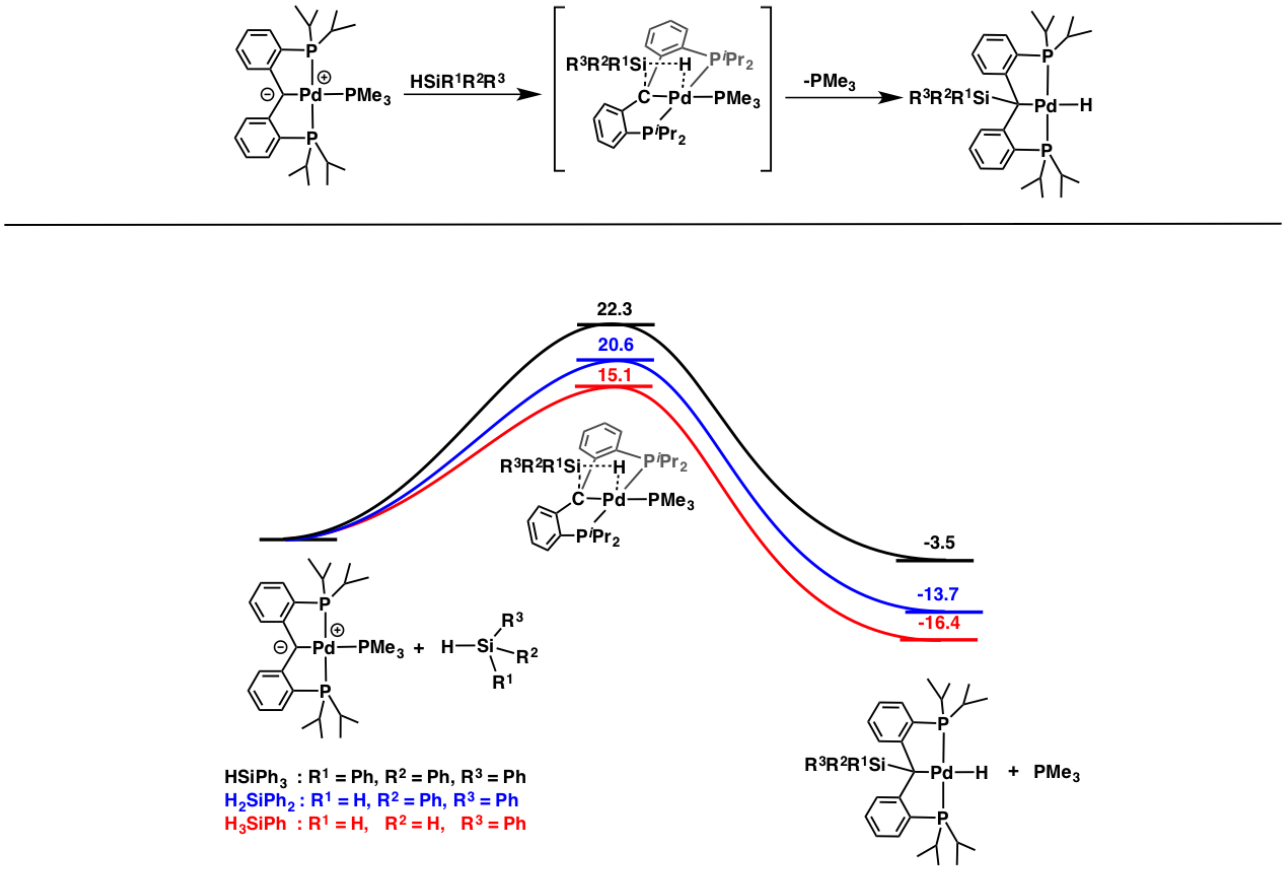


Figure S1. Calculated mechanism and reaction profile for the formation of the hydride products from [PC(sp^2)P]Pd(PMe$_3$) (**1**).

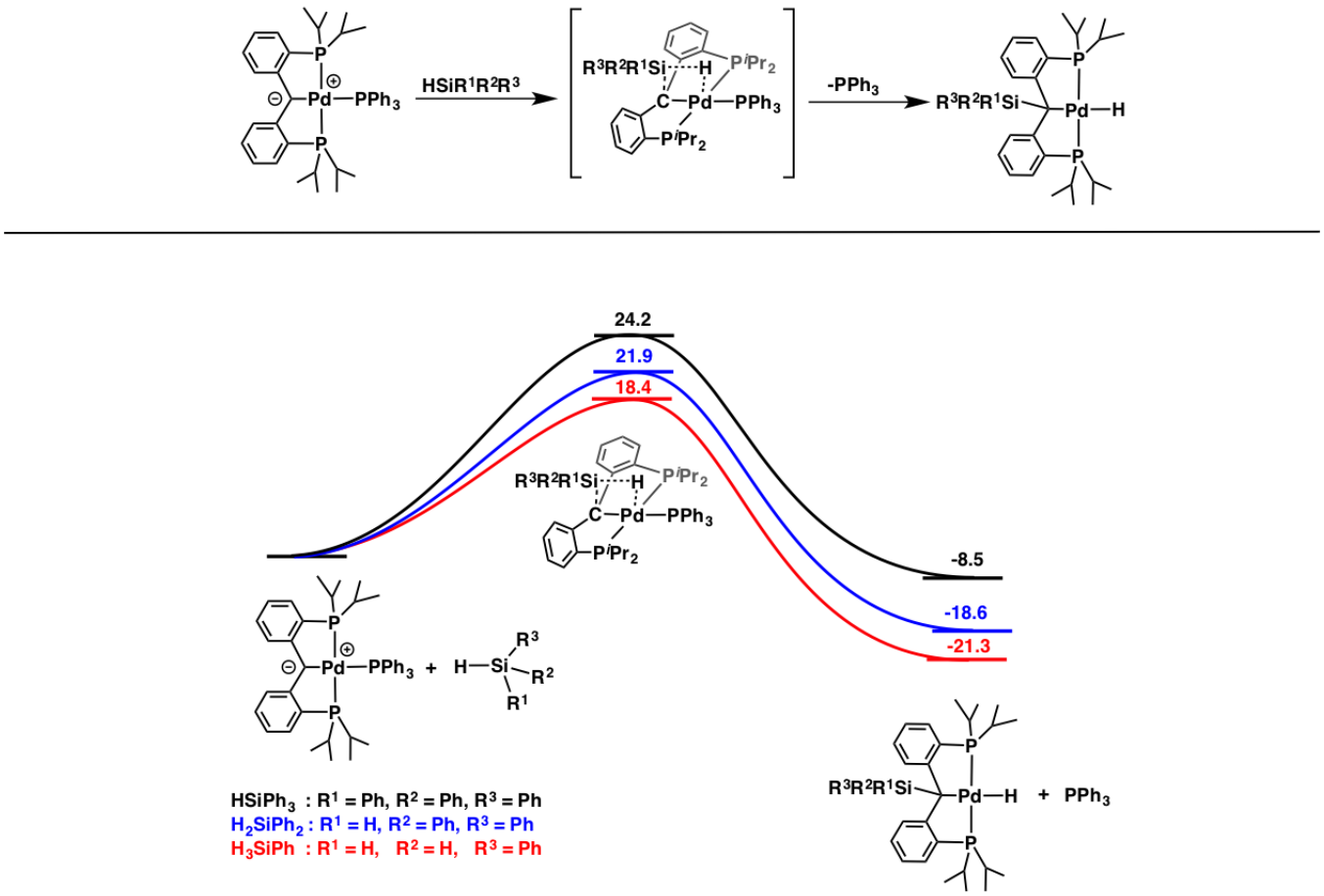


Figure S2. Calculated mechanism and reaction profile for the formation of the hydride products from [PC(sp^2)P]Pd(PPh_3) (**2**).

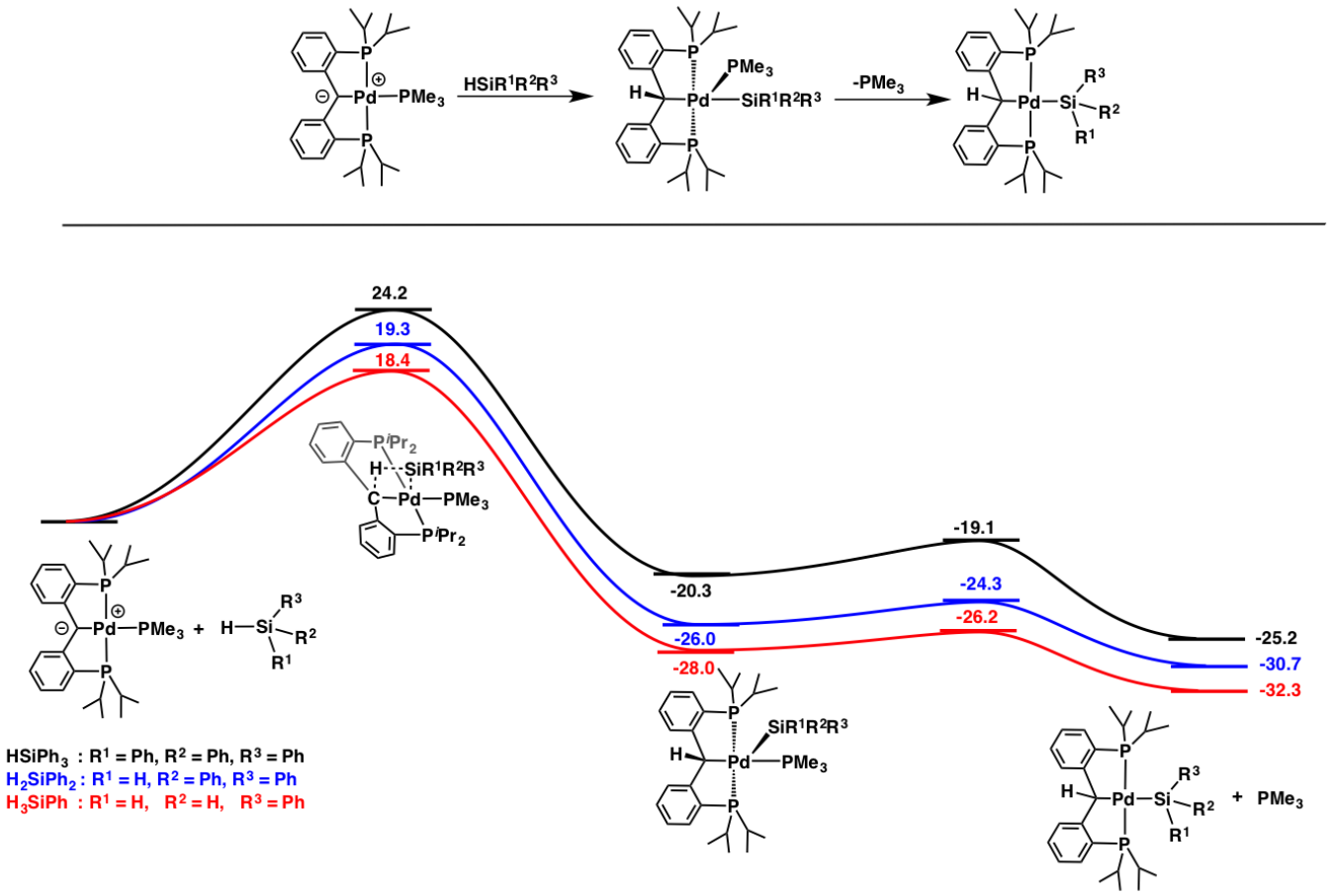


Figure S3. Calculated mechanism and reaction profile for the formation of the silyl products from [PC(sp^2)P]Pd(PMe$_3$) (**1**).

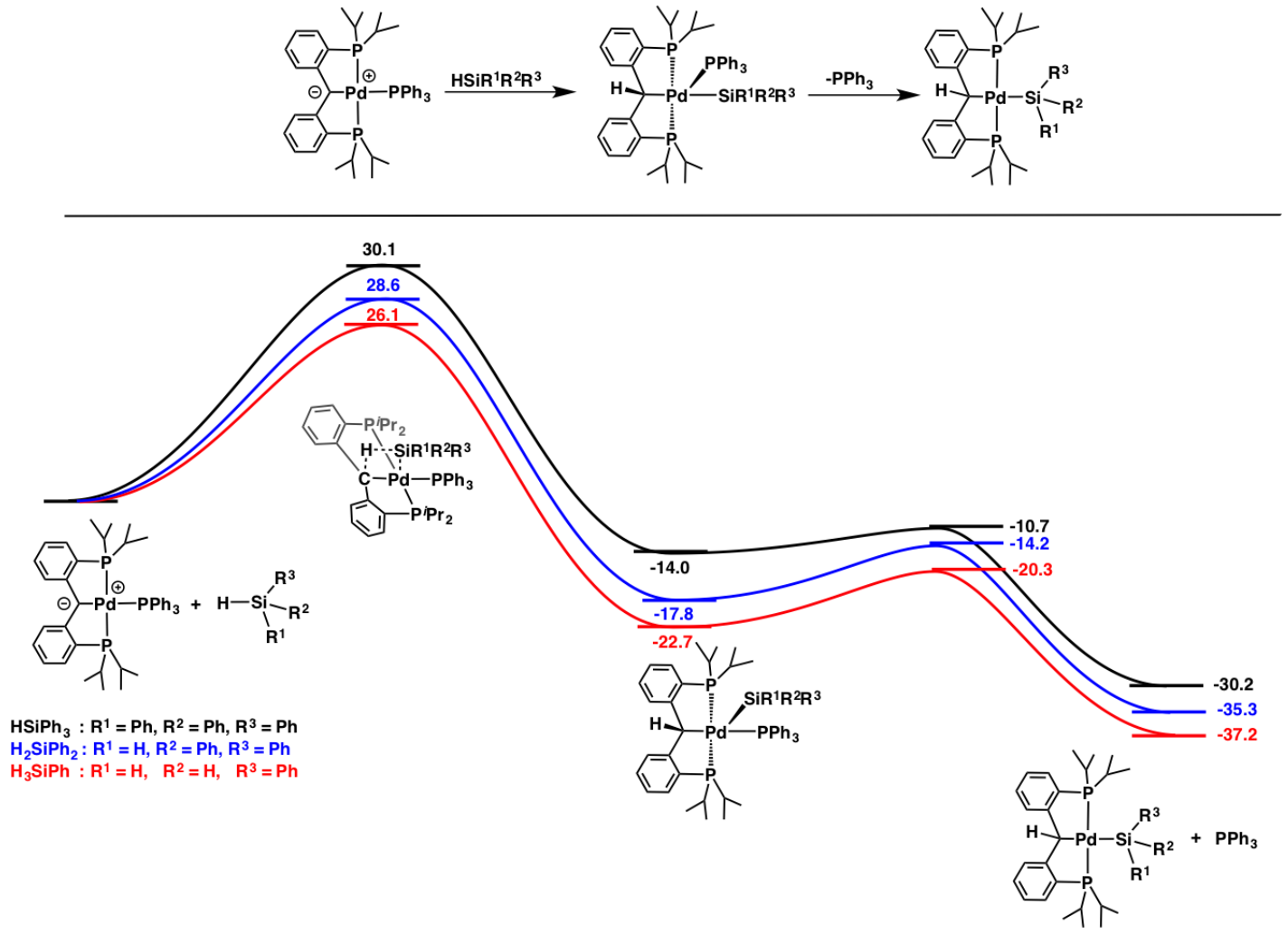


Figure S4. Calculated mechanism and reaction profile for the formation of the silyl products from [PC(sp^2)P]Pd(PPh$_3$) (**2**).

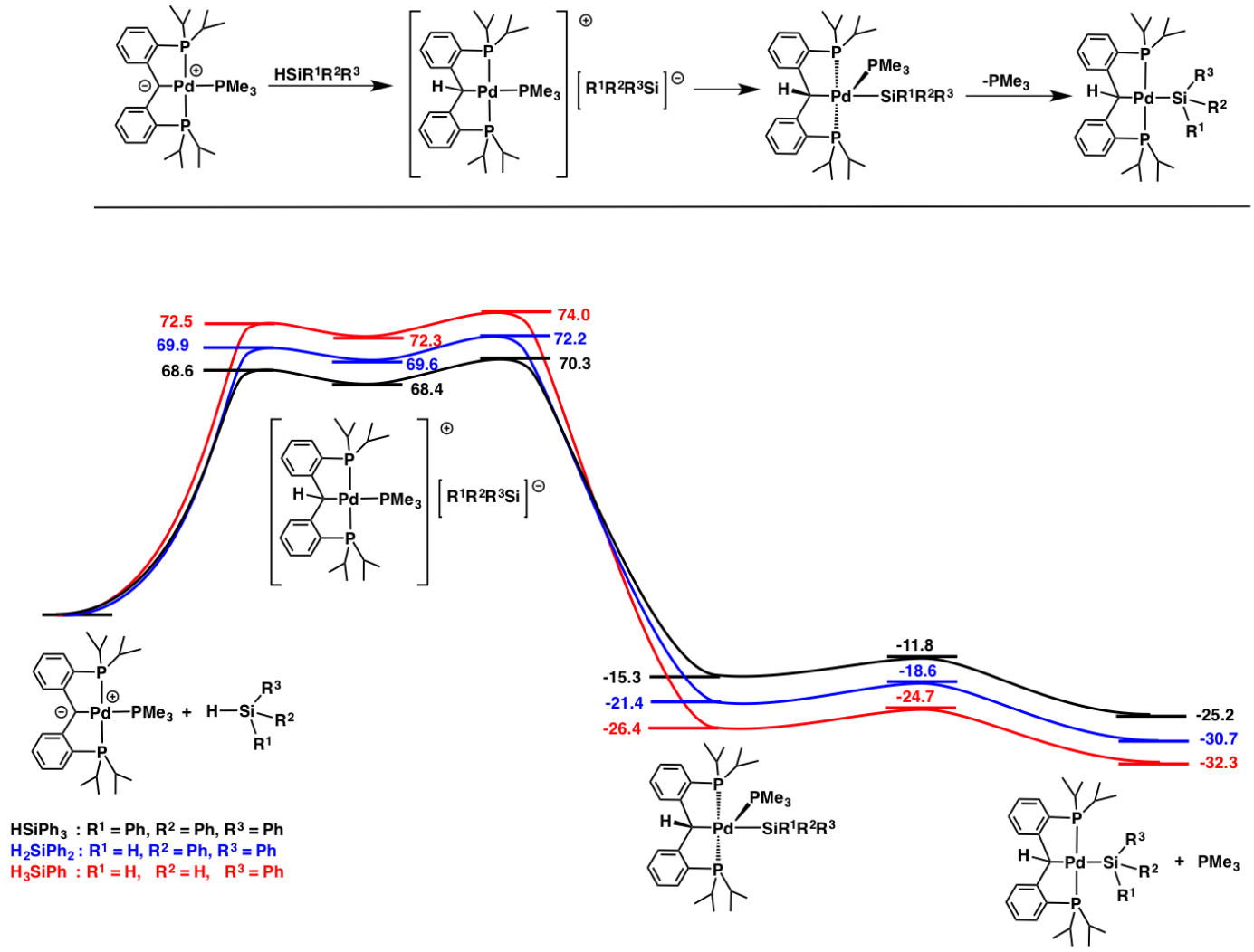


Figure S5. Calculated mechanism and reaction profile for the formation of the silyls from [PC(sp^2)P]Pd(PMe$_3$) (**1**) by a deprotonation mechanism.

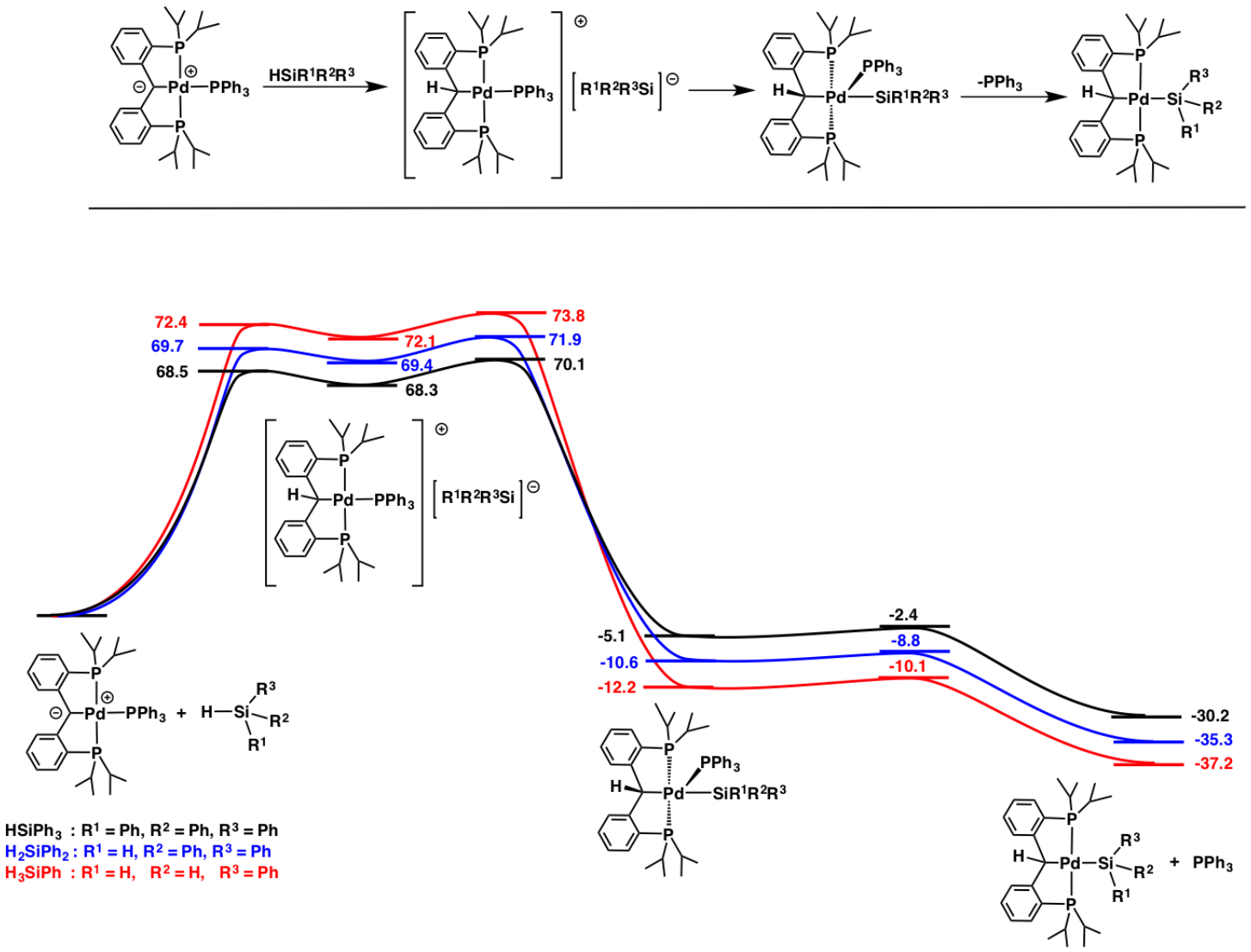


Figure S6. Calculated mechanism and reaction profile for the formation of the silyls from [PC(sp^2)P]Pd(PPh$_3$) (**2**) by a deprotonation mechanism.

3 NMR Spectra

3.1 NMR Spectra for [PC(SiH$_2$Ph)P]PdH (3)

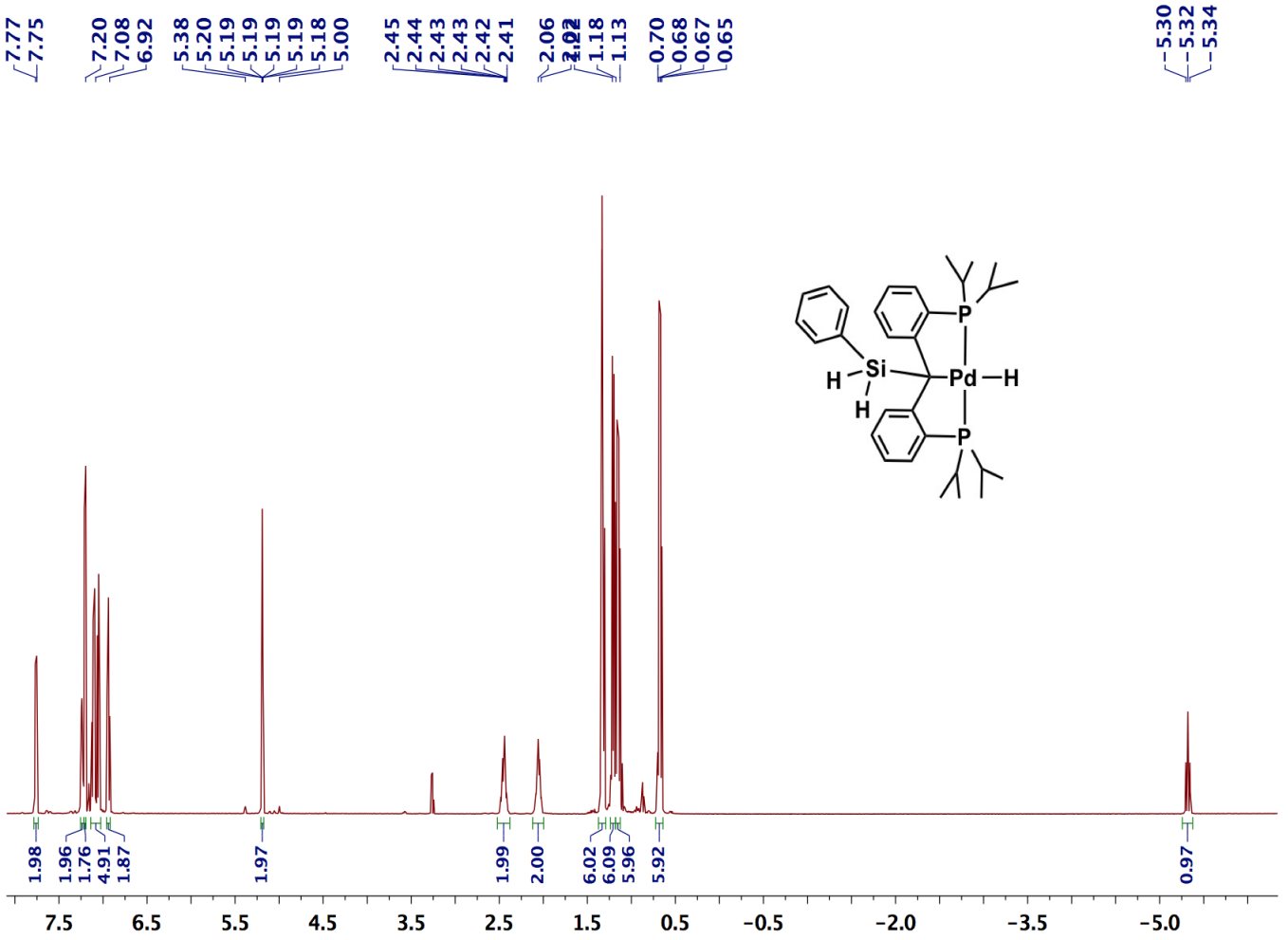


Figure S7. ^{1}H NMR spectrum for [PC(SiH$_2$Ph)P]PdH (**3**).

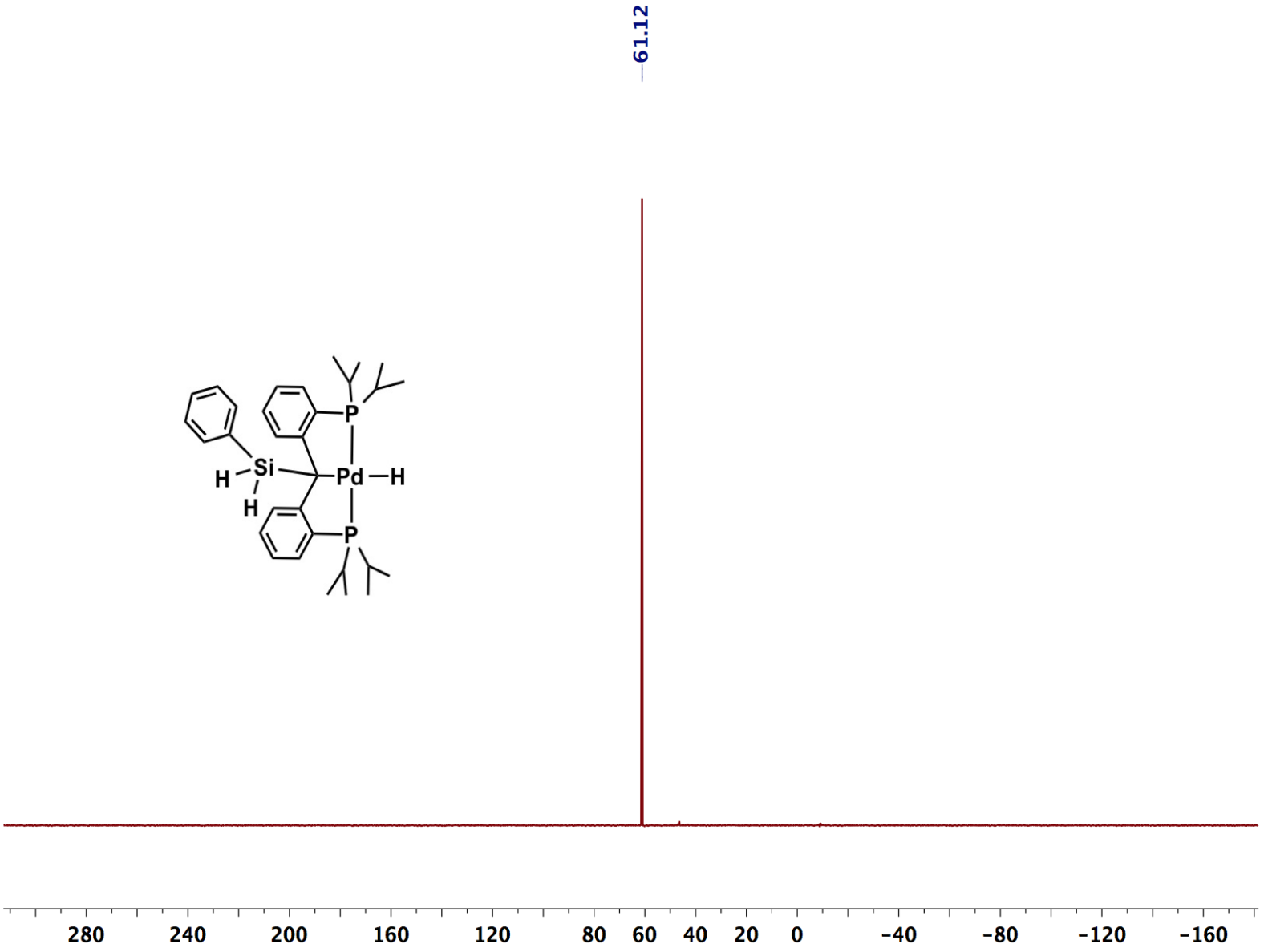


Figure S8. $^{31}P\{^{1}H\}$ NMR spectrum for [PC(SiH_2Ph)P]PdH (**3**).

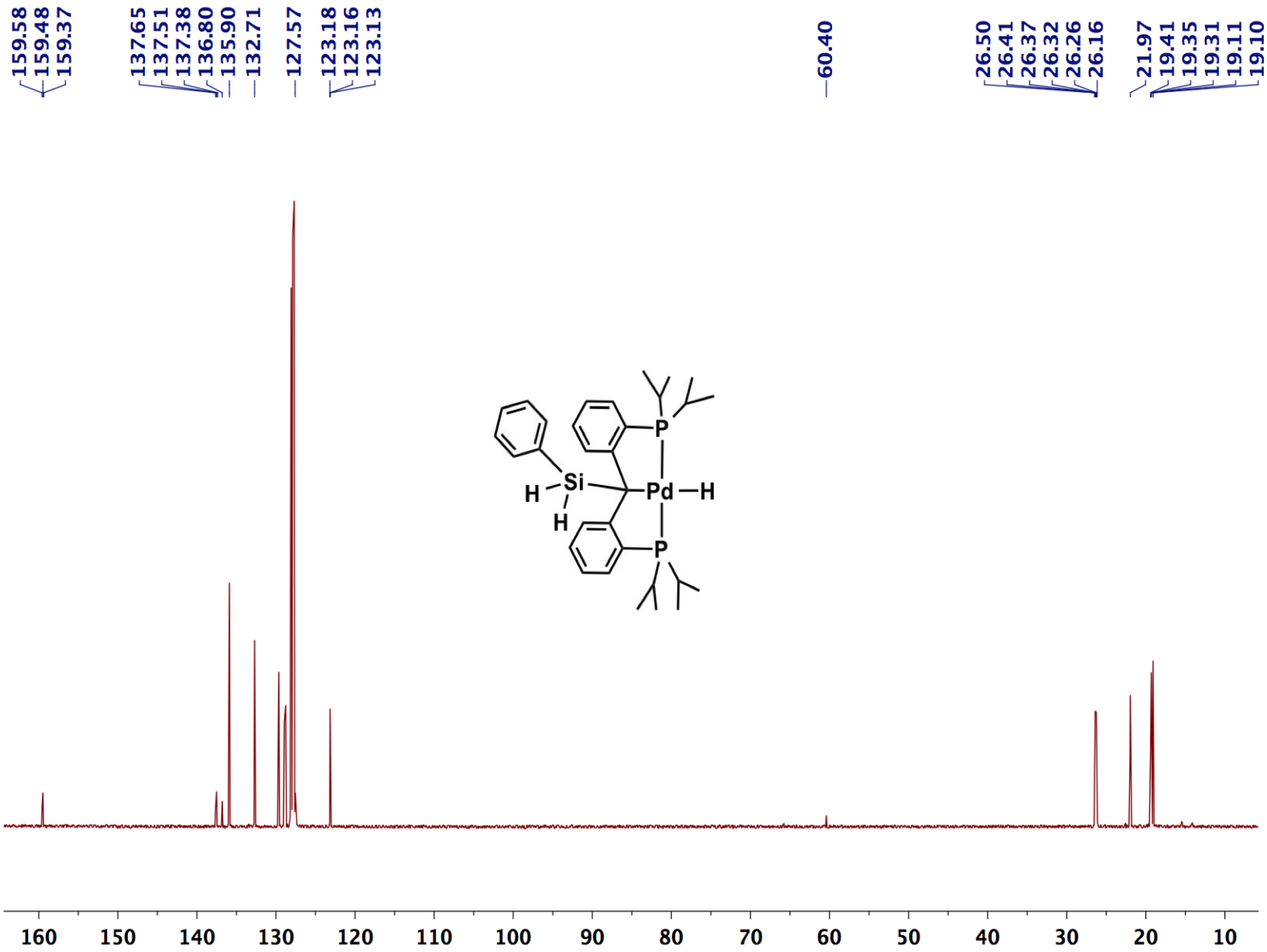


Figure S9. $^{13}C\{^{1}H\}$ NMR spectrum for [PC(SiH_2Ph)P]PdH (**3**).

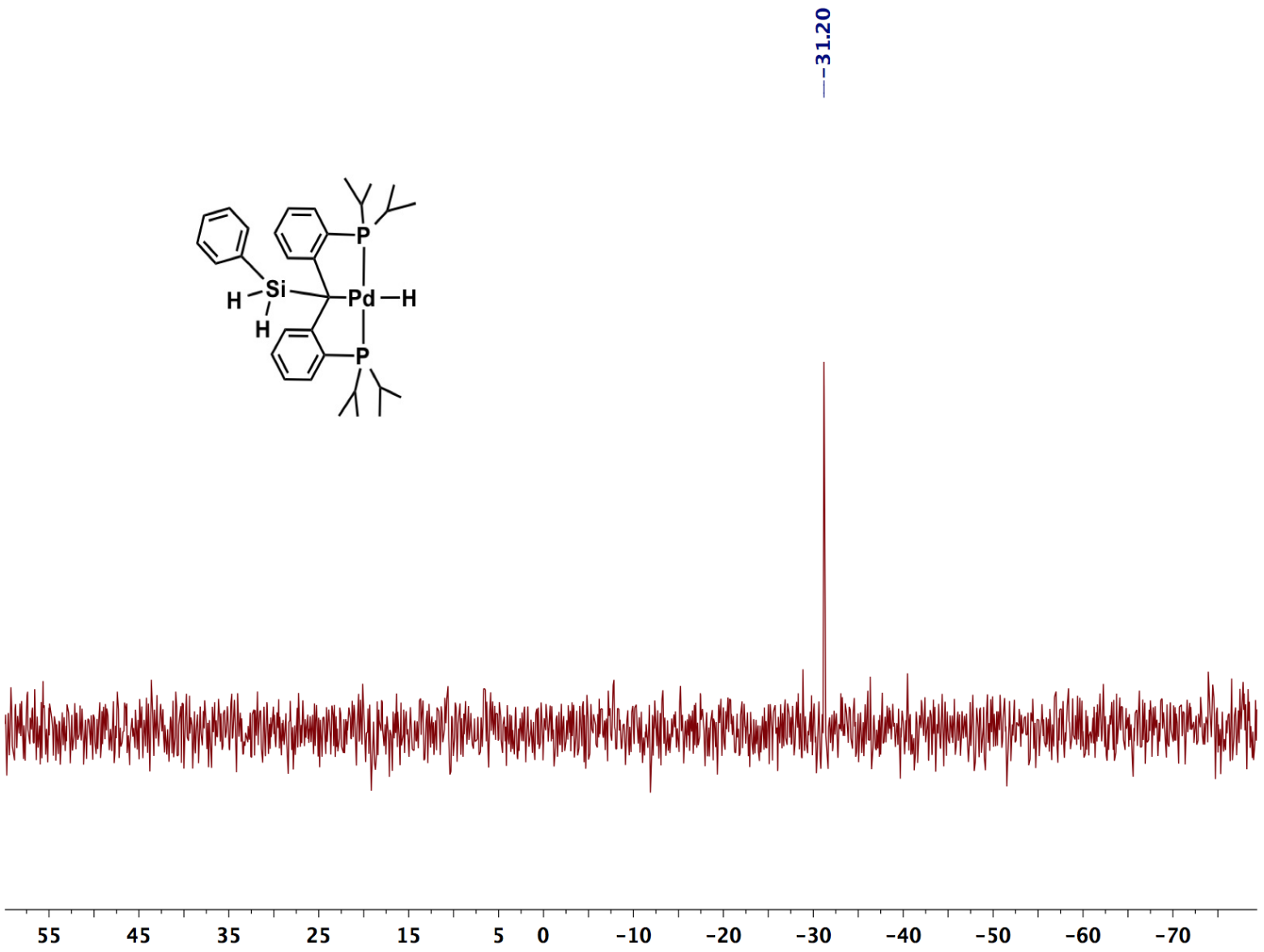


Figure S10. $^{29}Si\{^{1}H\}$ NMR spectrum for [PC(SiH_2Ph)P]PdH (**3**).

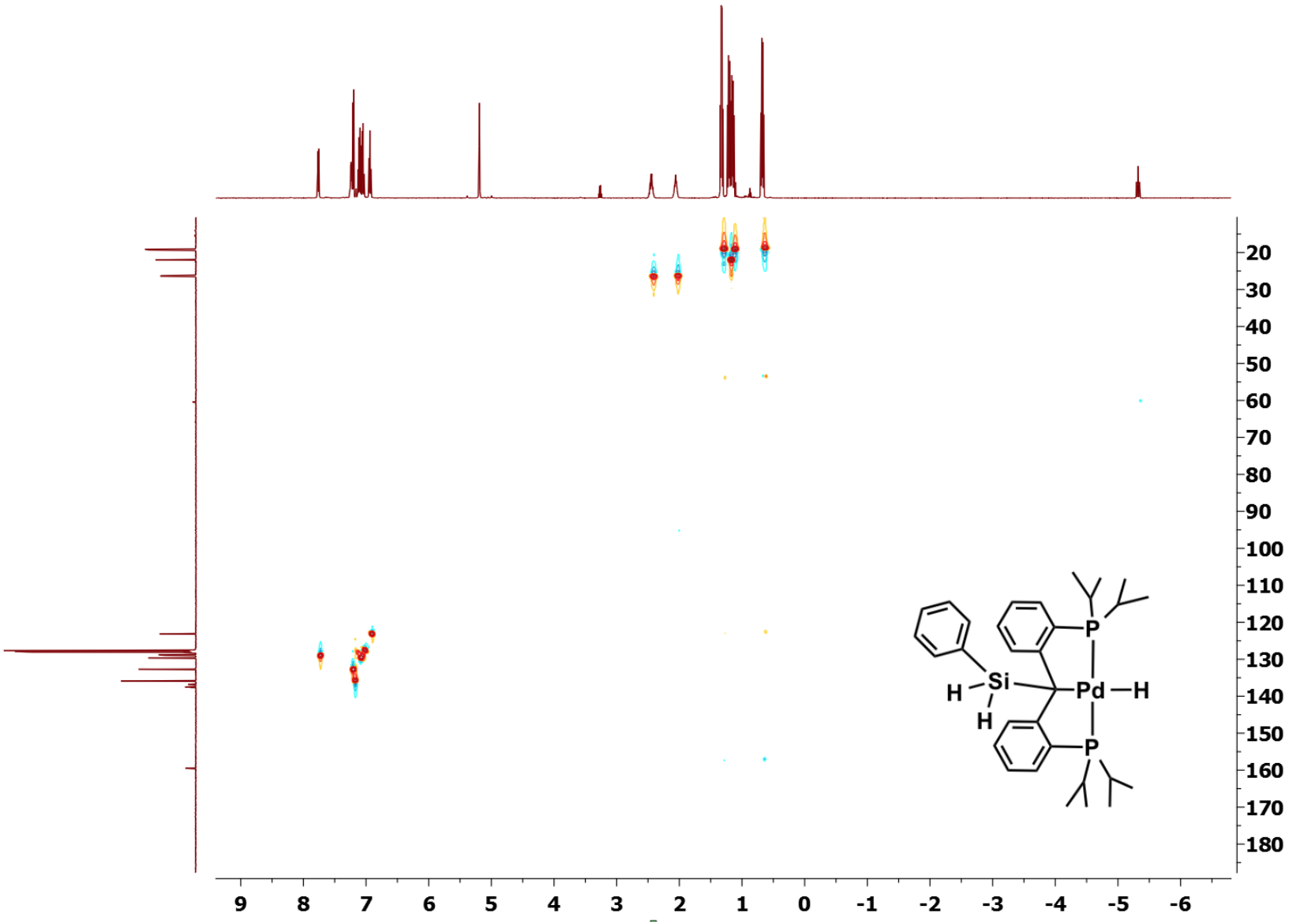


Figure S11. ^{1}H-^{13}C HSQC NMR spectrum for [PC(SiH_2Ph)P]PdH (**3**).

3.2 NMR Spectra for [PC(SiHPh$_2$)P]PdH (4)

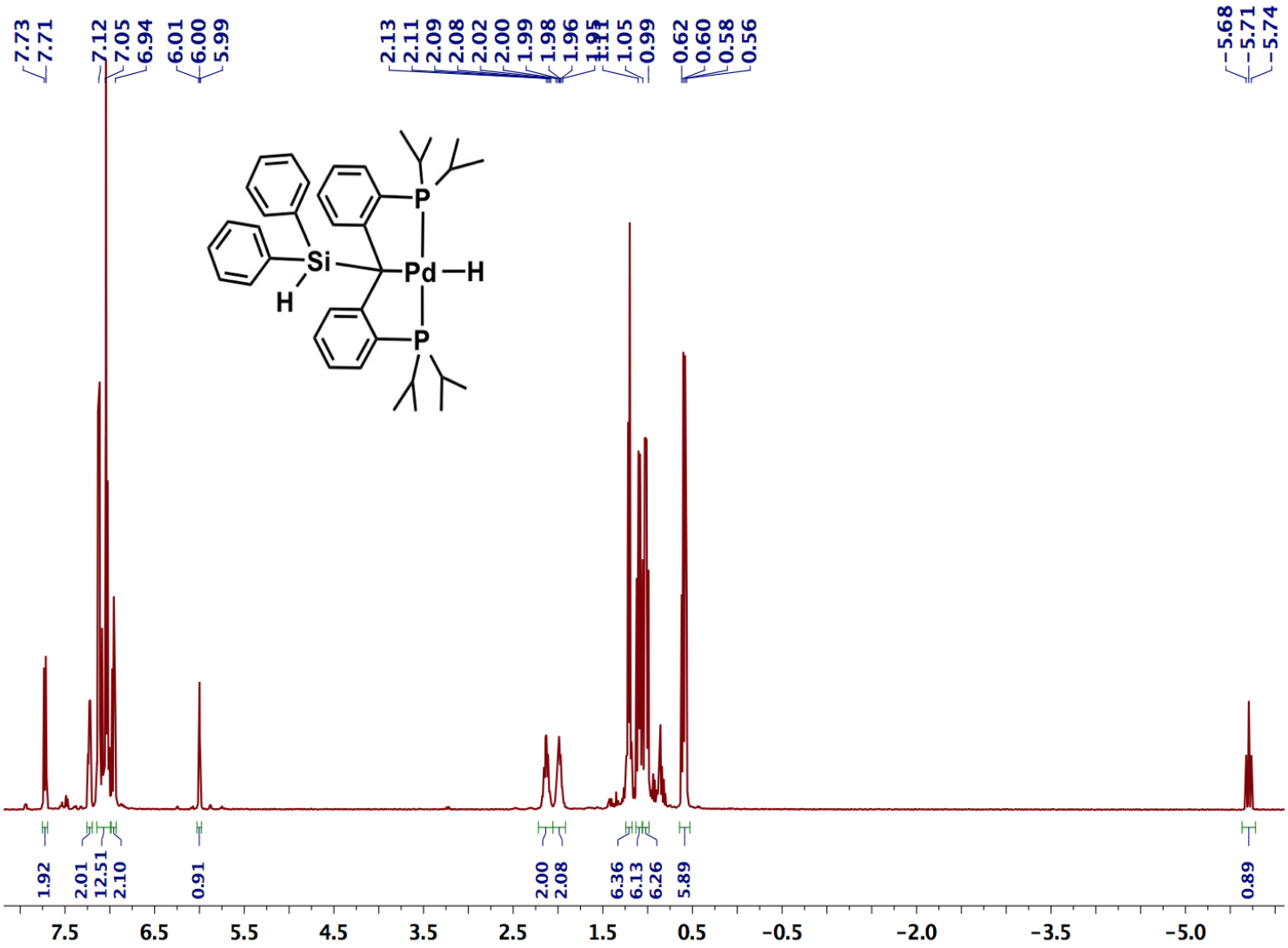


Figure S12. ^{1}H NMR spectrum for [PC(SiHPh$_2$)P]PdH (**4**).

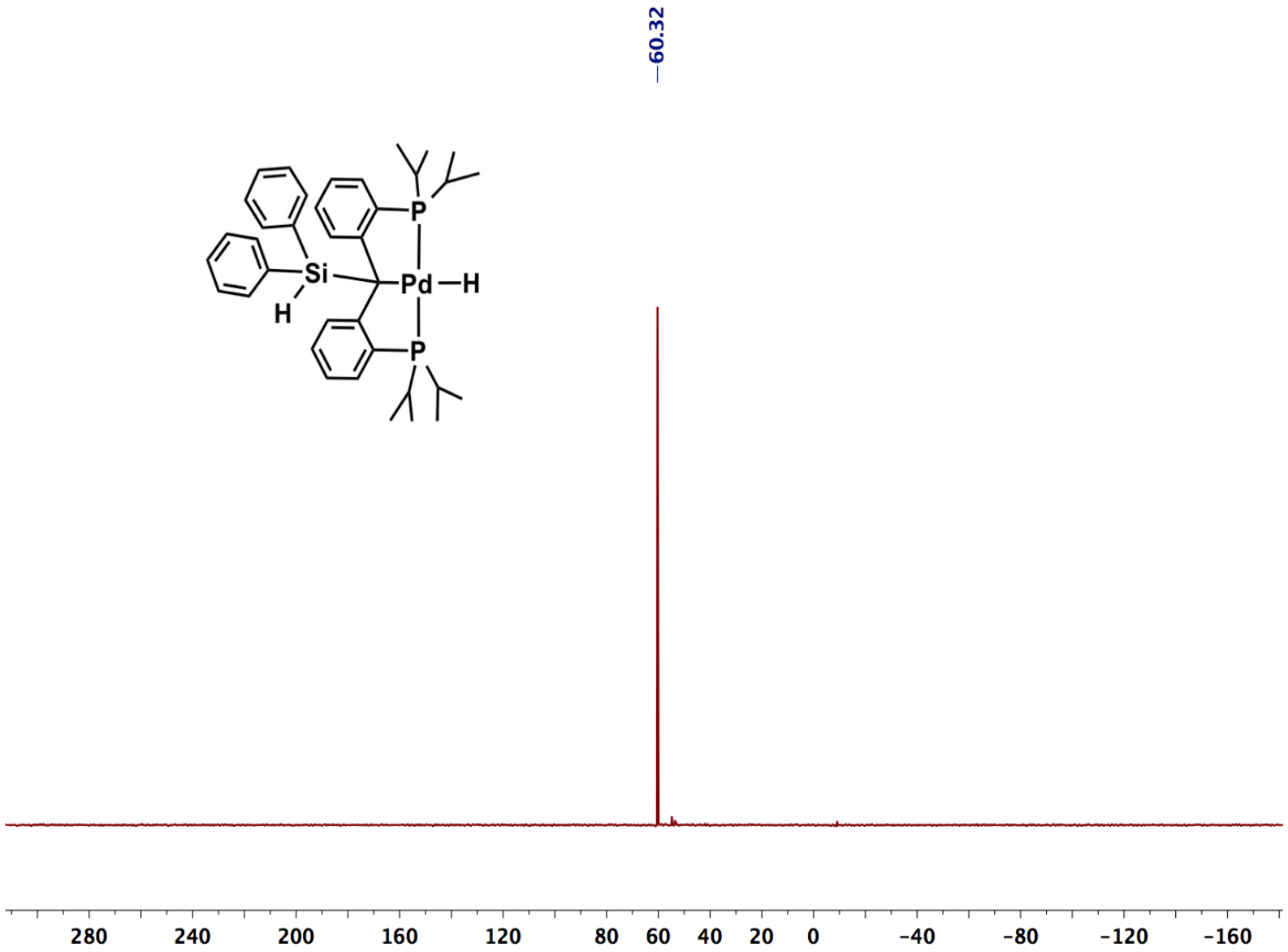


Figure S13. $^{31}P\{^{1}H\}$ NMR spectrum for [PC(SiHPh$_2$)P]PdH (**4**).

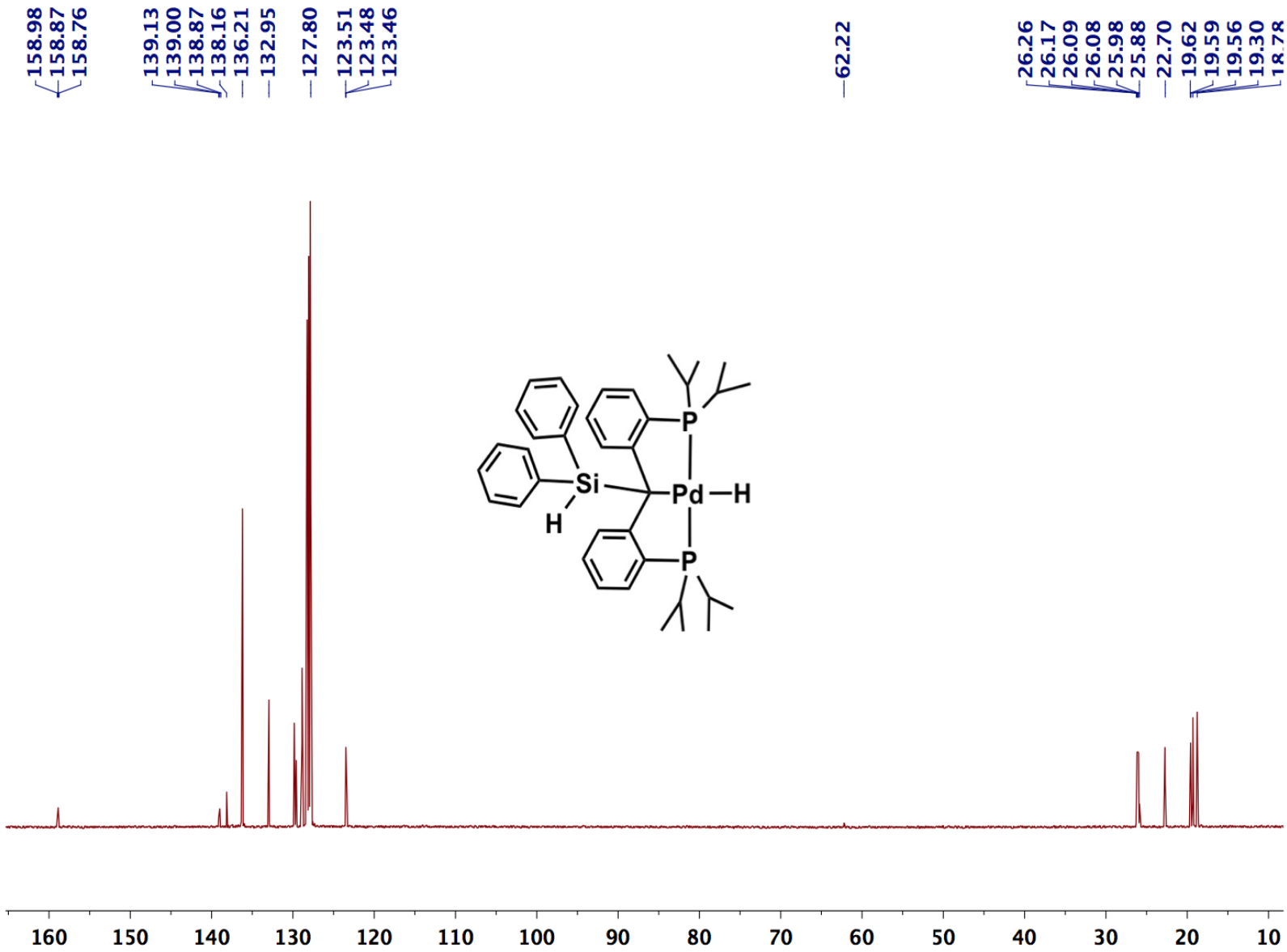


Figure S14. $^{13}C\{^{1}H\}$ NMR spectrum for [PC(SiHPh$_2$)P]PdH (**4**).

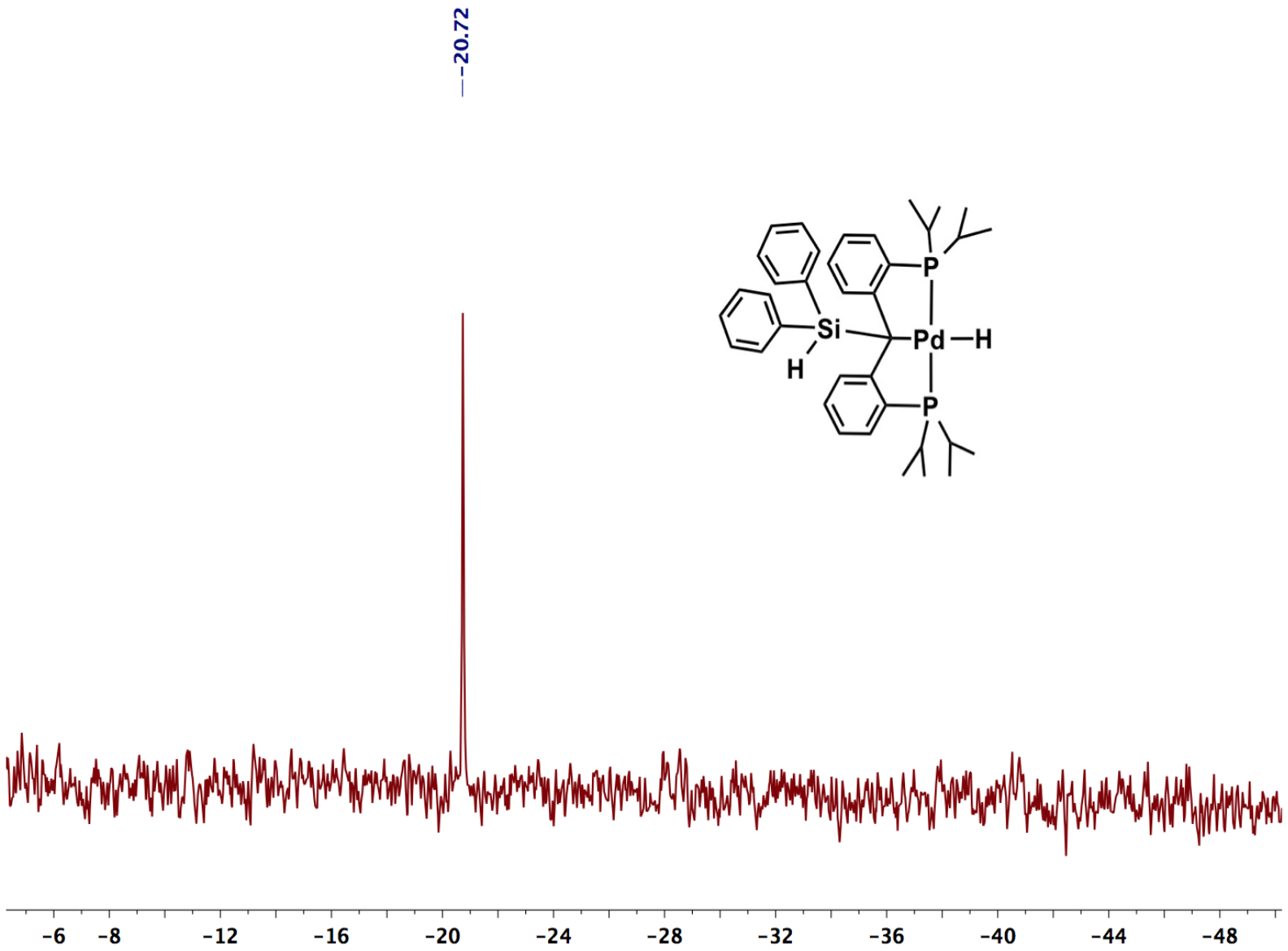


Figure S15. $^{29}Si\{^{1}H\}$ NMR spectrum for [PC(SiHPh$_2$)P]PdH (**4**).

3.3 NMR Spectra for [PC(SiPh$_3$)P]PdH (5)

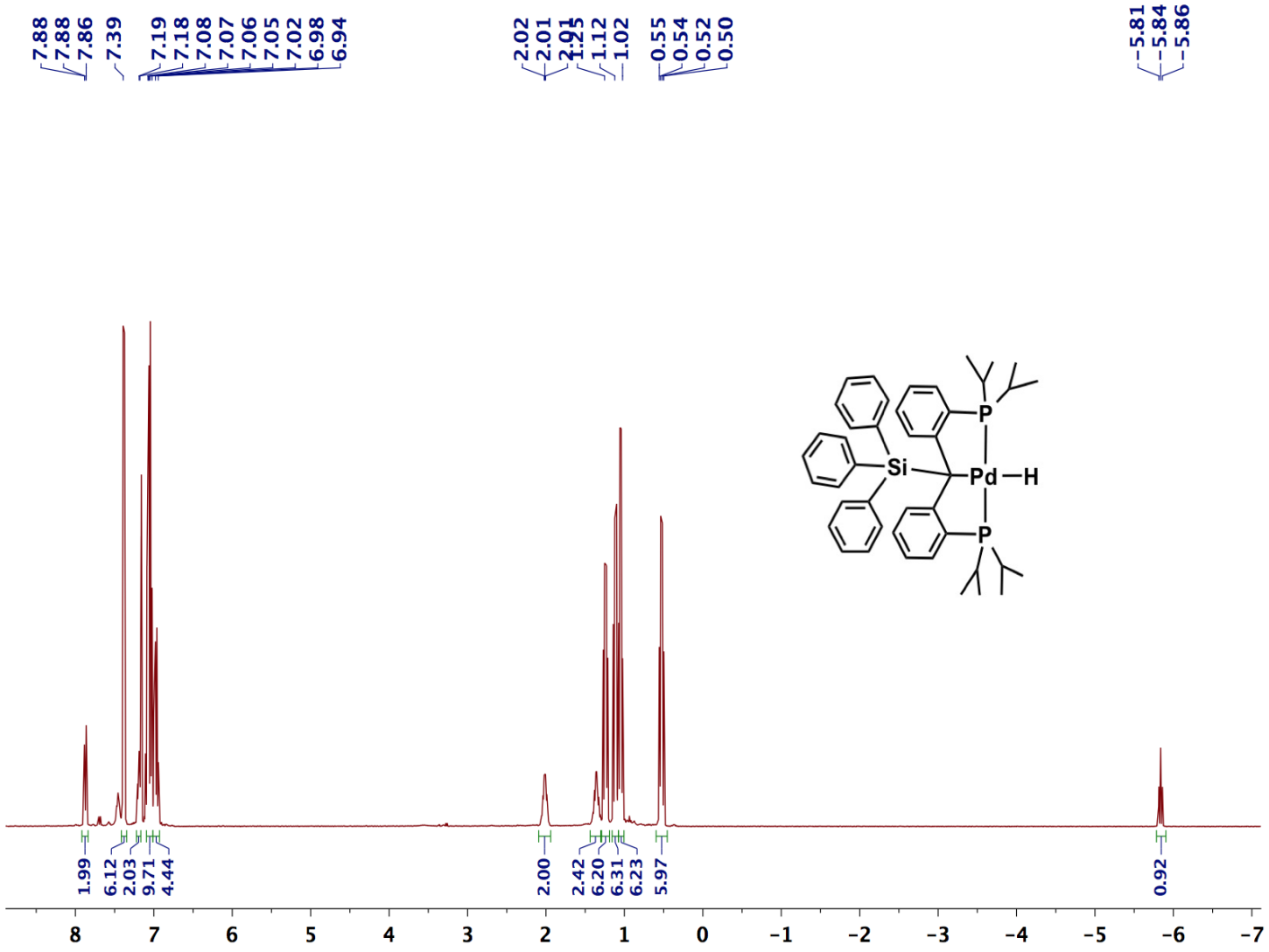


Figure S16. ^{1}H NMR spectrum for [PC(SiPh$_3$)P]PdH (**5**).

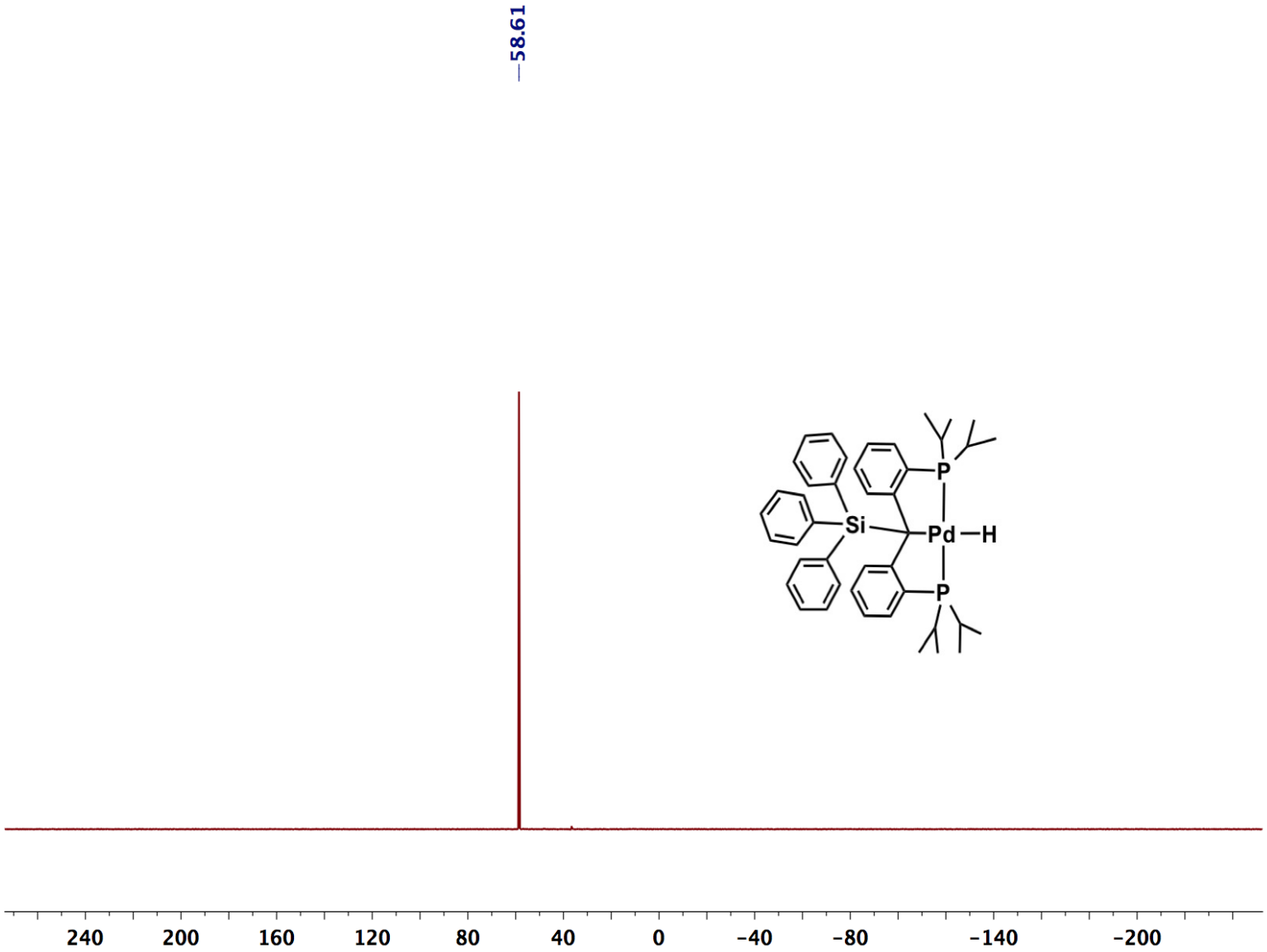


Figure S17. $^{31}P\{^{1}H\}$ NMR spectrum for [PC(SiPh$_3$)P]PdH (**5**).

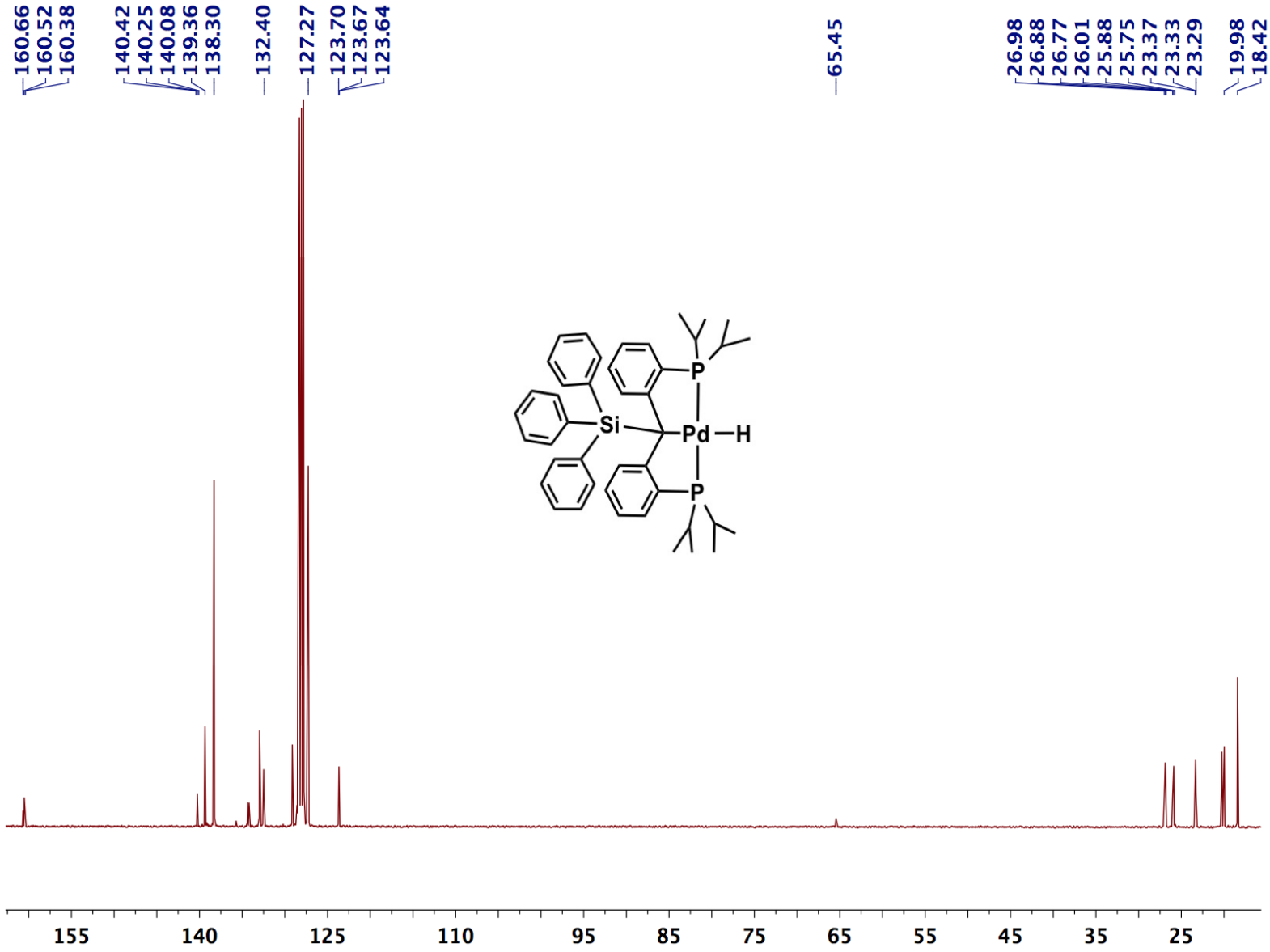


Figure S18. $^{13}C\{^{1}H\}$ NMR spectrum for [PC(SiPh$_3$)P]PdH (**5**).

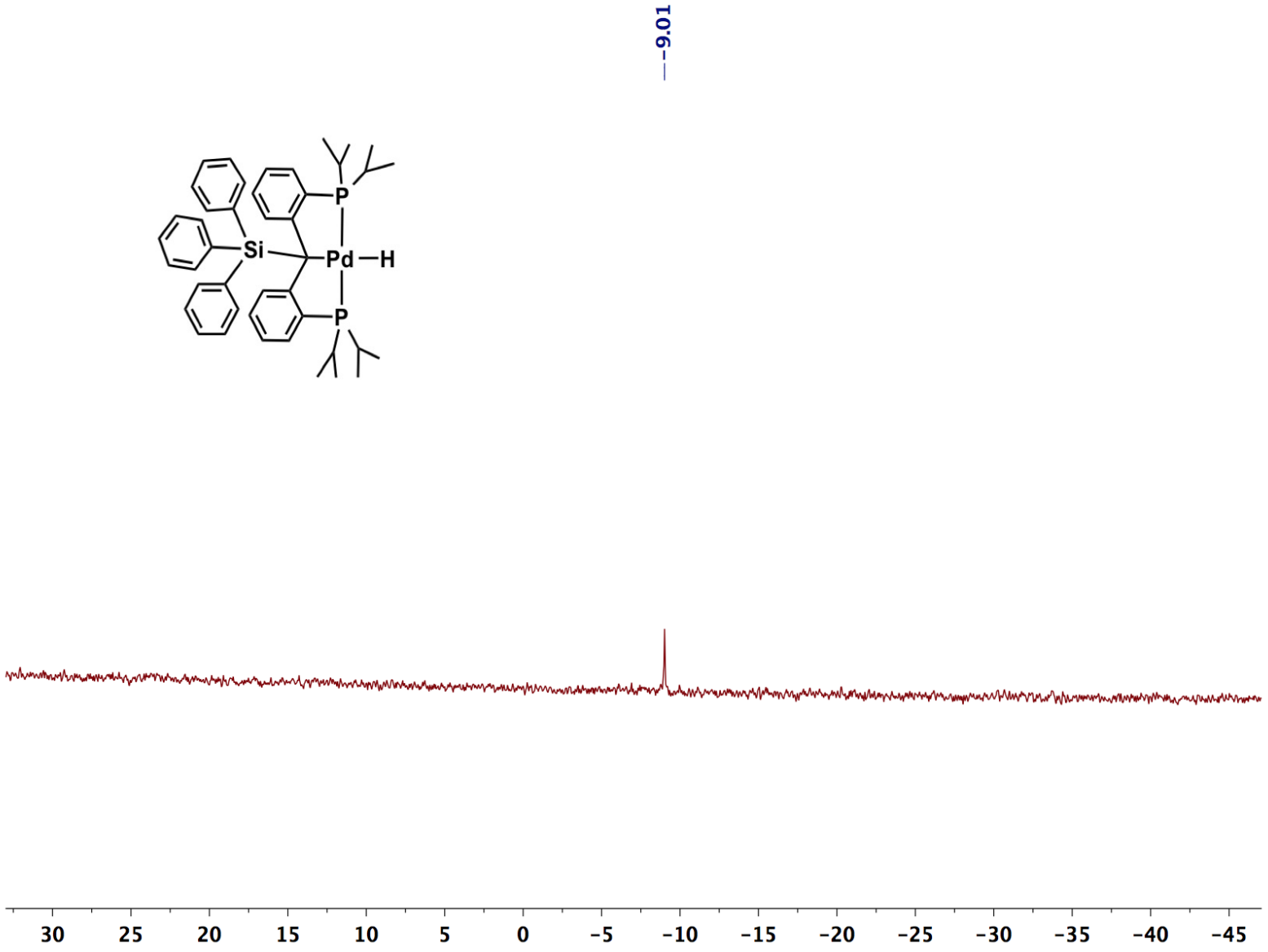


Figure S19. $^{29}Si\{^{1}H\}$ NMR spectrum for [PC(SiPh$_3$)P]PdH (**5**).

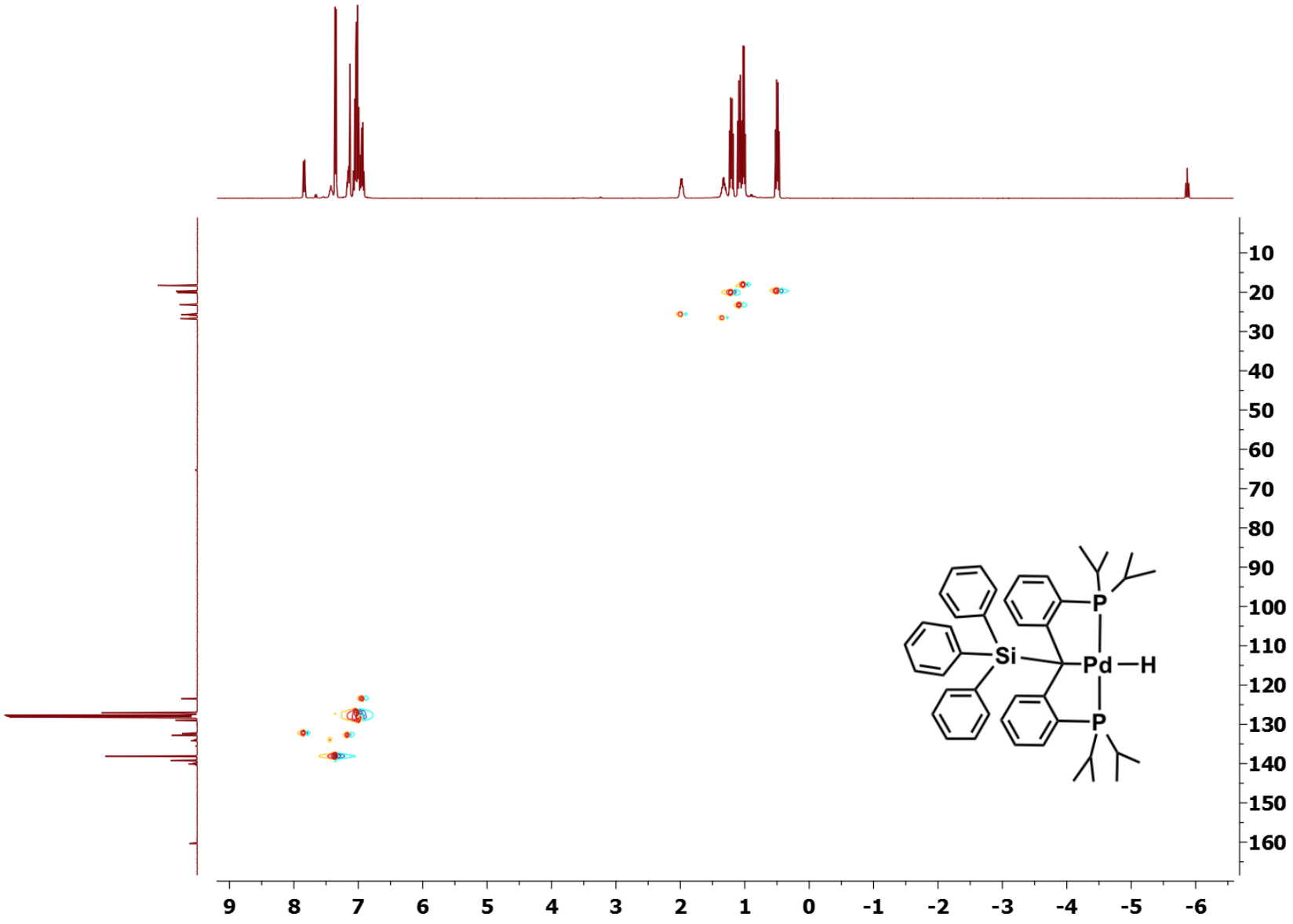


Figure S20. ^{1}H-^{13}C HSQC NMR spectrum for [PC($SiPh_3$)P]PdH (**5**).

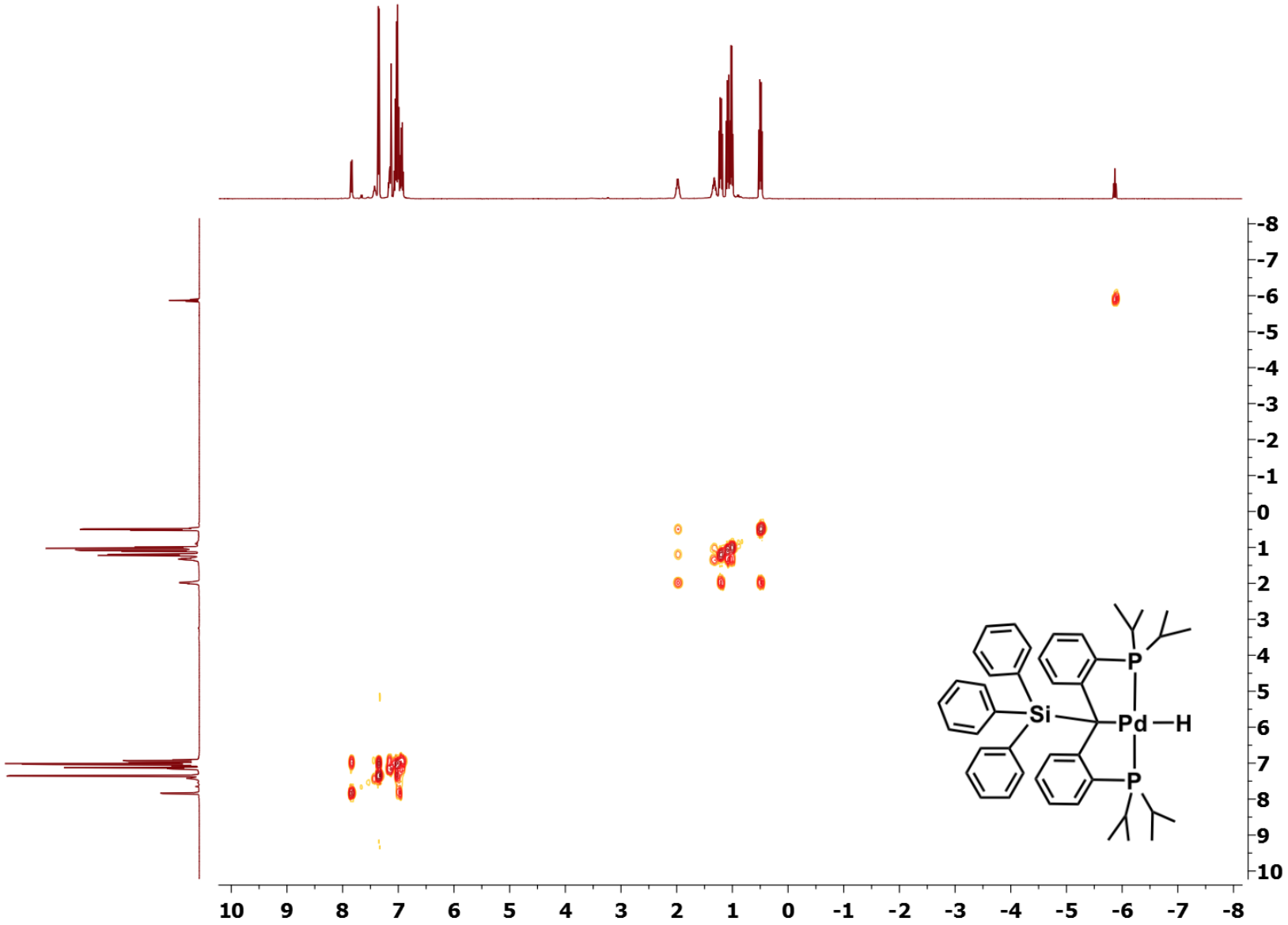


Figure S21. ^{1}H-^{1}H COSY NMR spectrum for [PC(SiPh$_3$)P]PdH (**5**).

3.4 NMR Spectra for [PC(H)P]Pd(SiHPh$_2$) (7)

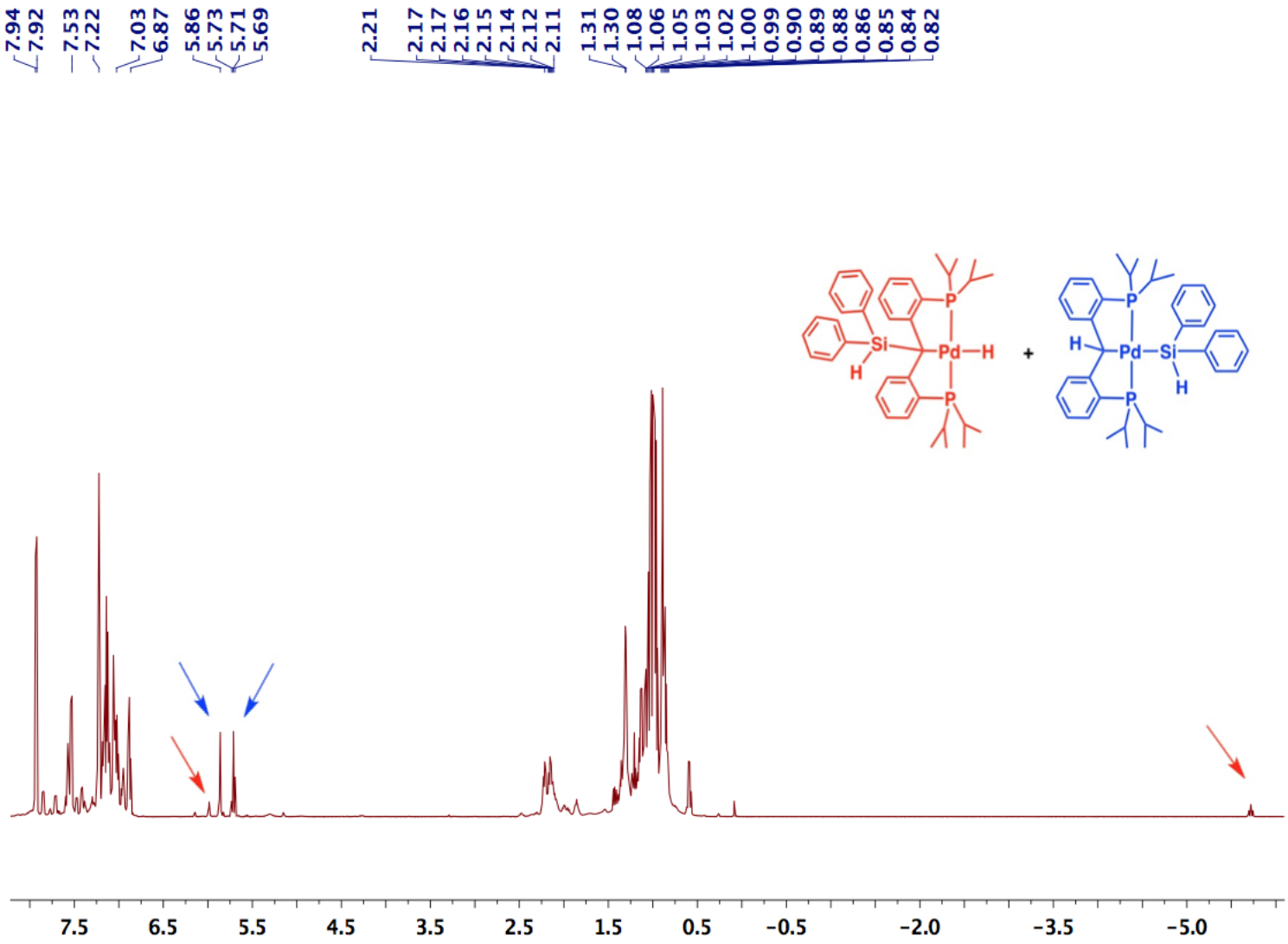


Figure S22. ^{1}H NMR spectrum for the mixture of [PC(H)P]Pd(SiHPh$_2$) (**7**) and [PC(SiHPh$_2$)P]PdH (**4**).

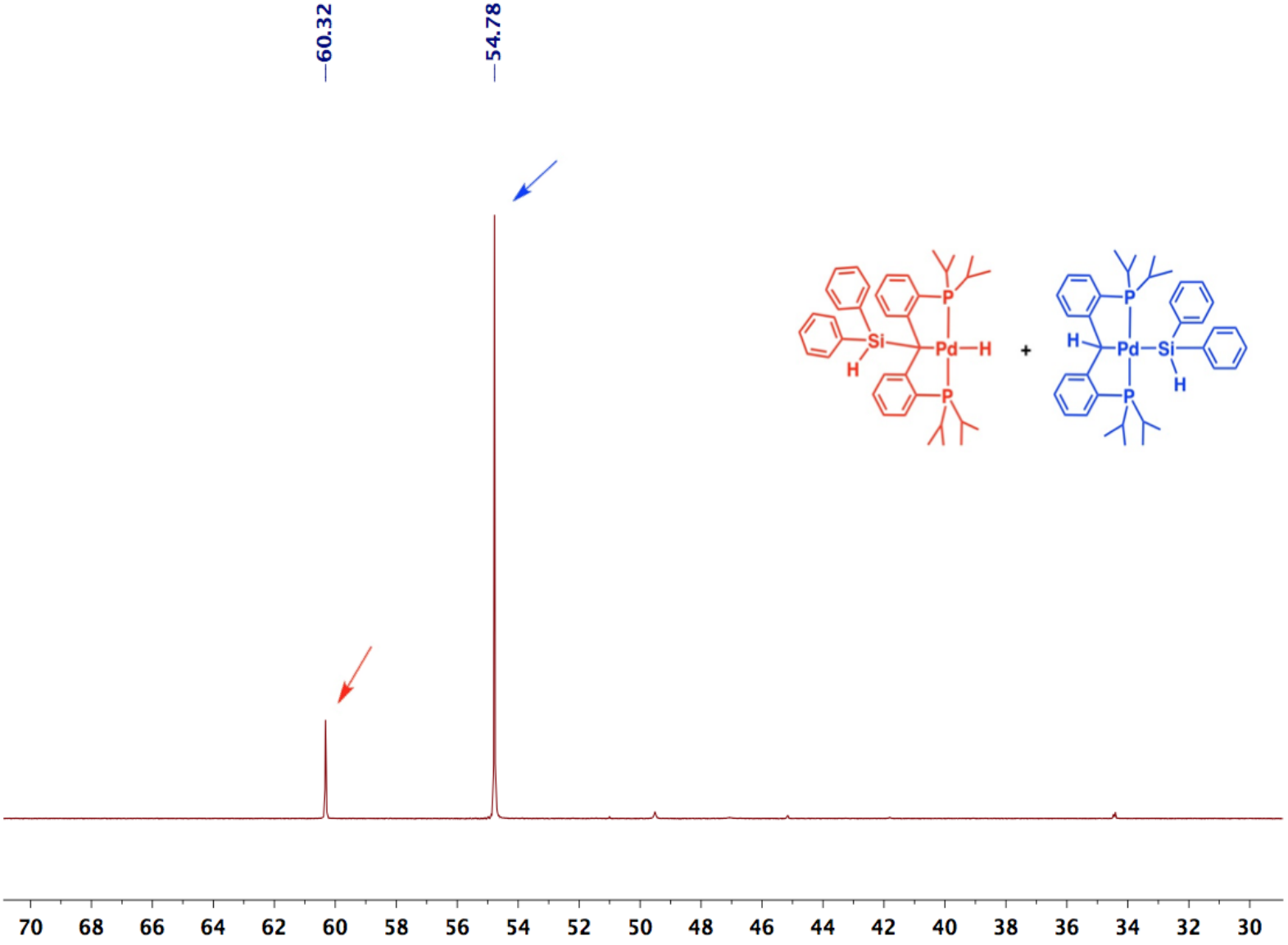


Figure S23. $^{31}P\{^{1}H\}$ NMR spectrum for the mixture of [PC(H)P]Pd($SiHPh_2$) (**7**) and [PC($SiHPh_2$)P]PdH (**4**)

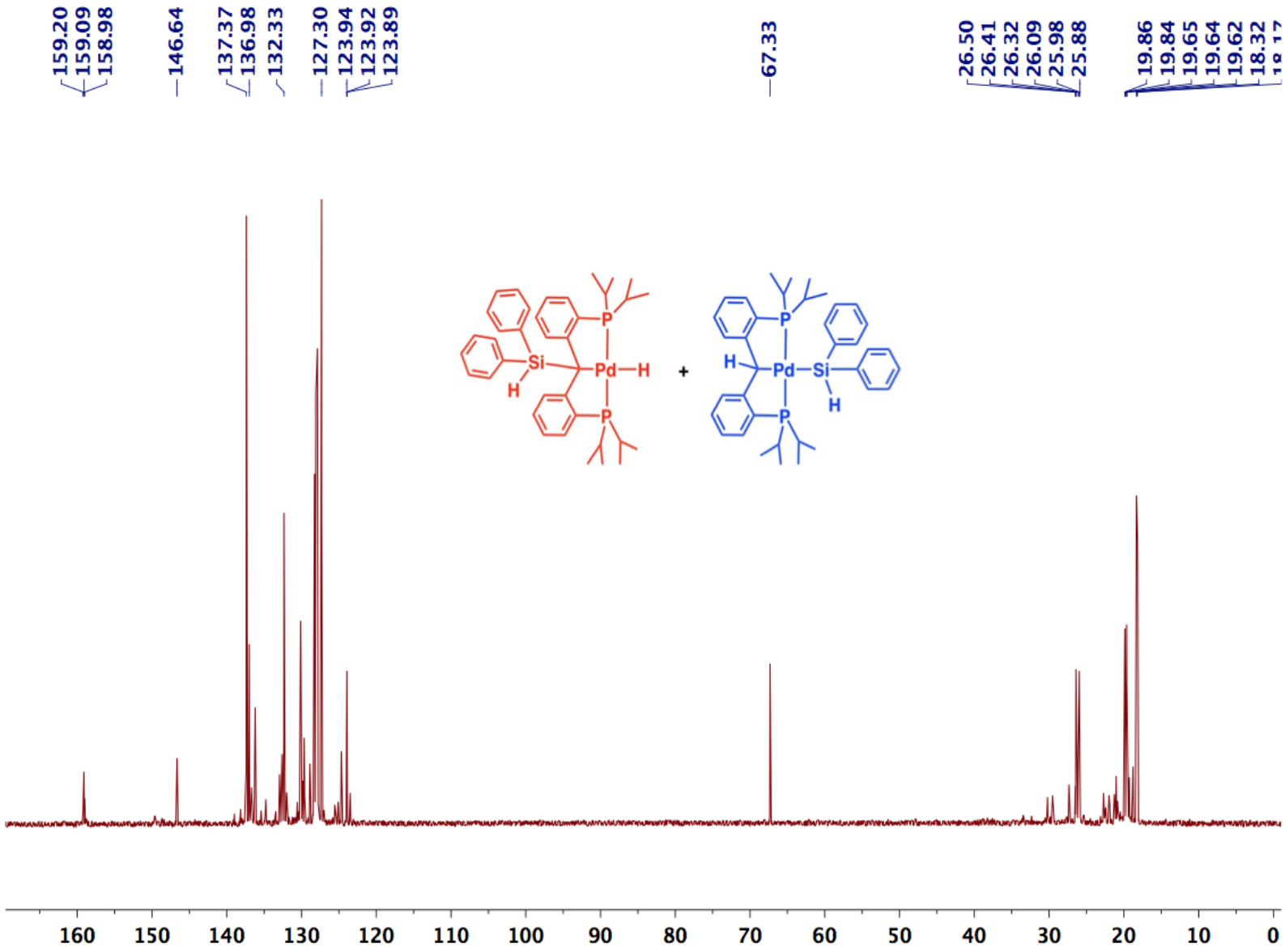


Figure S24. $^{13}C\{^{1}H\}$ NMR spectrum for the mixture of [PC(H)P]Pd($SiHPh_2$) (**7**) and [PC($SiHPh_2$)P]PdH (**4**).

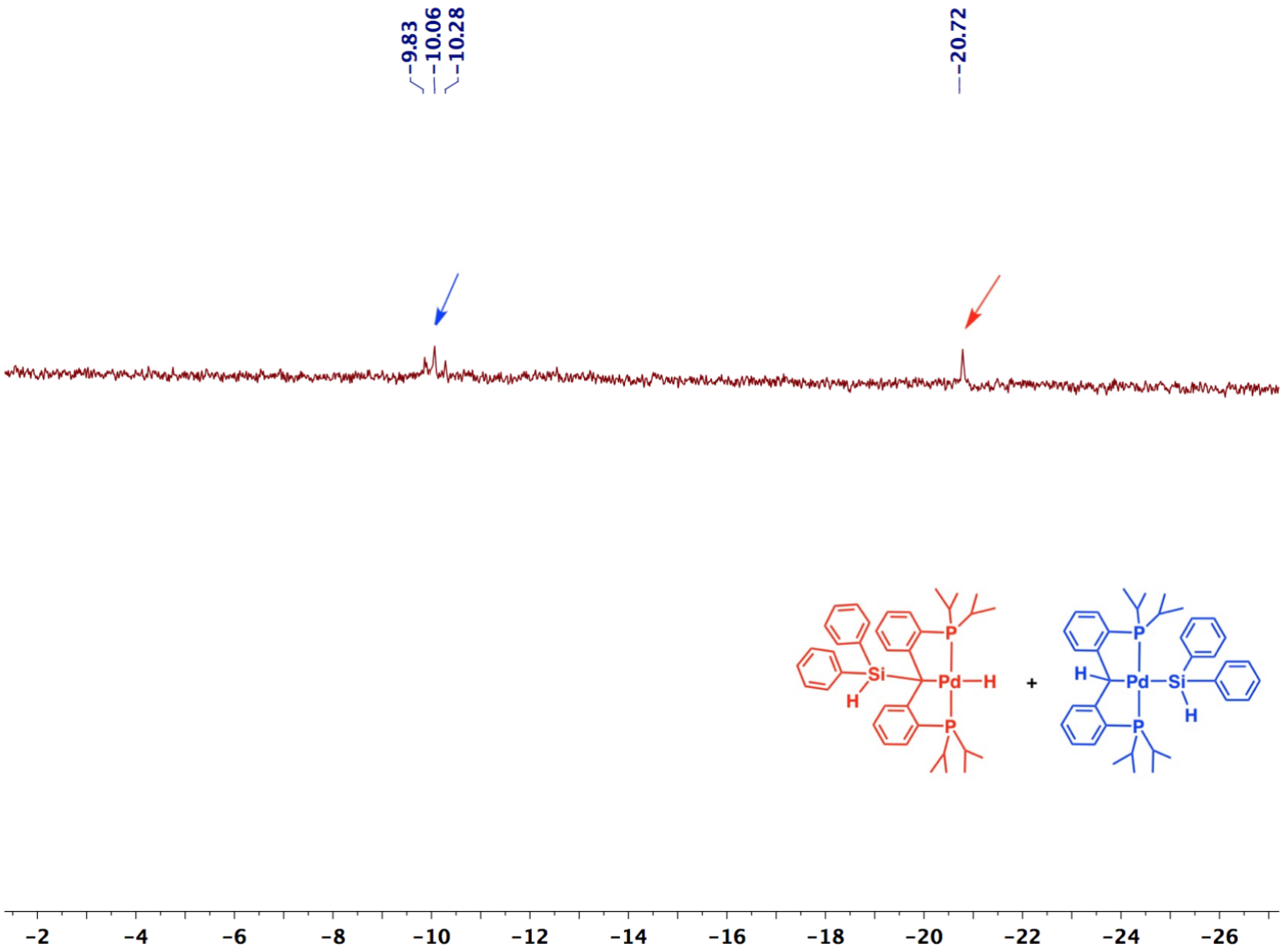


Figure S25. $^{29}Si\{^{1}H\}$ NMR spectrum for the mixture of [PC(H)P]Pd($SiHPh_2$) (**7**) and [PC($SiHPh_2$)P]PdH (**4**).

3.5 NMR Spectra for [PC(H)P]Pd($SiPh_3$) (8)

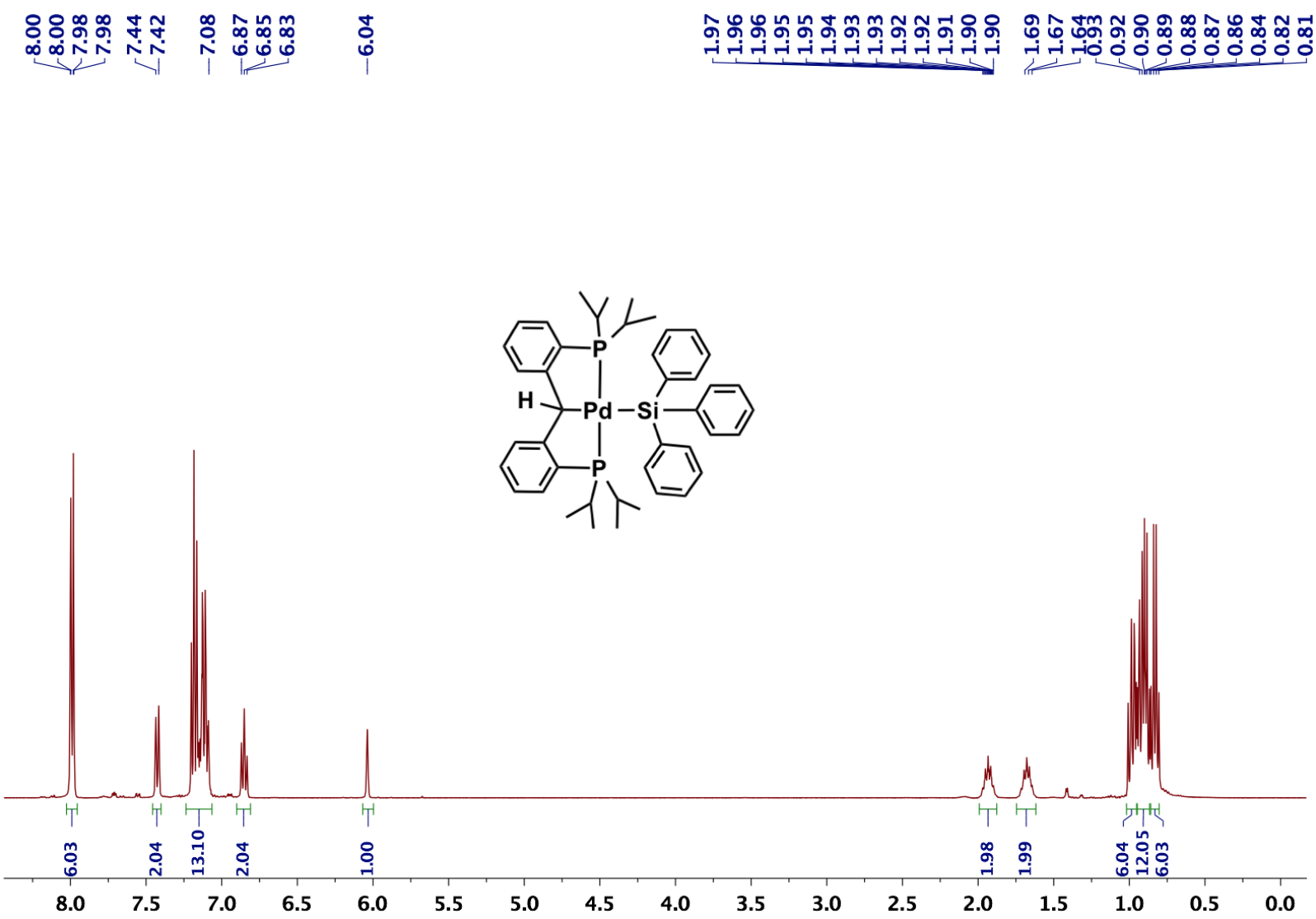


Figure S26. ^{1}H NMR spectrum for [PC(H)P]Pd($SiPh_3$) (**8**).

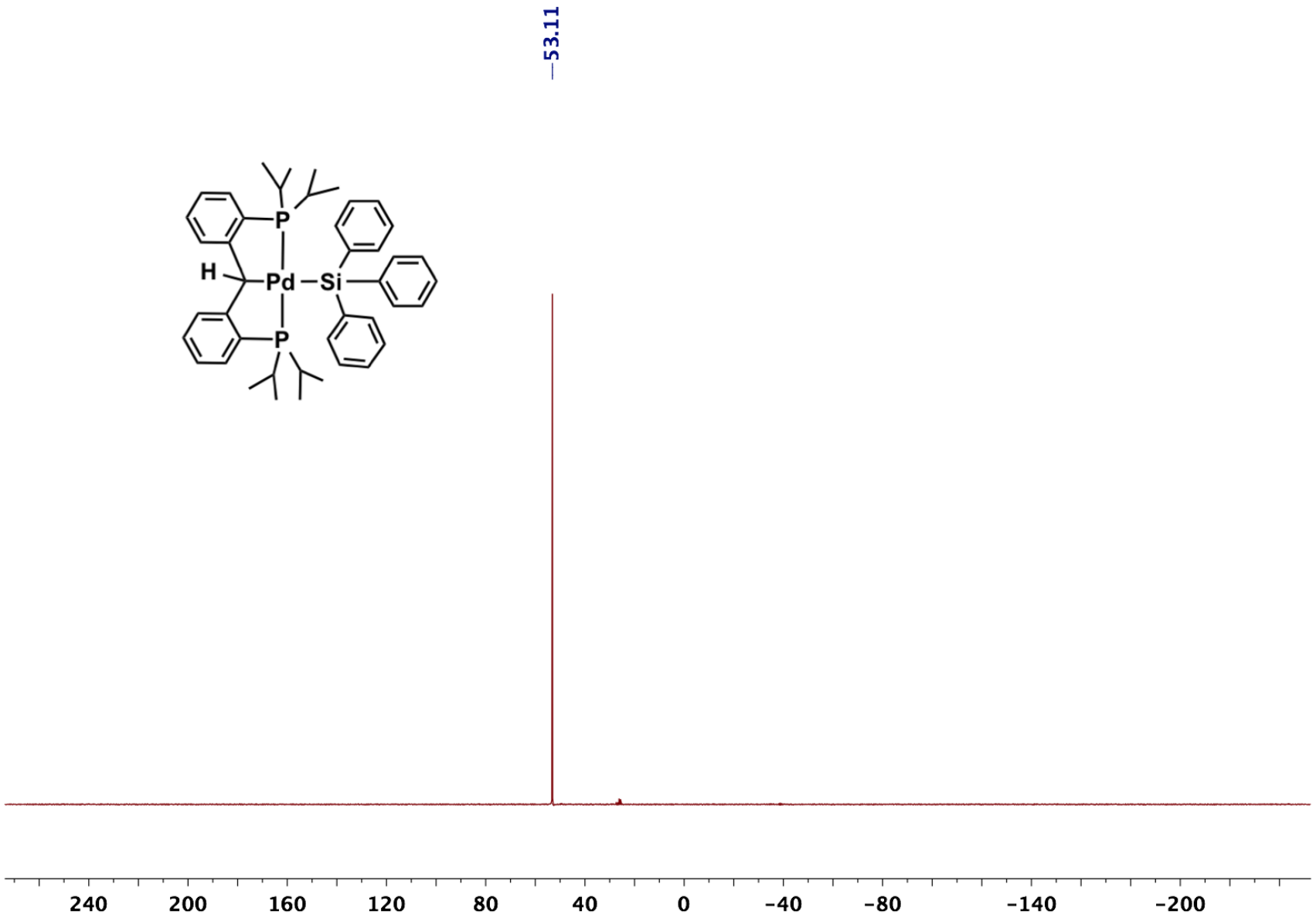


Figure S27. $^{31}P\{^{1}H\}$ NMR spectrum for [PC(H)P]Pd($SiPh_3$) (**8**).

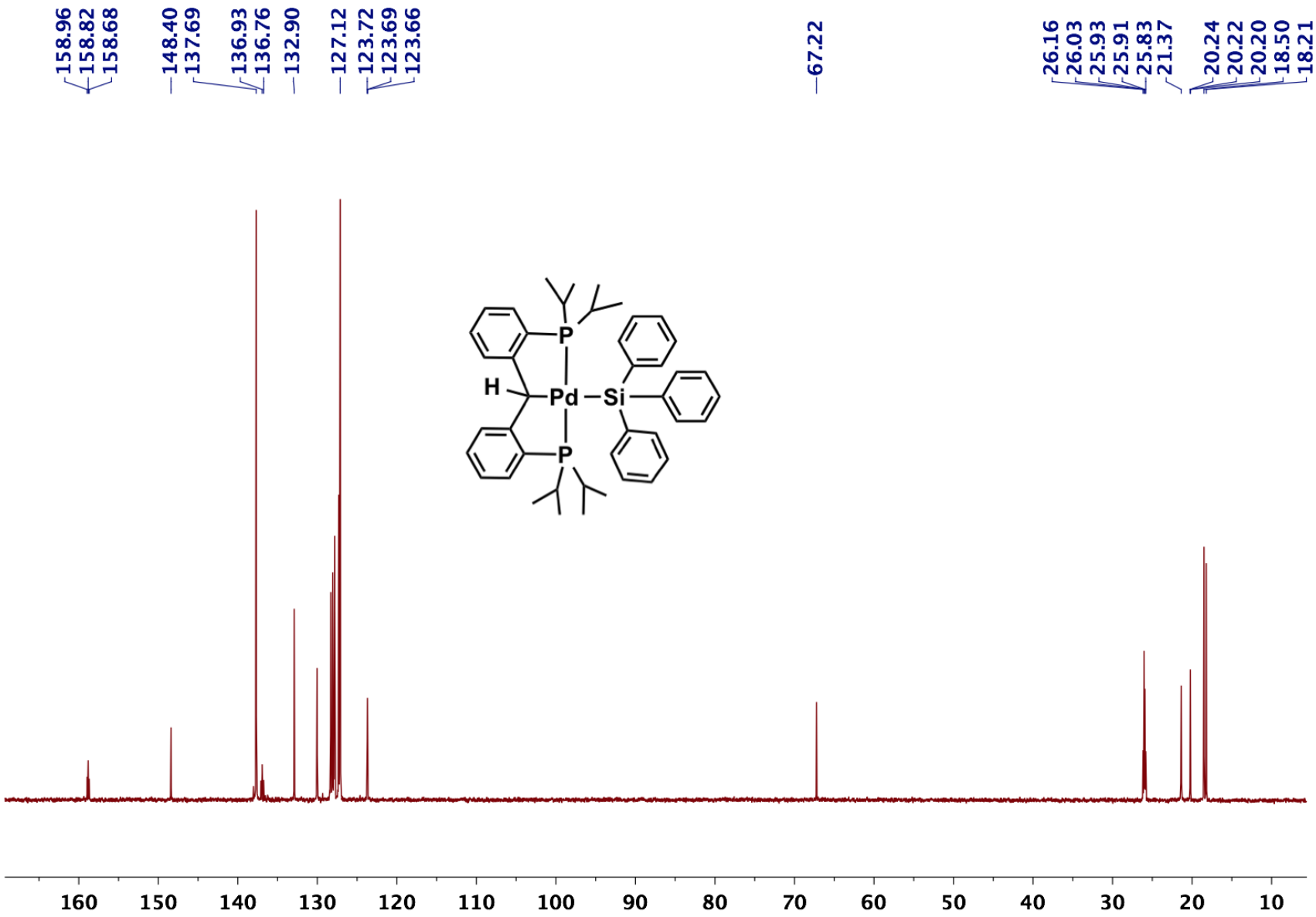


Figure S28. $^{13}C\{^{1}H\}$ NMR spectrum for [PC(H)P]Pd($SiPh_3$) (**8**).

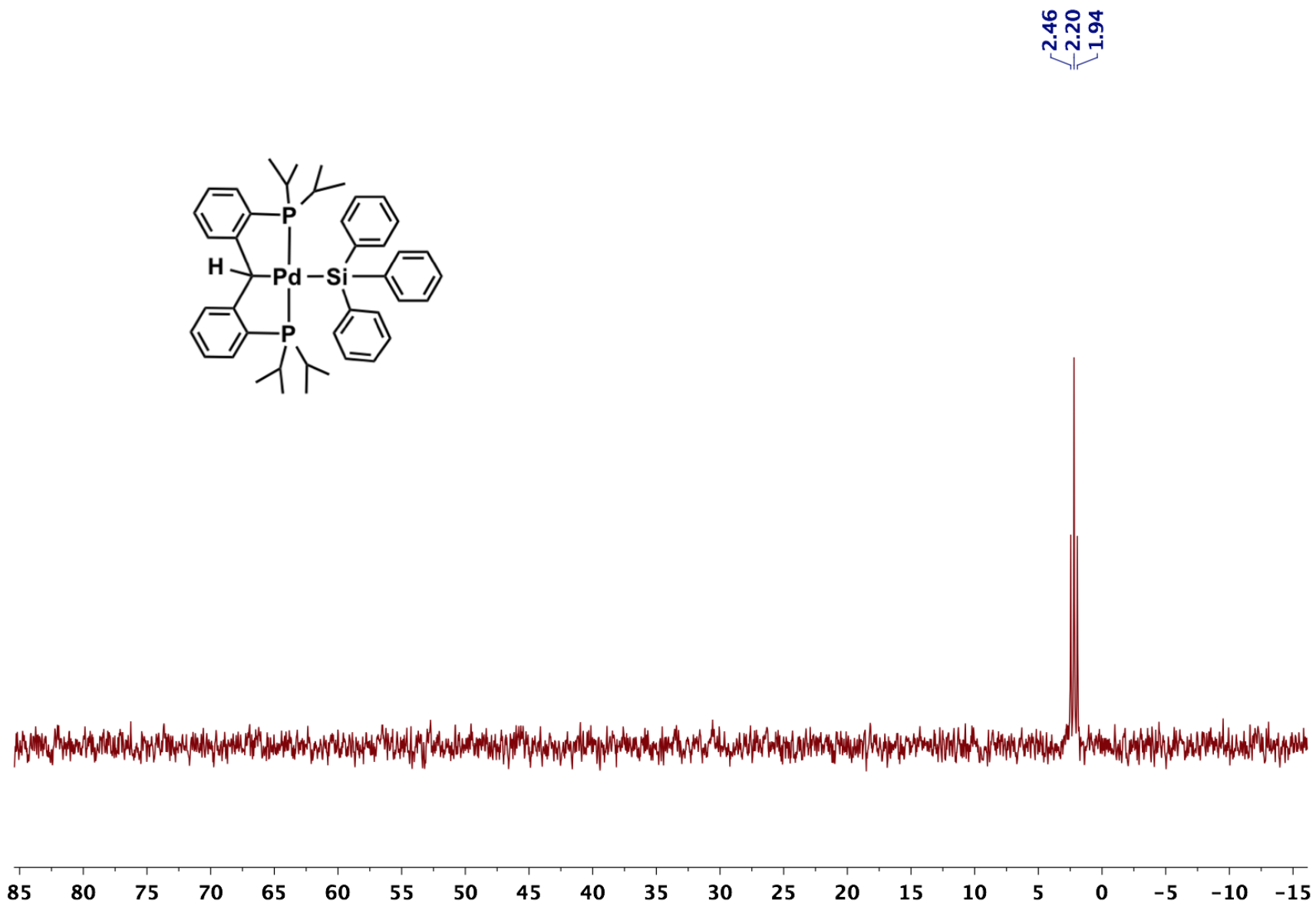


Figure S29. $^{29}Si\{^{1}H\}$ NMR spectrum for [PC(H)P]Pd($SiPh_3$) (**8**).

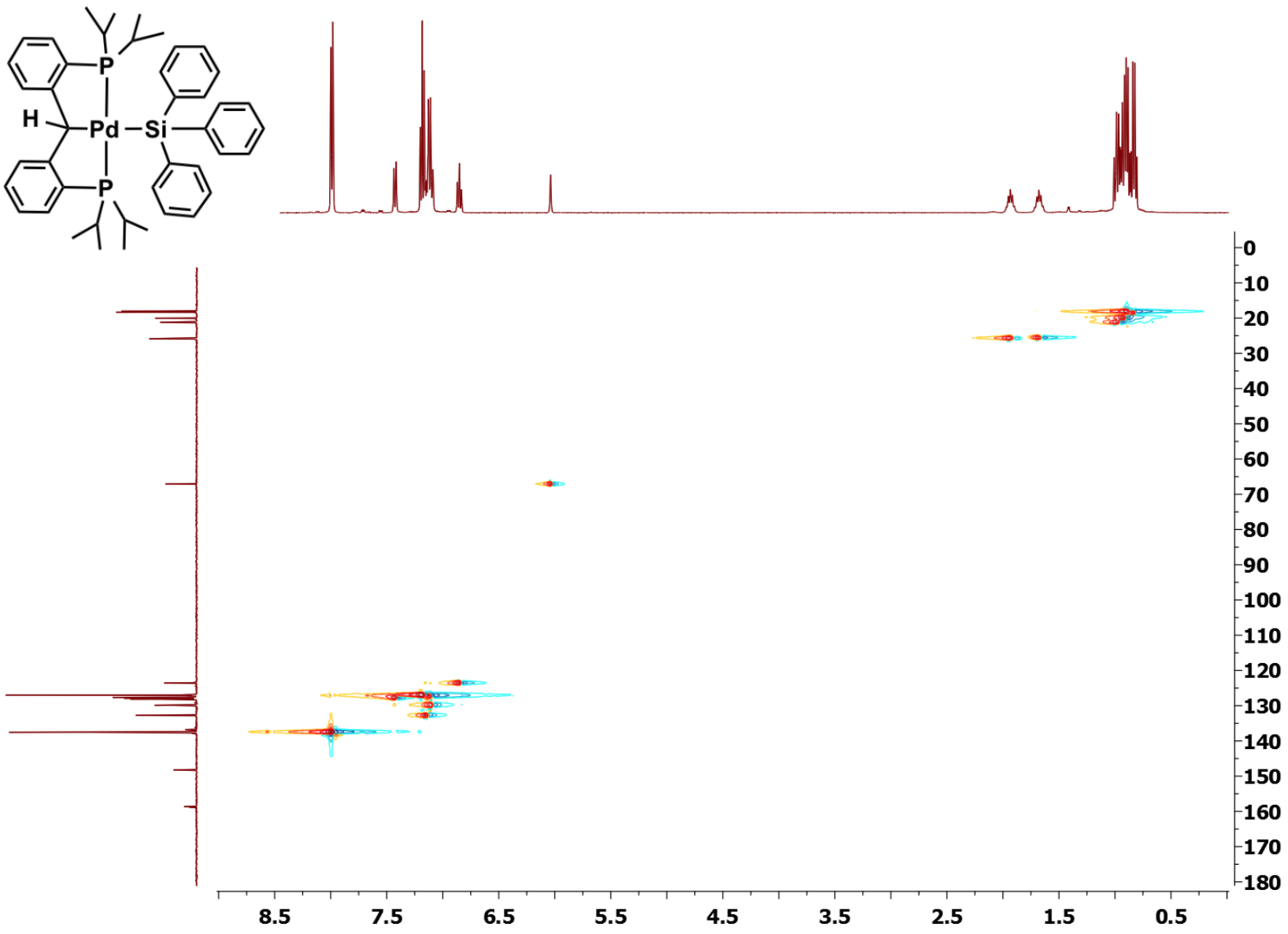


Figure S30. ^{1}H-^{13}C HSQC NMR spectrum for [PC(H)P]Pd($SiPh_3$) (**8**).

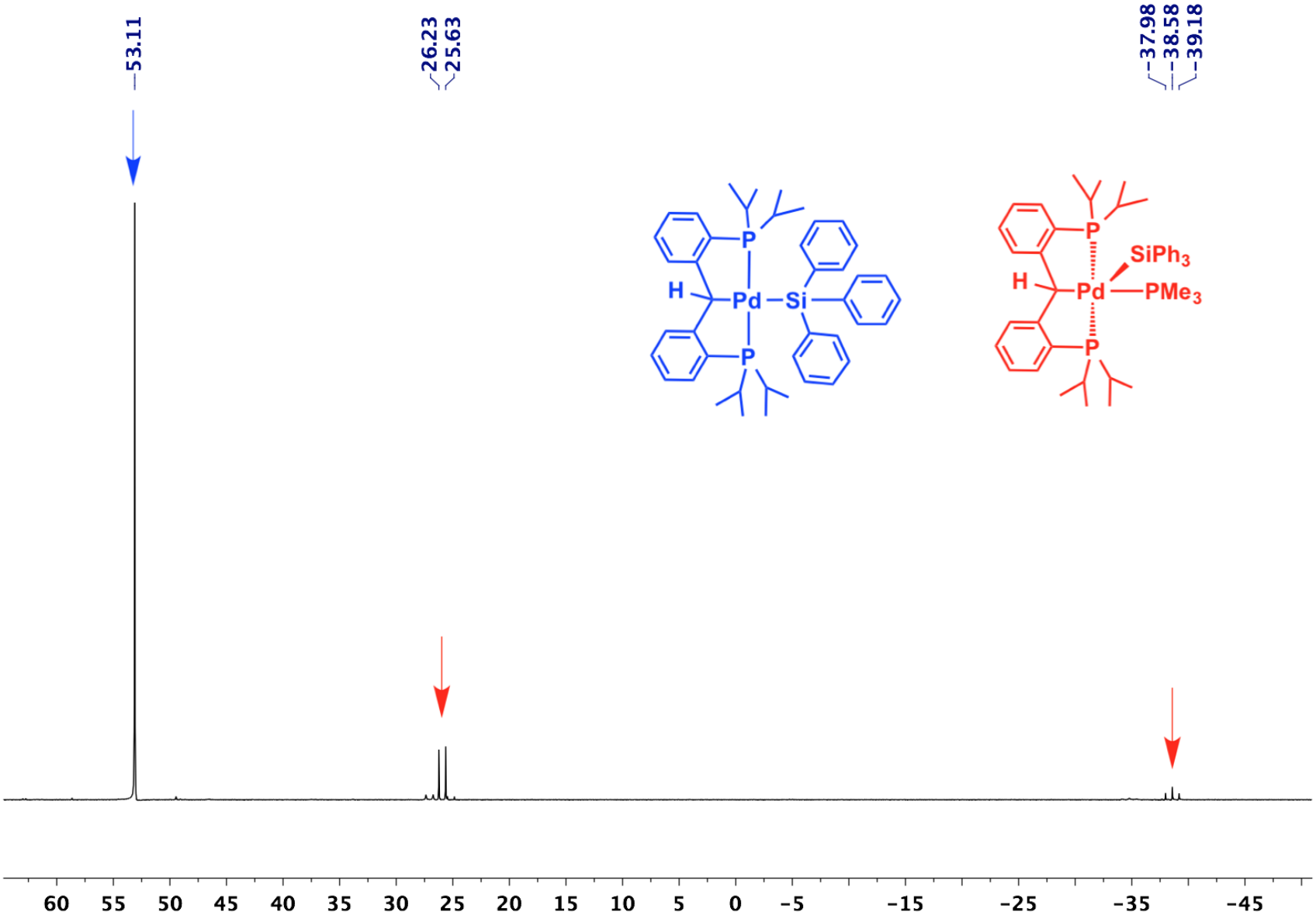


Figure S31. $^{31}P\{^{1}H\}$ NMR spectrum for [PC(H)P]Pd(PMe_3)($SiPh_3$) (**14**).

3.6 NMR Spectra for [PC(Bpin)P]PdH (9)

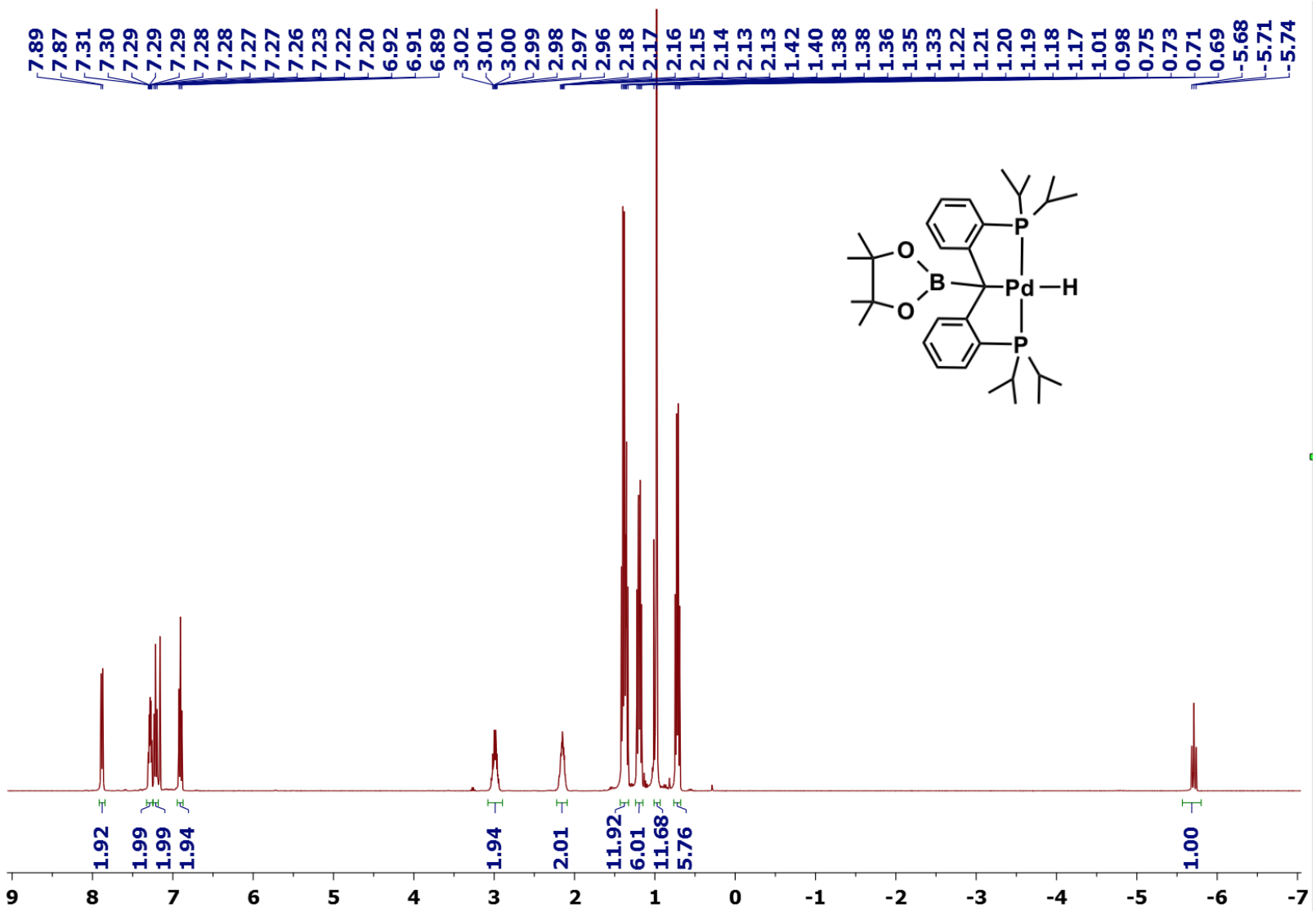


Figure S32. ^{1}H NMR spectrum for [PC(Bpin)P]PdH (**9**).

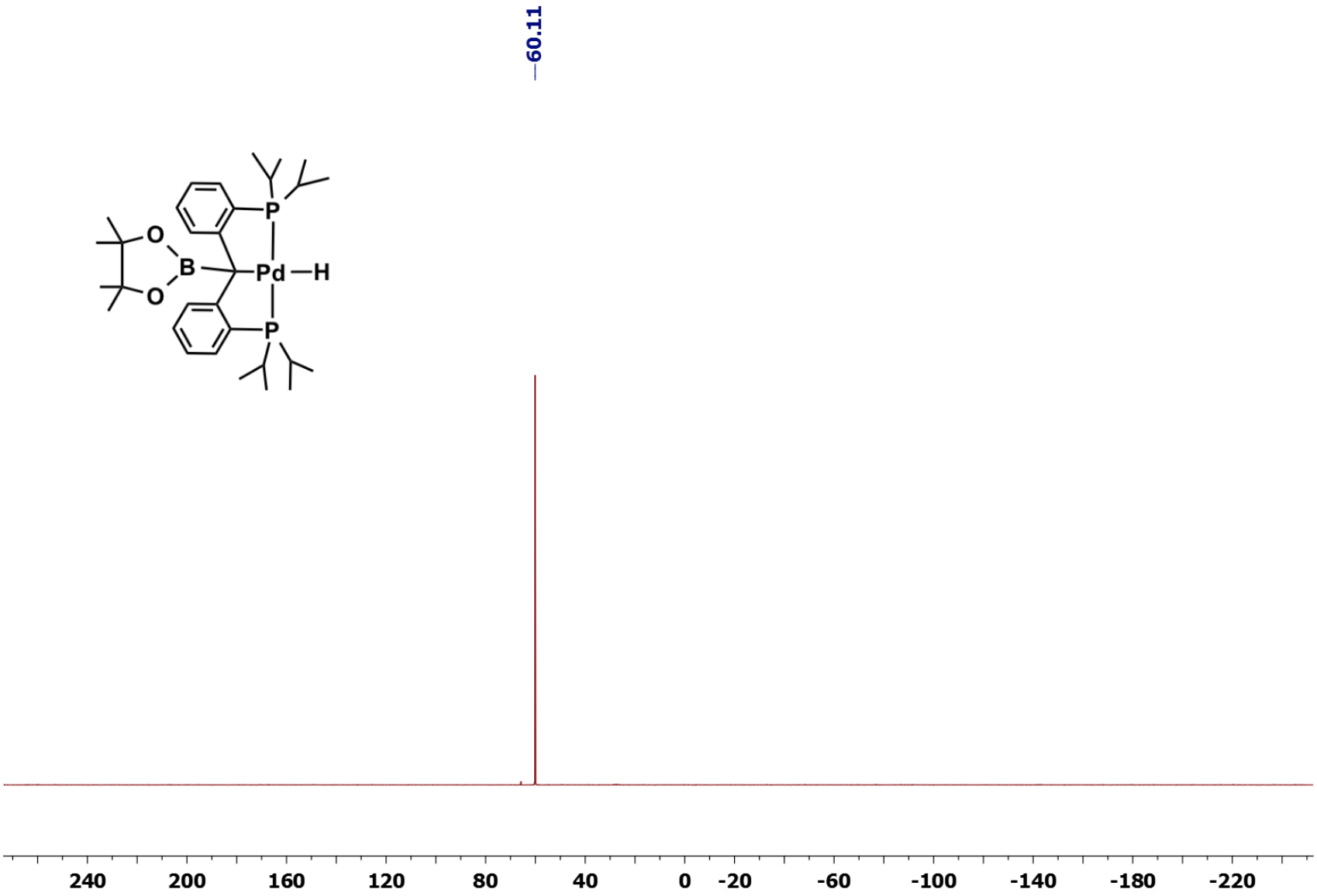


Figure S33. $^{31}P\{^{1}H\}$ NMR spectrum for [PC(Bpin)P]PdH (**9**).

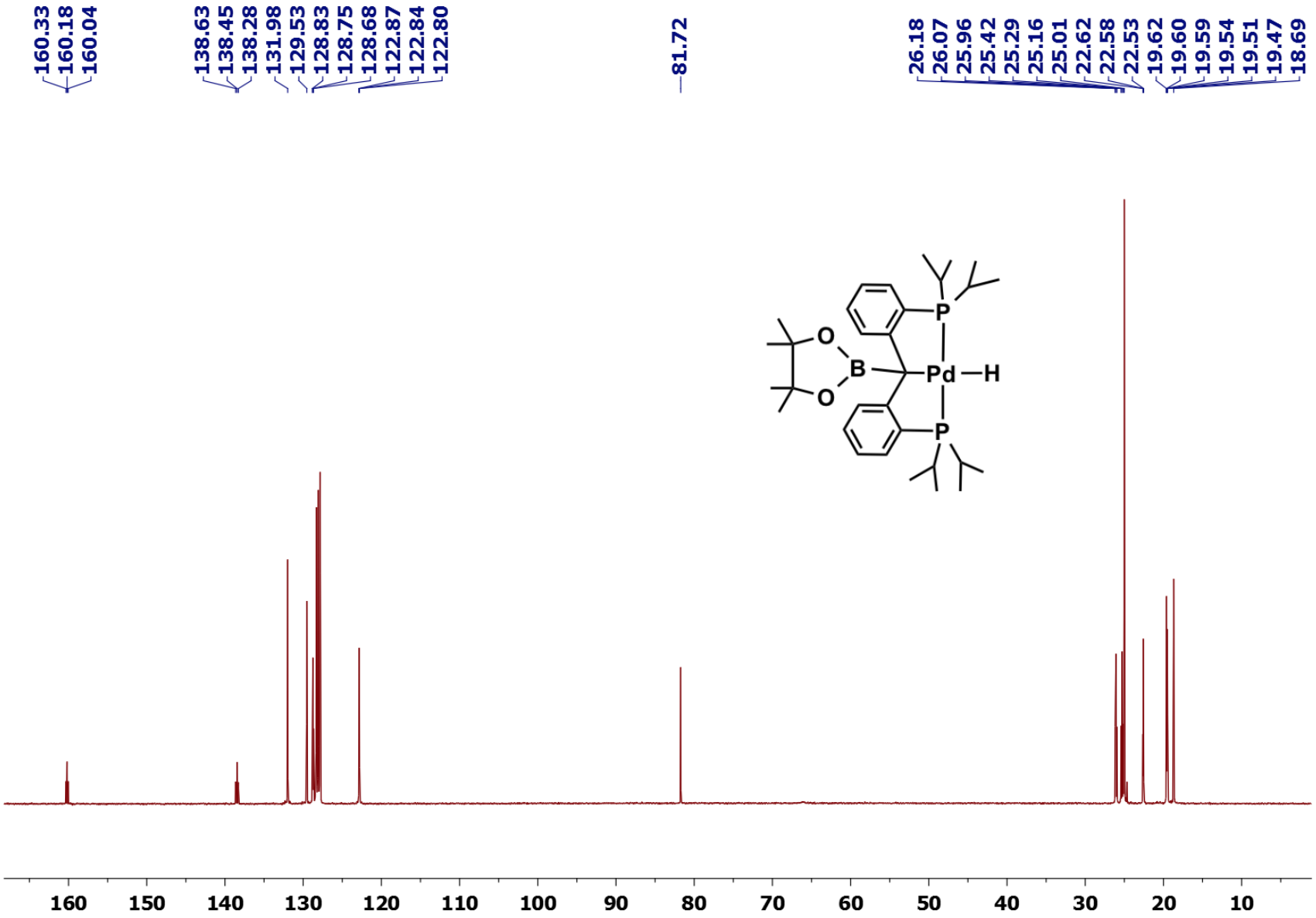


Figure S34. $^{13}C\{^{1}H\}$ NMR spectrum for [PC(Bpin)P]PdH (**9**).

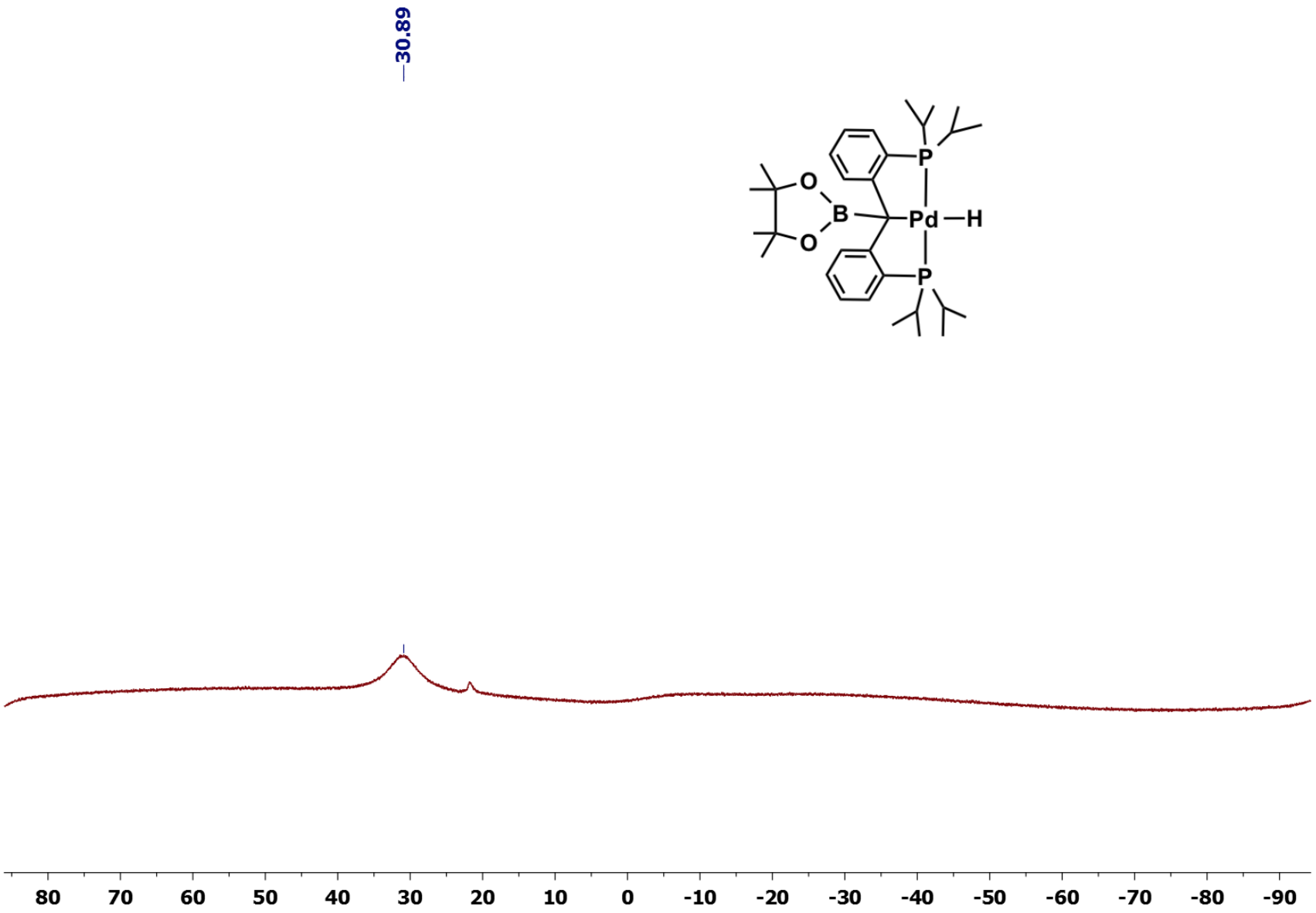


Figure S35. ^{11}B NMR spectrum for [PC(Bpin)P]PdH (**9**).

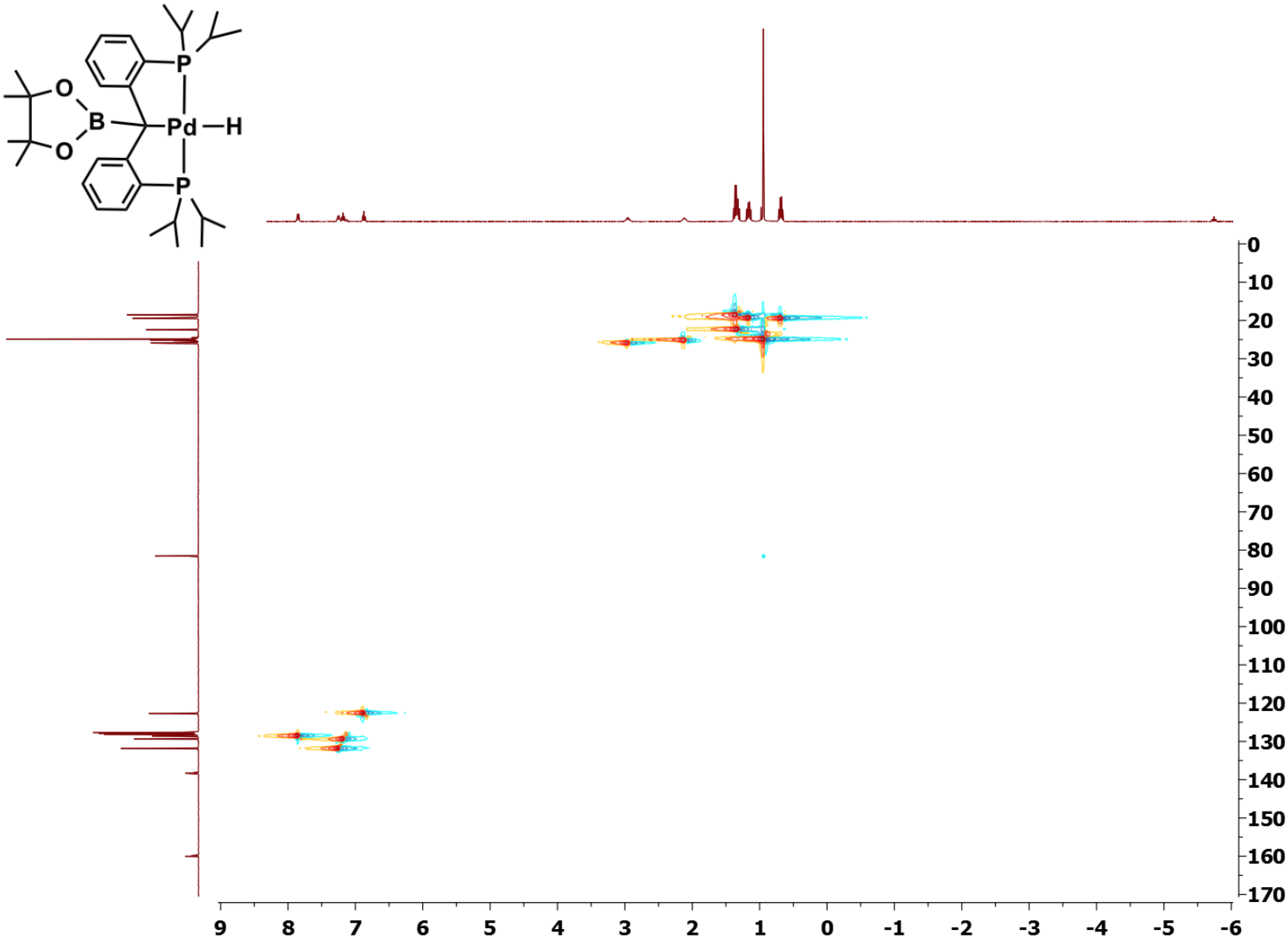


Figure S36. ^{1}H-^{13}C HSQC NMR spectrum for [PC(Bpin)P]PdH (**9**).

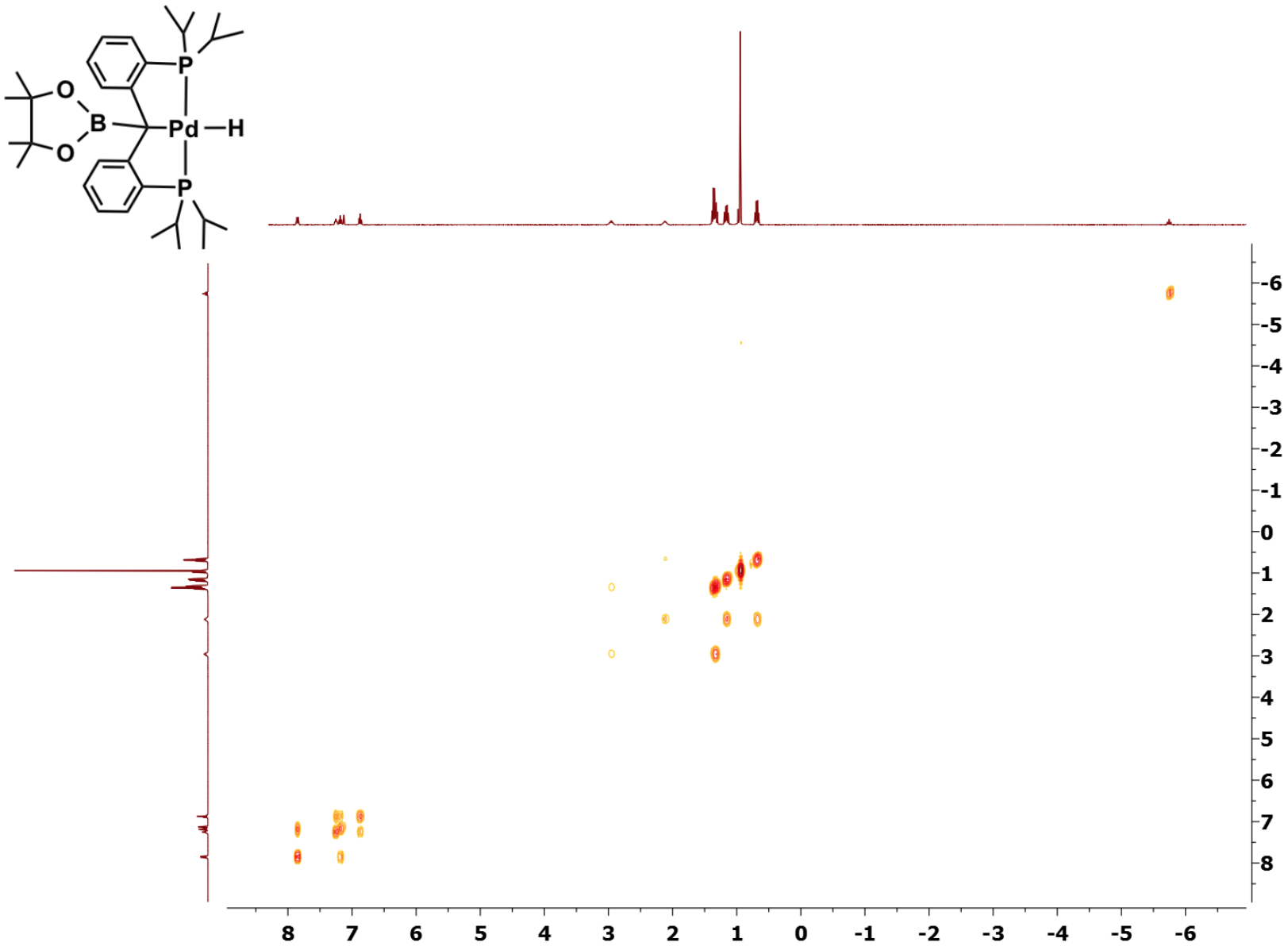


Figure S37. ^{1}H-^{1}H COSY NMR spectrum for [PC(Bpin)P]PdH (**9**).

3.7 NMR Spectra for [PC(H)P]Pd(GeH_2Ph) (10)

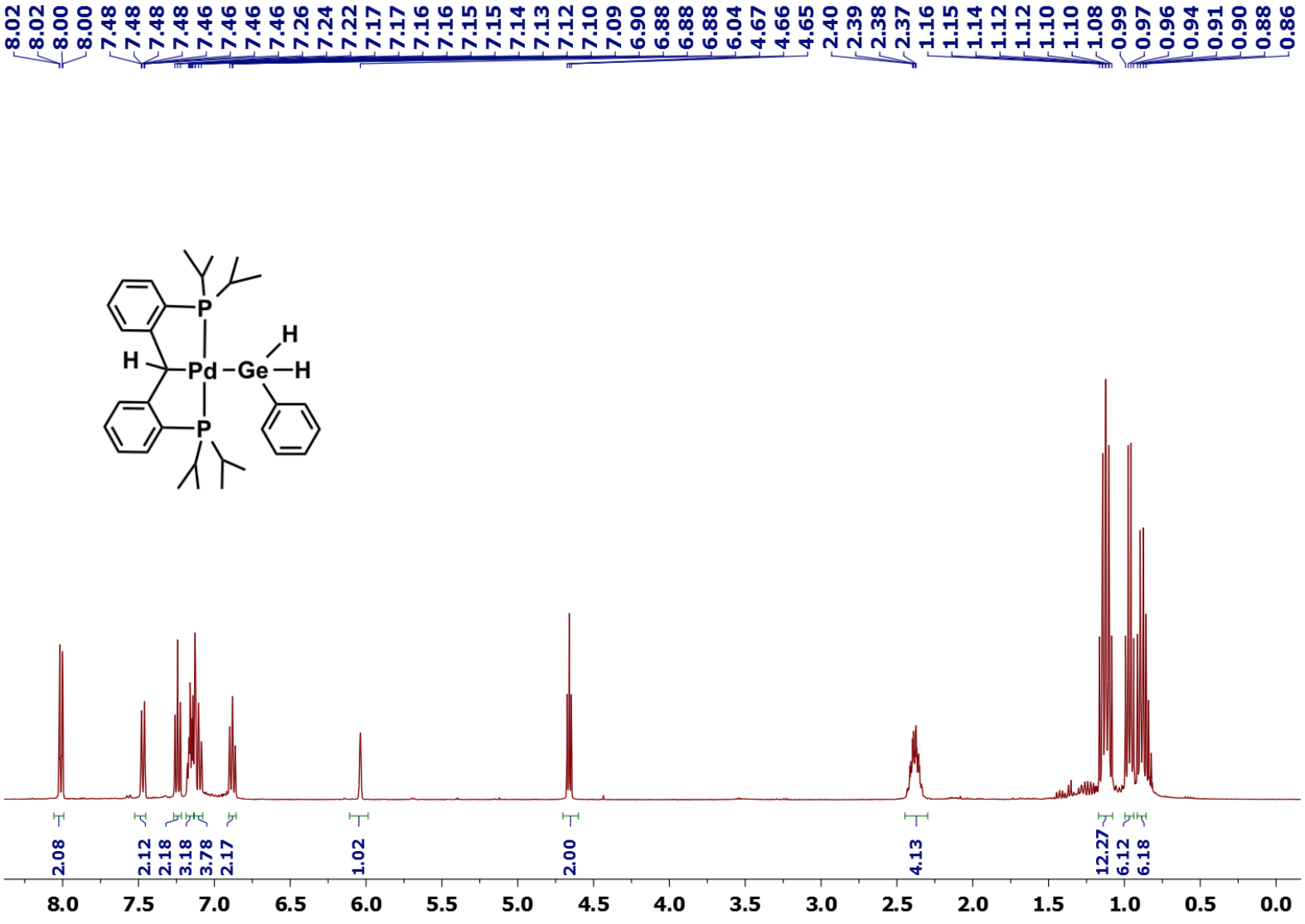


Figure S38. ^{1}H NMR spectrum for [PC(H)P]Pd(GeH_2Ph) (**10**).

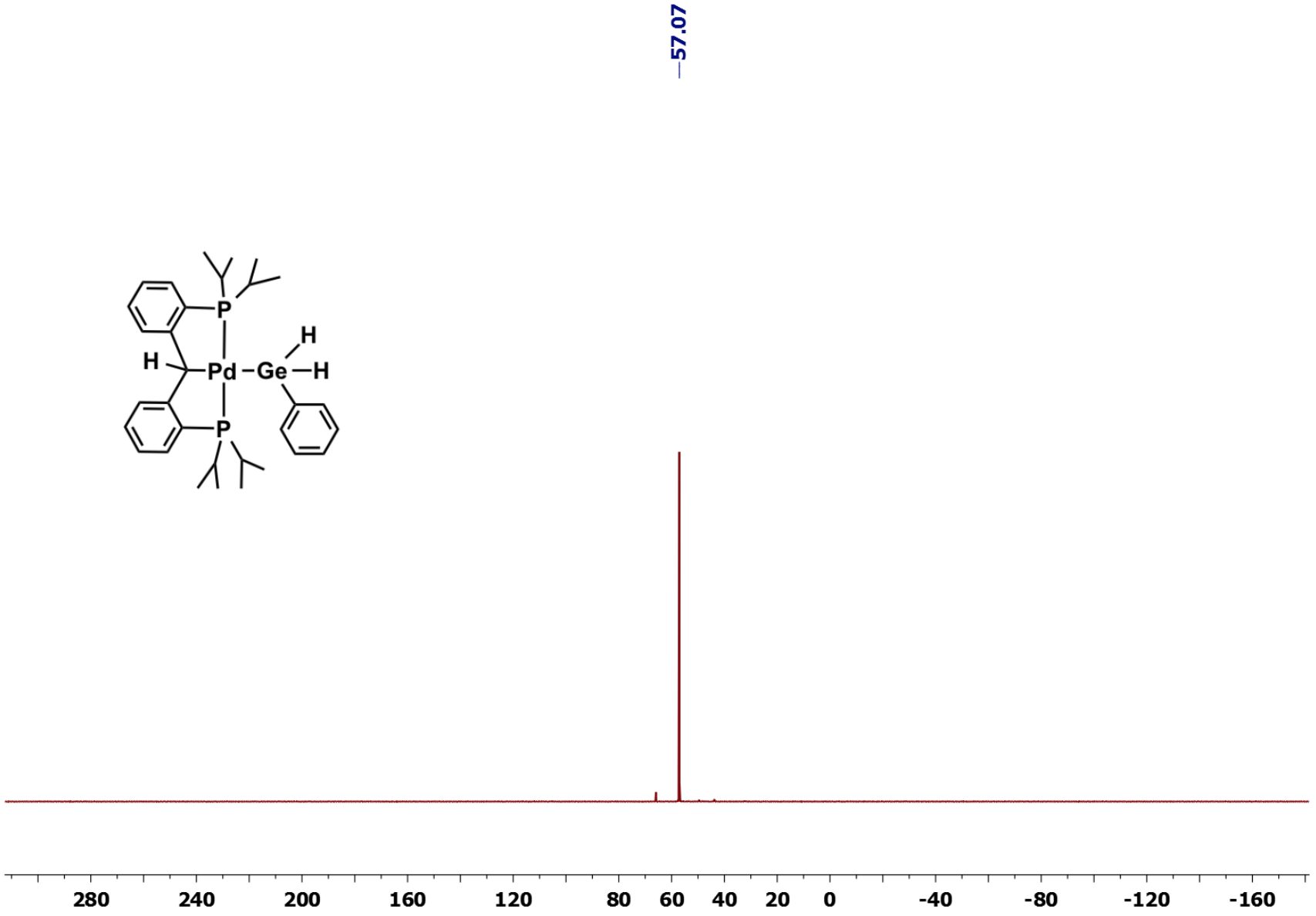


Figure S39. $^{31}P\{^{1}H\}$ NMR spectrum for [PC(H)P]Pd(GeH_2Ph) (**10**).

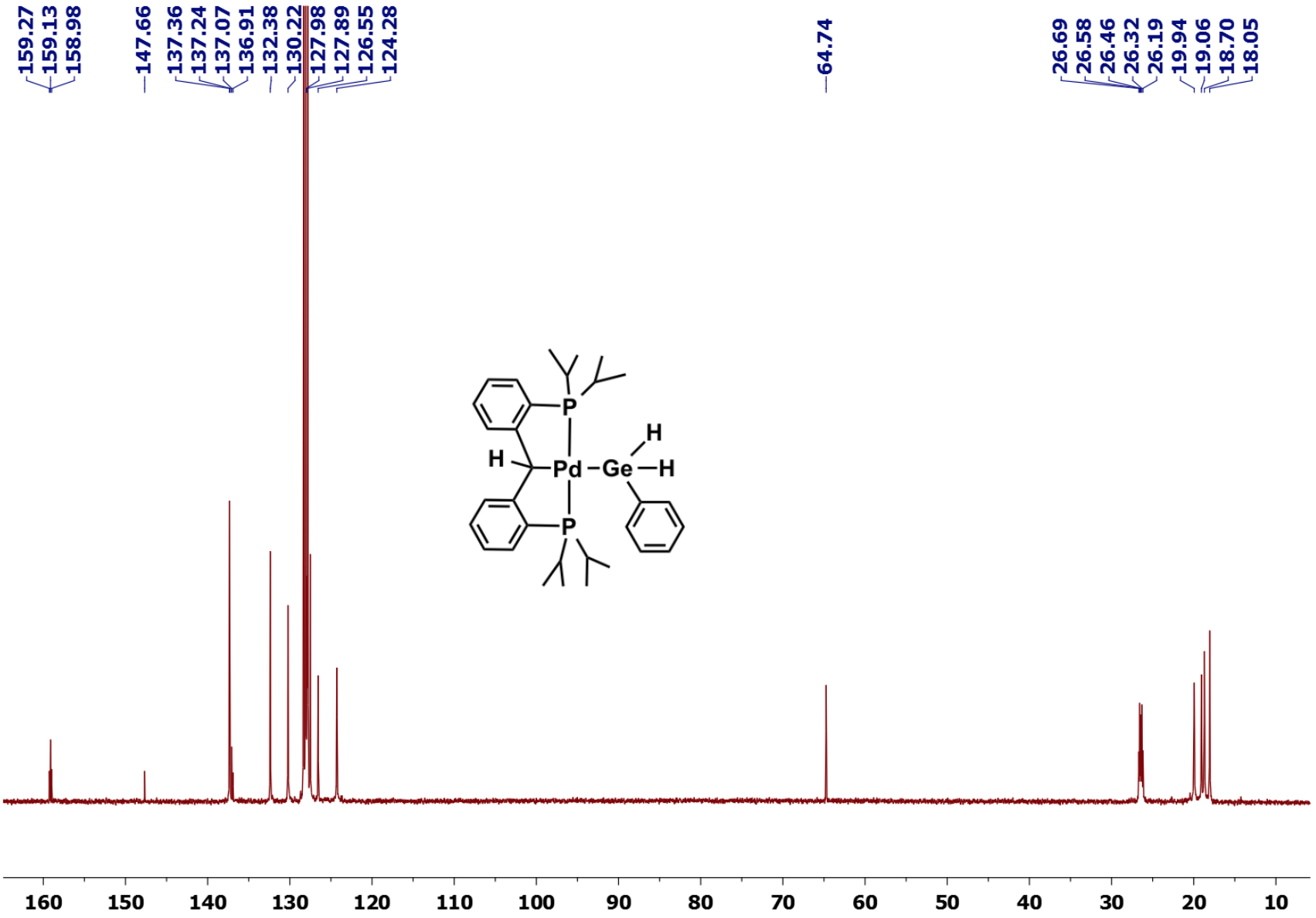


Figure S40. $^{13}C\{^{1}H\}$ NMR spectrum for [PC(H)P]Pd(GeH_2Ph) (**10**).

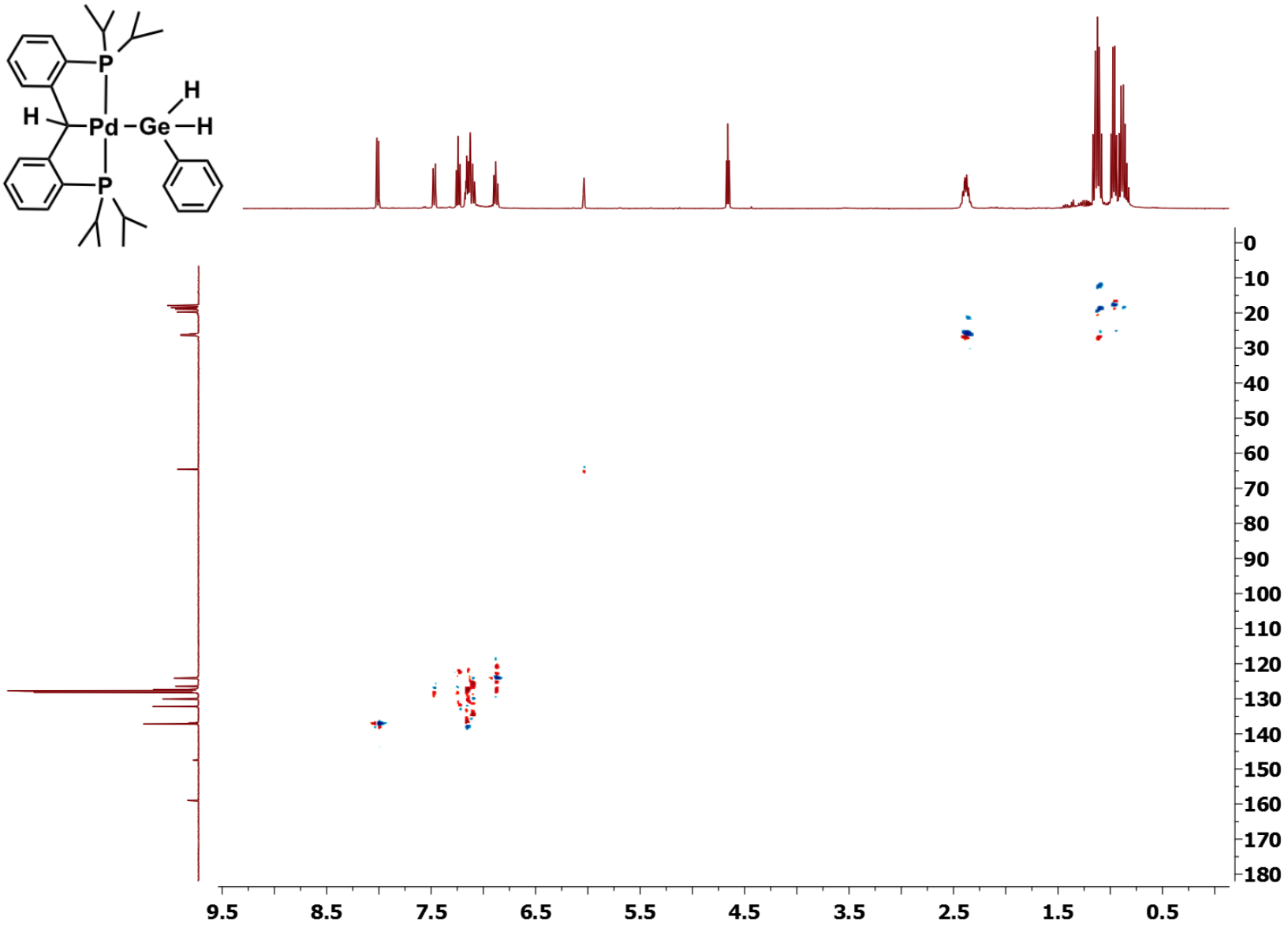


Figure S41. ^{1}H-^{13}C HSQC NMR spectrum for [PC(H)P]Pd(GeH_2Ph) (**10**).

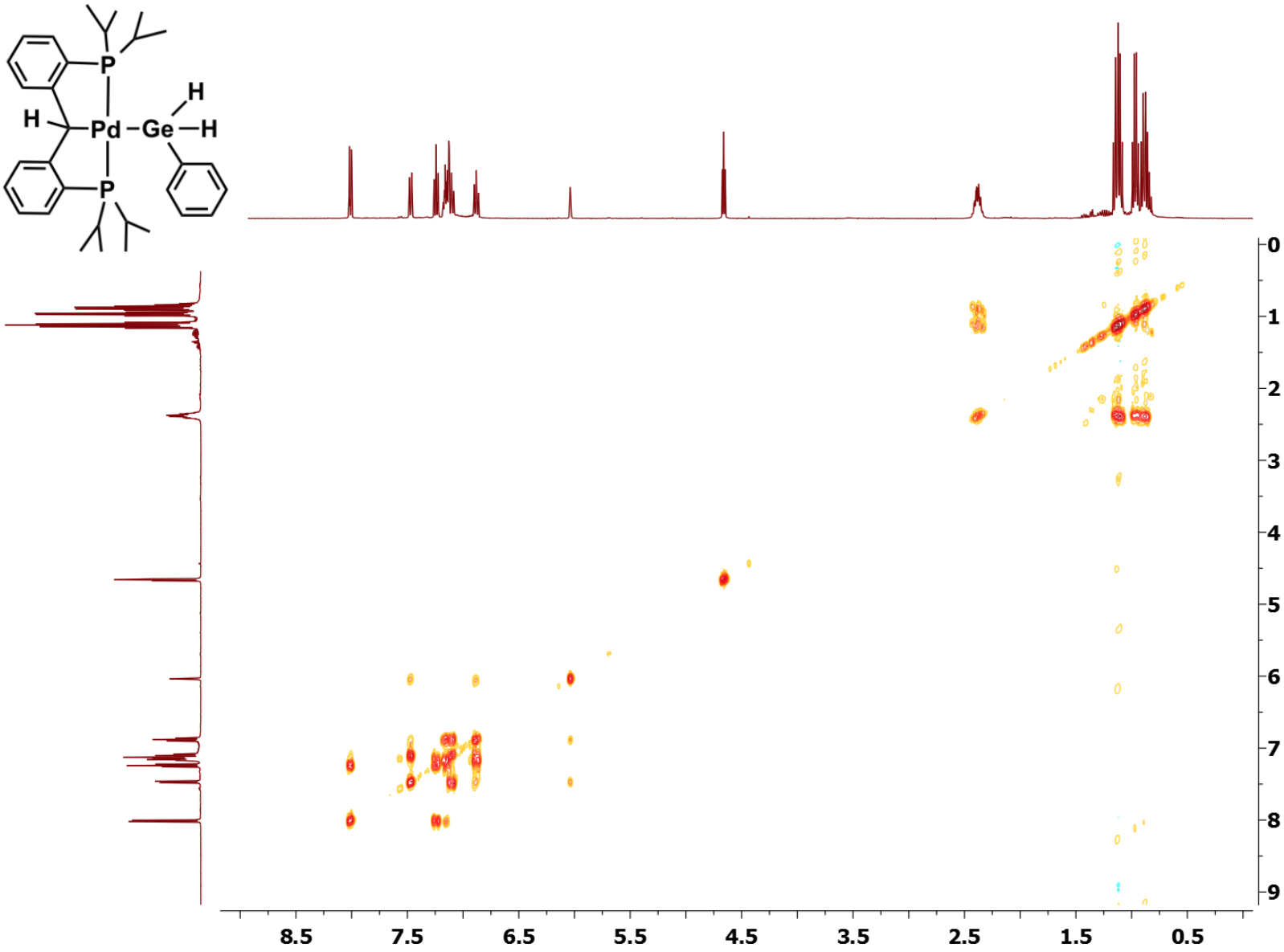


Figure S42. ^{1}H-^{1}H COSY NMR spectrum for [PC(H)P]Pd(GeH_2Ph) (**10**).

3.8 NMR Spectra for [PC(H)P]Pd(GeHPh$_2$) (11)

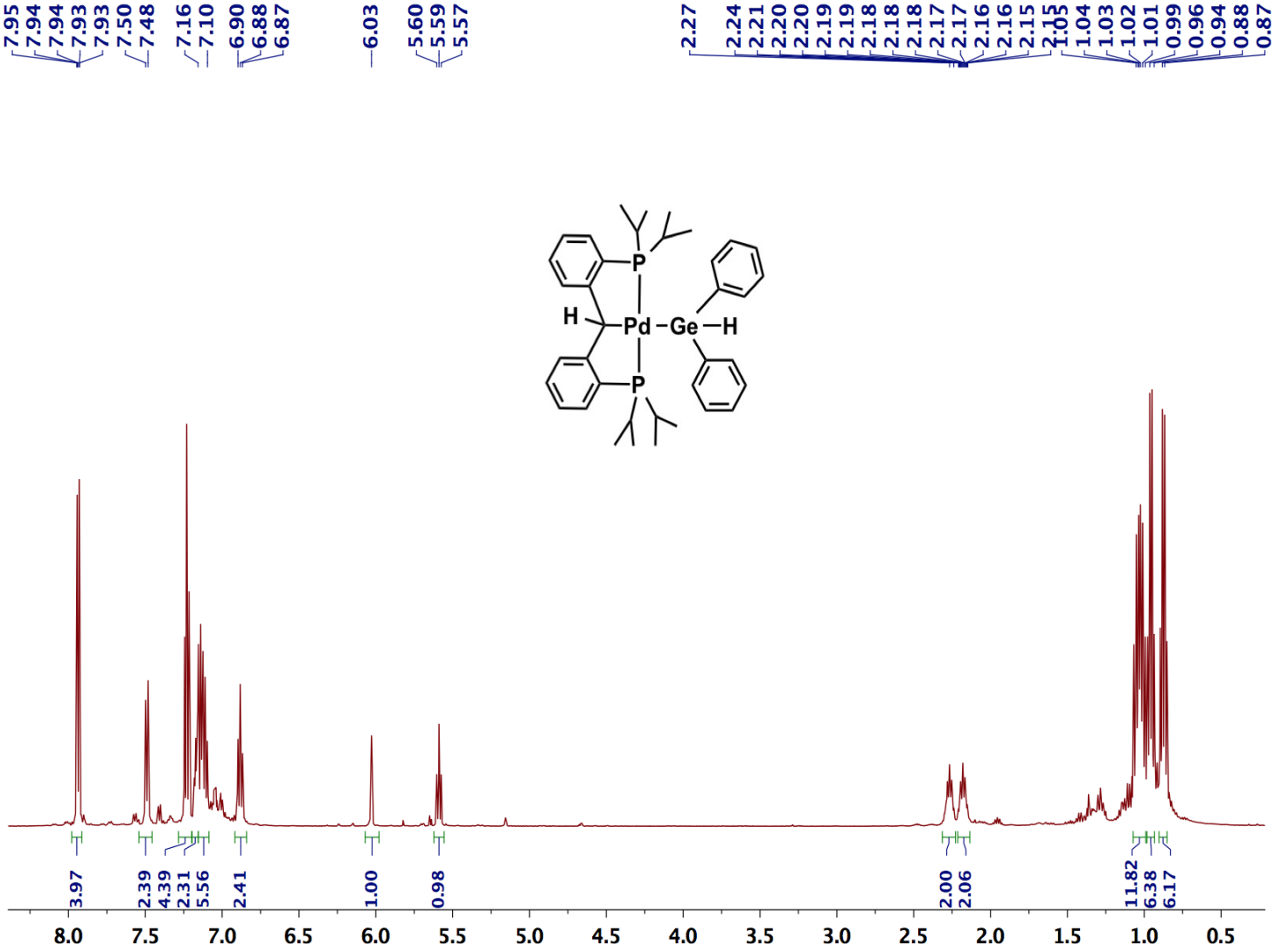


Figure S43. ^{1}H NMR spectrum for [PC(H)P]Pd(GeHPh$_2$) (**11**).

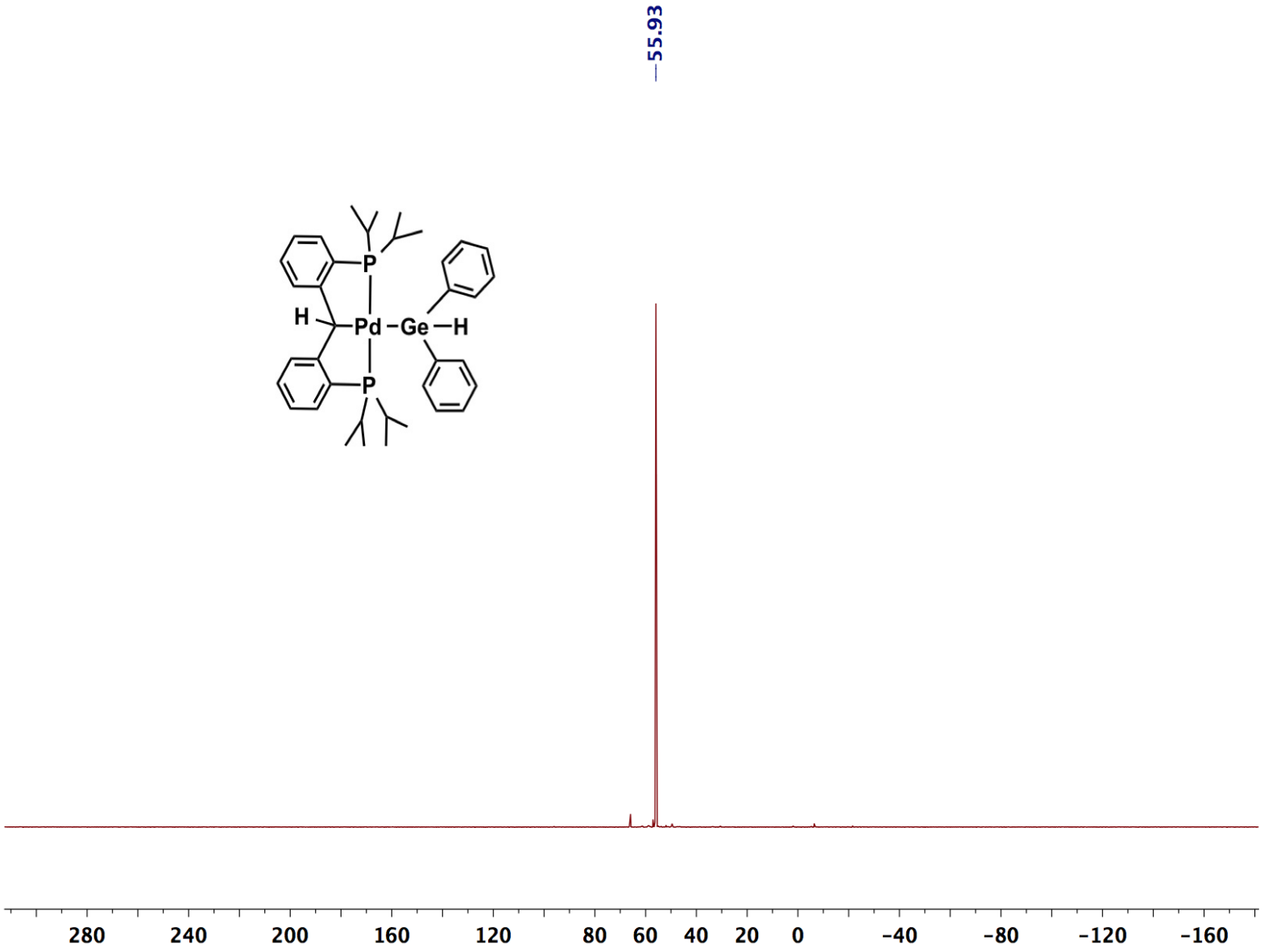


Figure S44. $^{31}P\{^{1}H\}$ NMR spectrum for [PC(H)P]Pd($GeHPh_2$) (**11**).

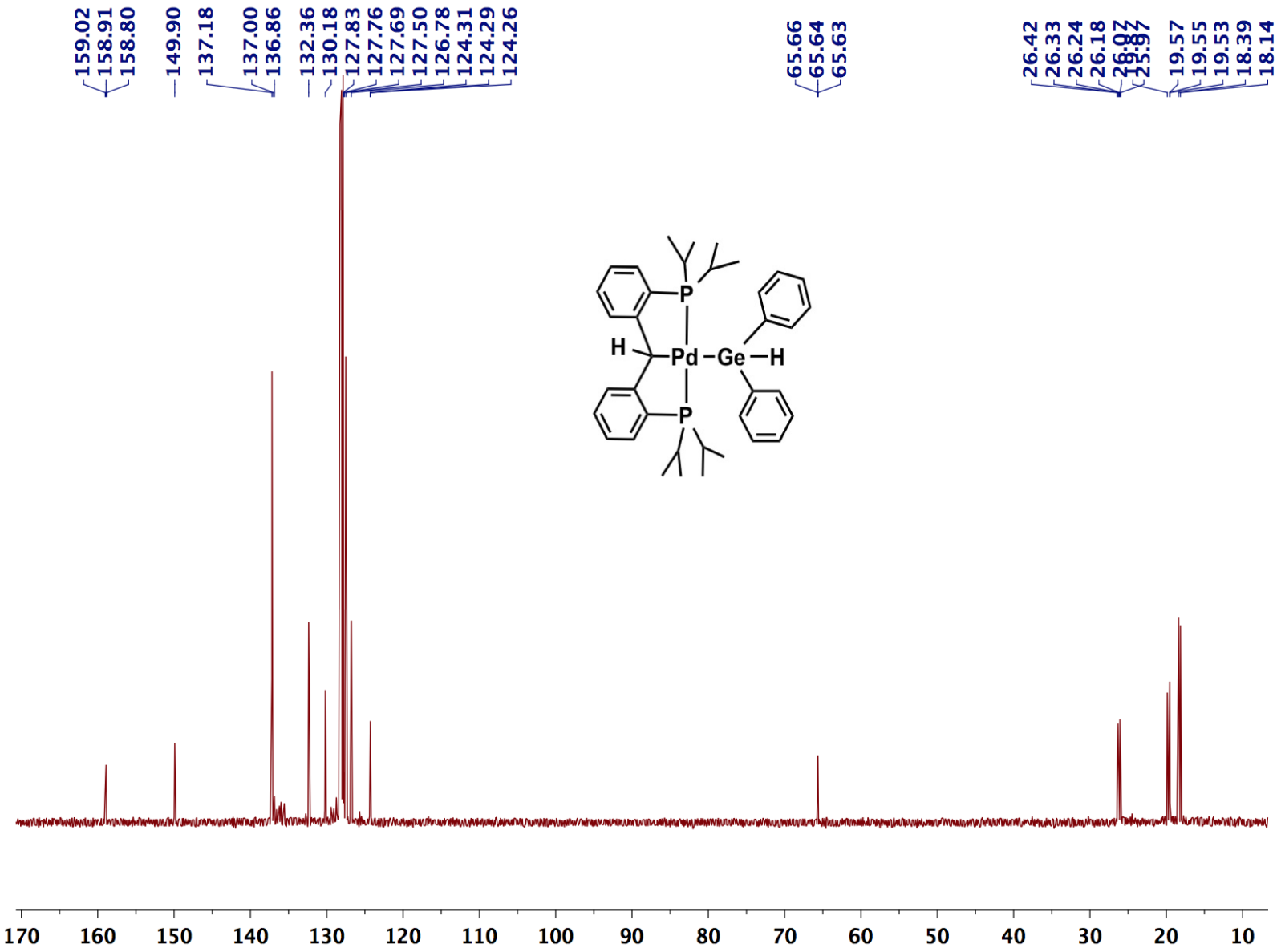


Figure S45. $^{13}C\{^{1}H\}$ NMR spectrum for [PC(H)P]Pd(GeHPh$_2$) (**11**).

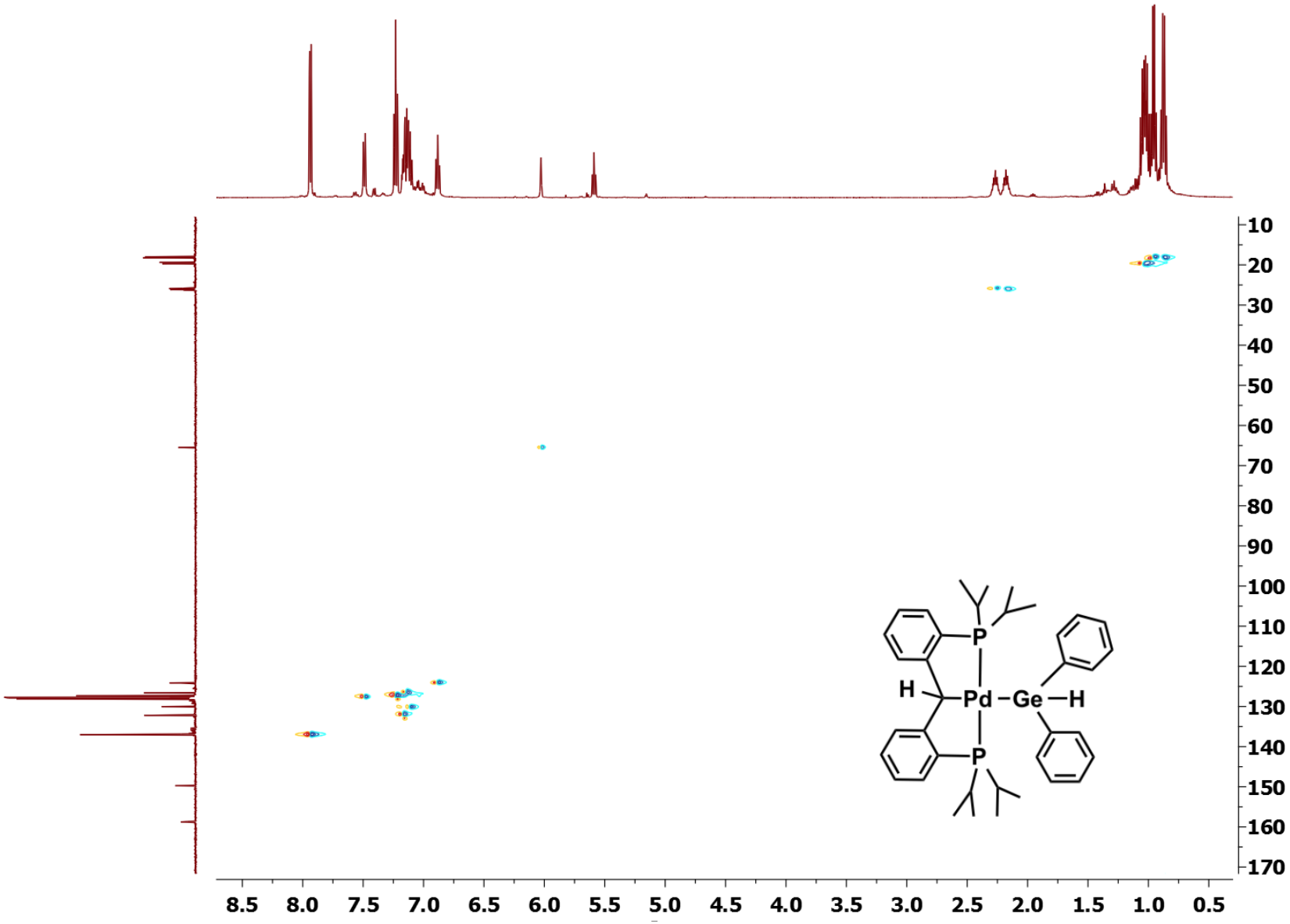


Figure S46. ^{1}H-^{13}C HSQC NMR spectrum for [PC(H)P]Pd($GeHPh_2$) (**11**).

3.9 NMR Spectra for [PC(H)P]Pd($GePh_3$) (12)

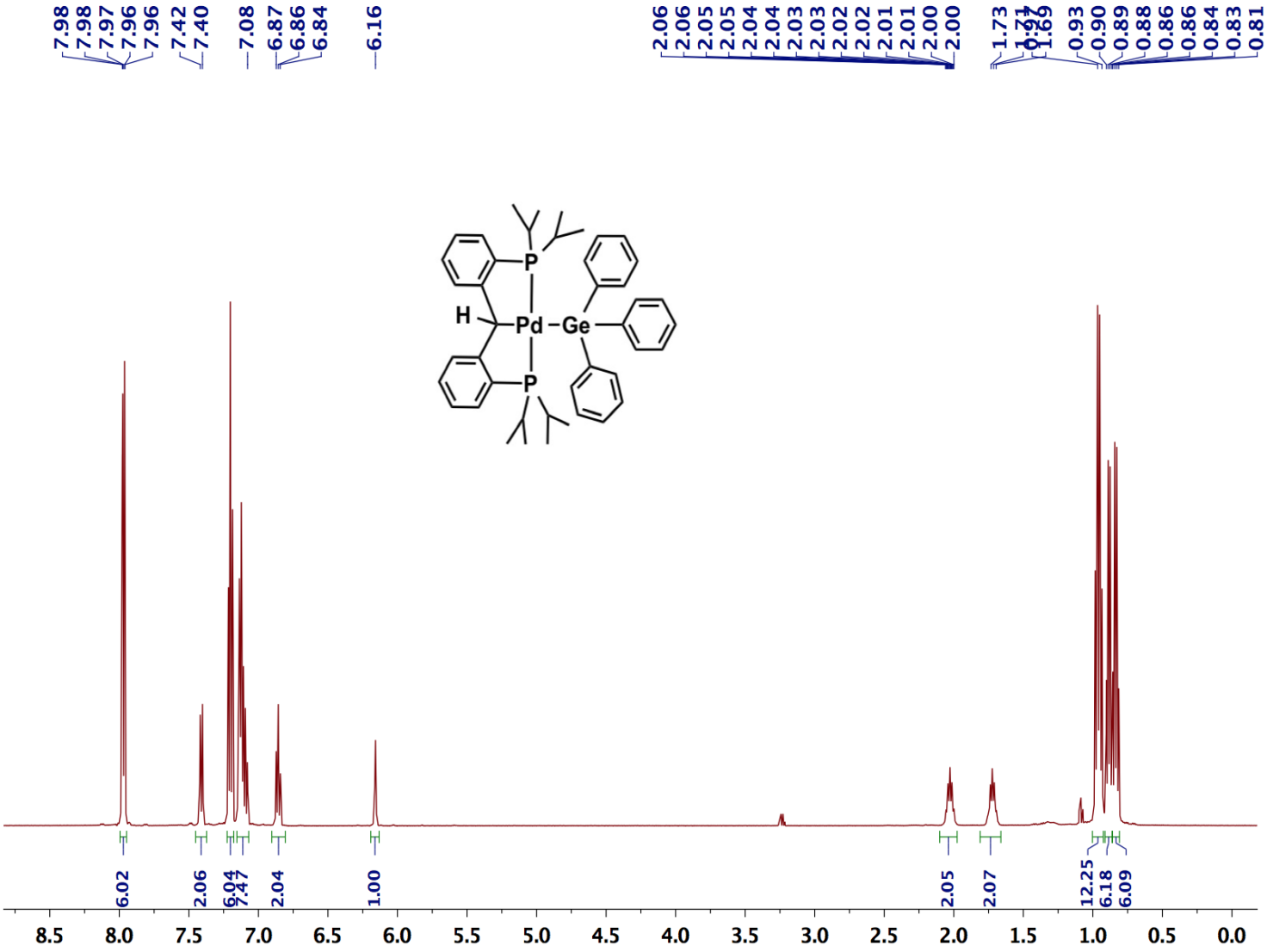


Figure S47. ^{1}H NMR spectrum for [PC(H)P]Pd($GePh_3$) (**12**).

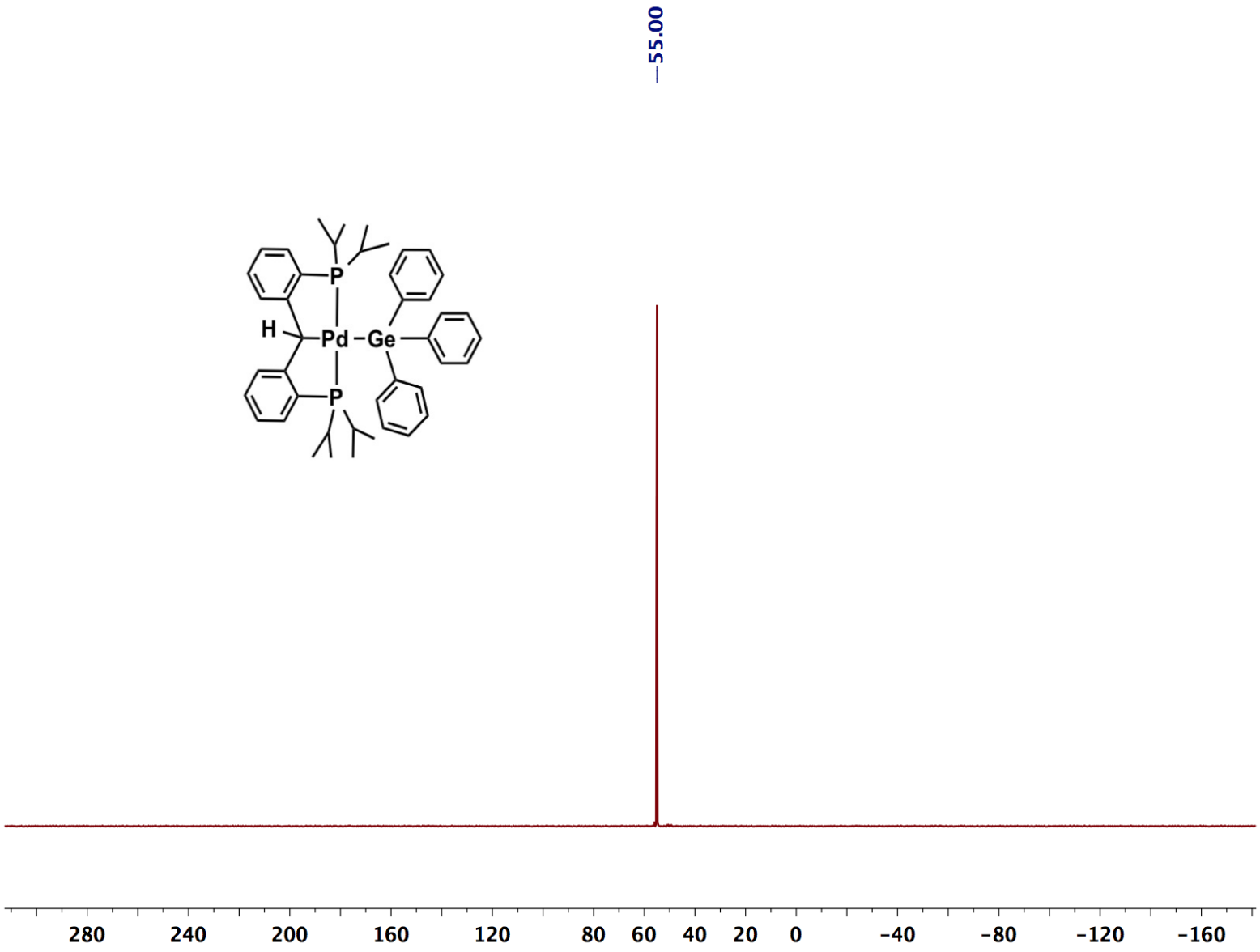


Figure S48. $^{31}P\{^{1}H\}$ NMR spectrum for [PC(H)P]Pd($GePh_3$) (**12**).

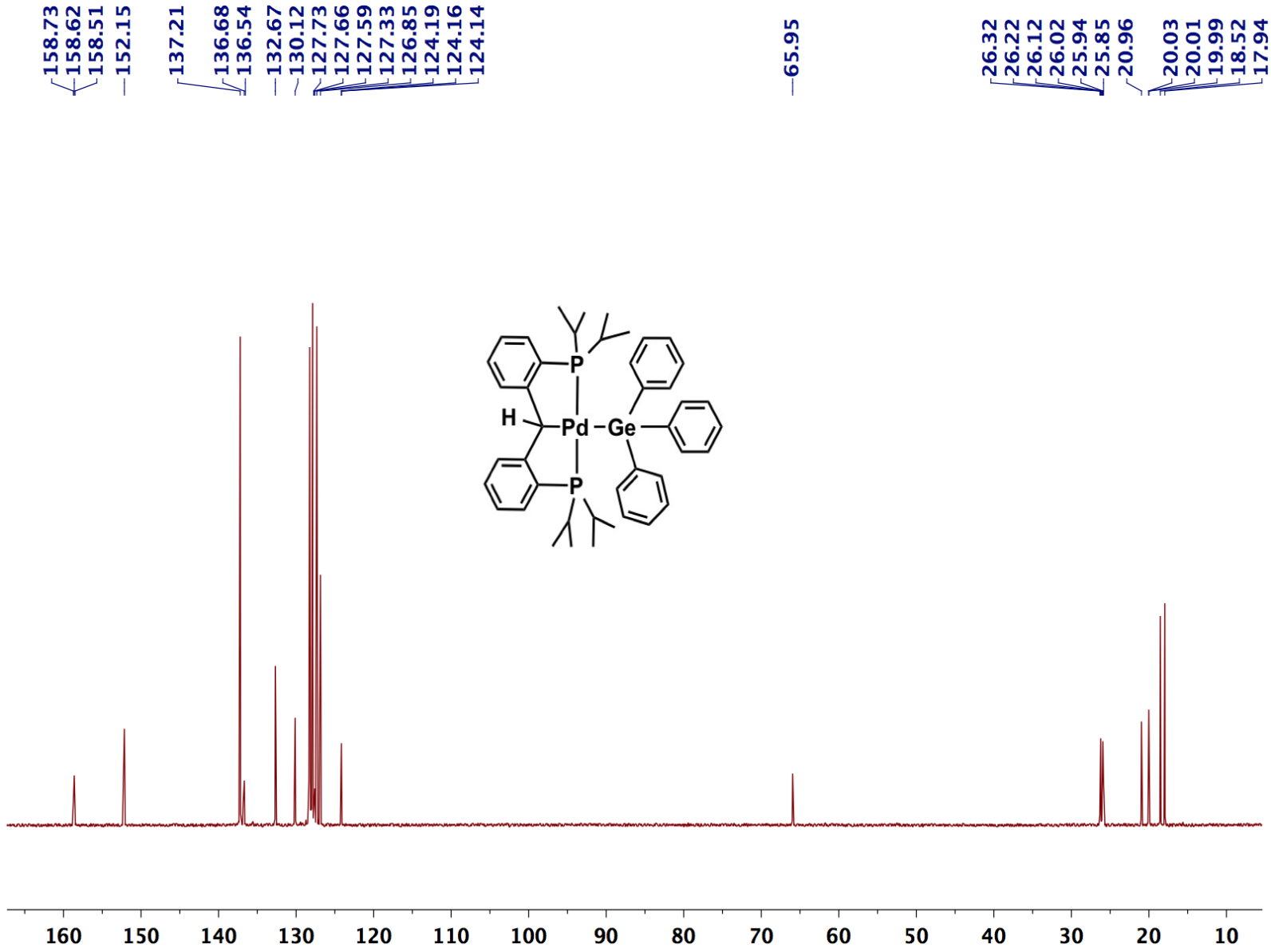


Figure S49. $^{13}C\{^{1}H\}$ NMR spectrum for [PC(H)P]Pd($GePh_3$) (**12**).

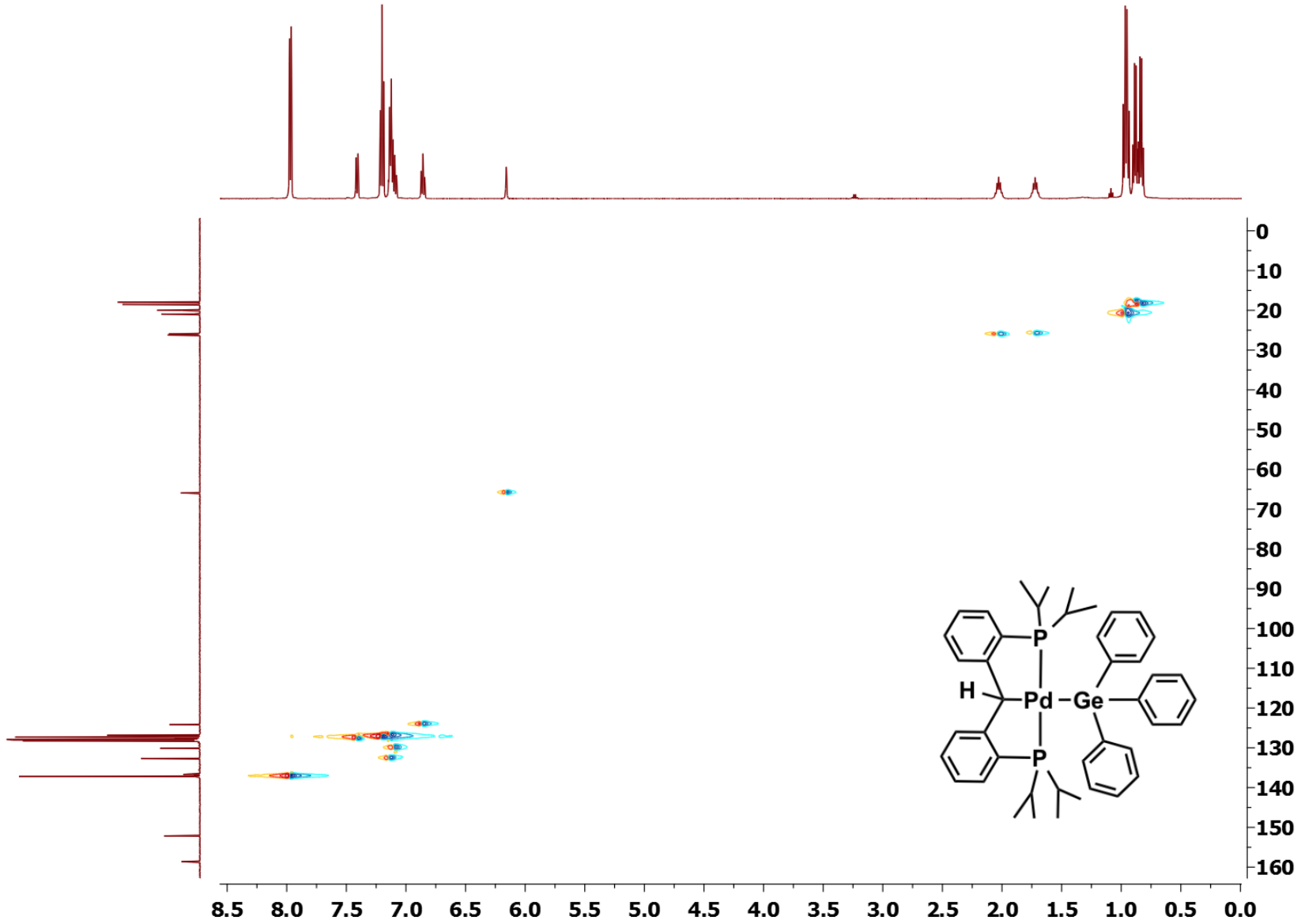


Figure S50. ^{1}H-^{13}C HSQC NMR spectrum for [PC(H)P]Pd($GePh_3$) (**12**).

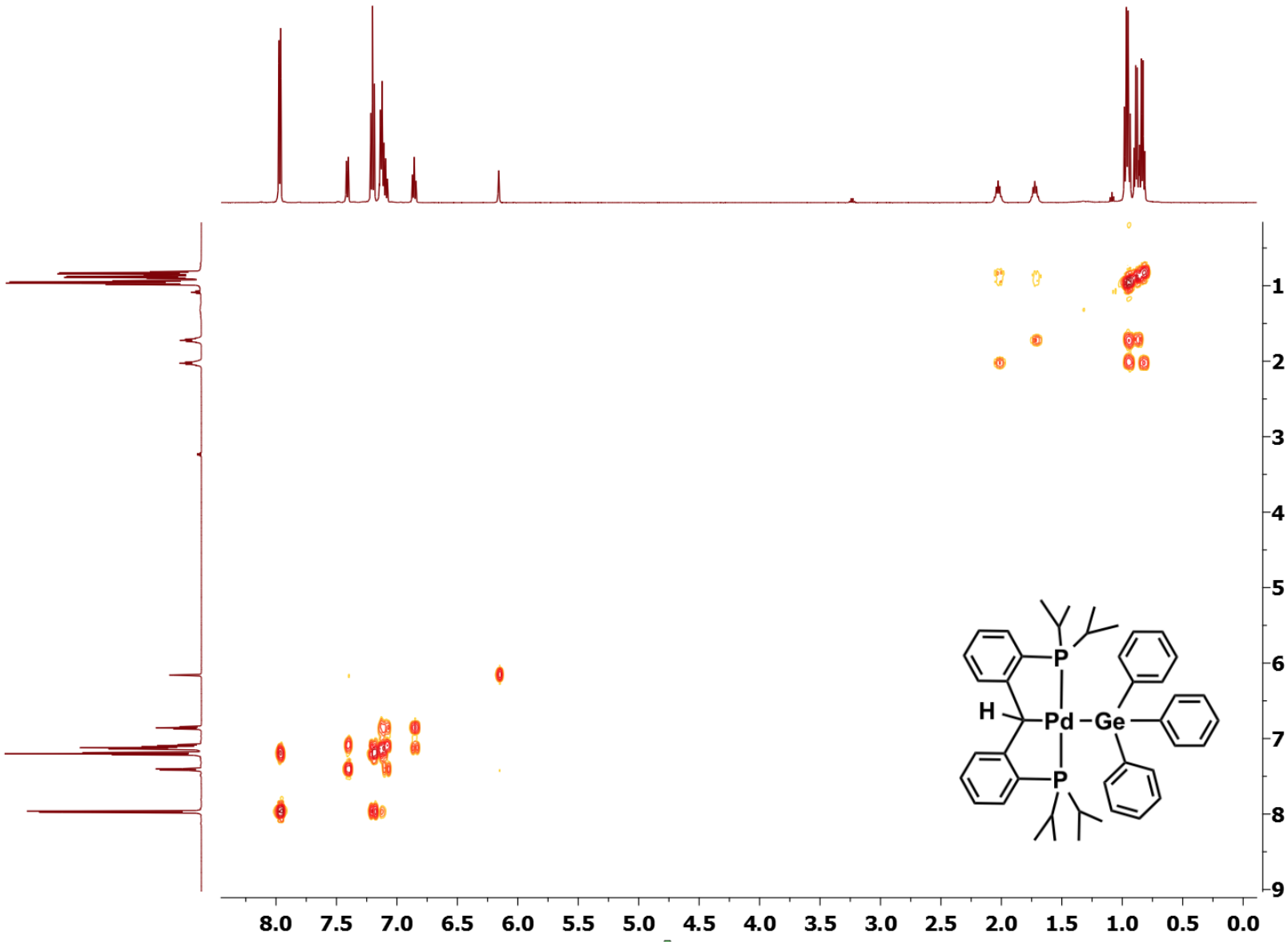


Figure S51. ^{1}H-^{1}H COSY NMR spectrum for [PC(H)P]Pd($GePh_3$) (**12**).

3.10 NMR Spectra for [PC(H)P]Pd(PMe$_3$)(GeH$_2$Ph) (15)

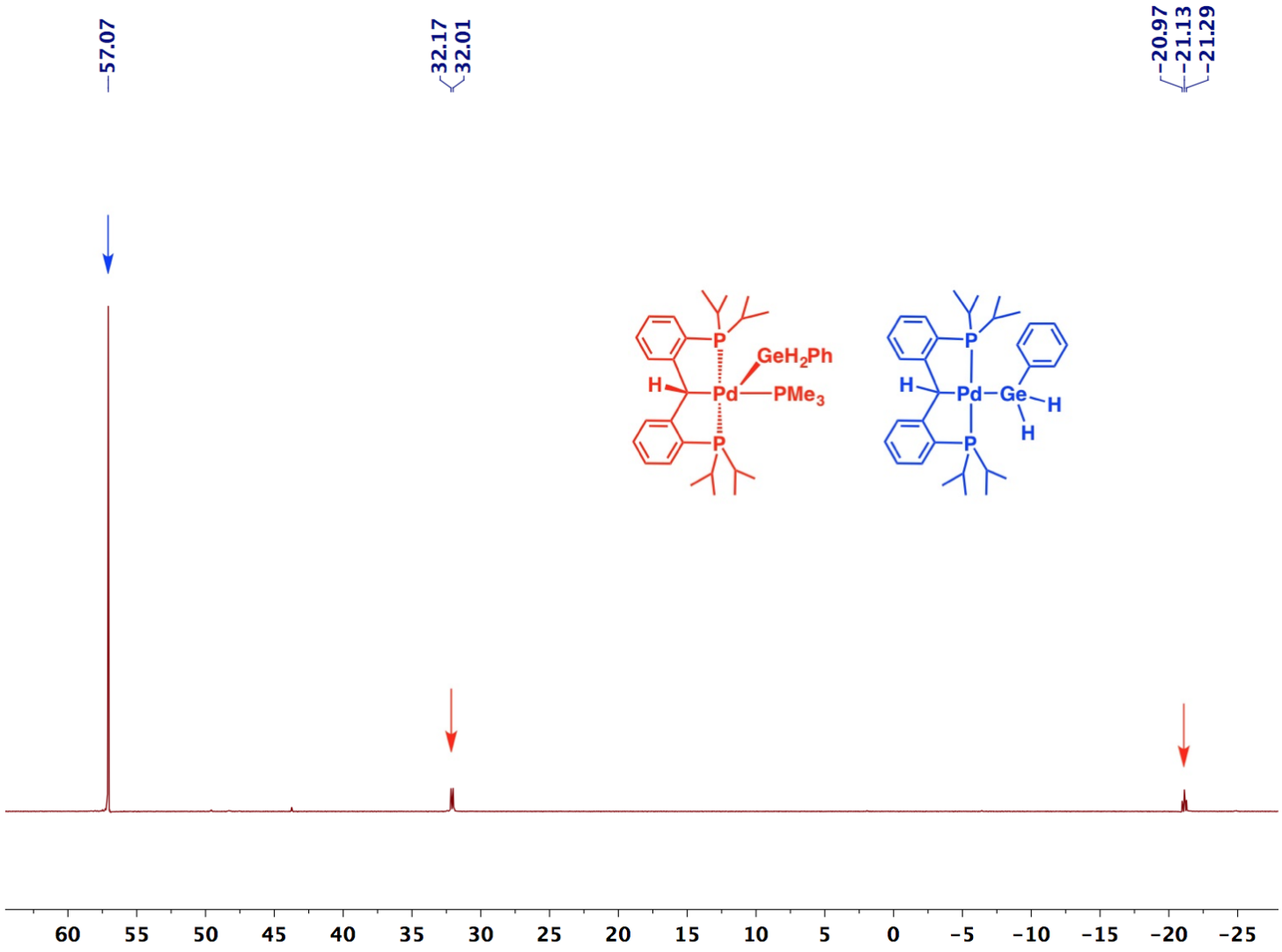


Figure S52. $^{31}P\{^{1}H\}$ NMR spectrum for the mixture of [PC(H)P]Pd(GeH$_2$Ph) (**10**) and [PC(H)P]Pd(PMe$_3$)(GeH$_2$Ph) (**15**).

3.11 NMR Spectra for [PC(H)P]Pd(PMe_3)($GeHPh_2$) (13)

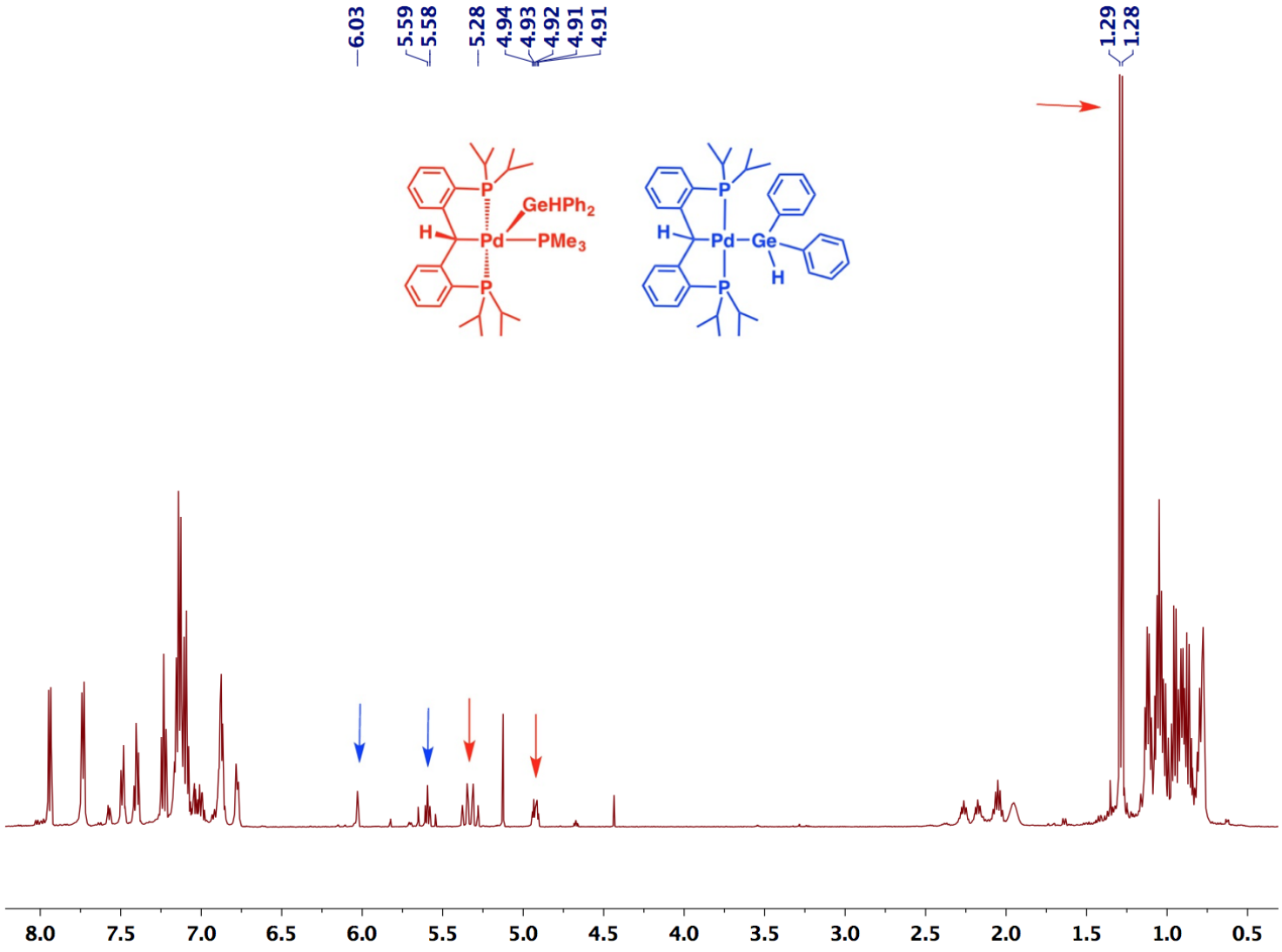


Figure S53. ^{1}H NMR spectrum for the mixture of [PC(H)P]Pd(PMe_3)($GeHPh_2$) (**13**) and [PC(H)P]Pd($GeHPh_2$) (**11**).

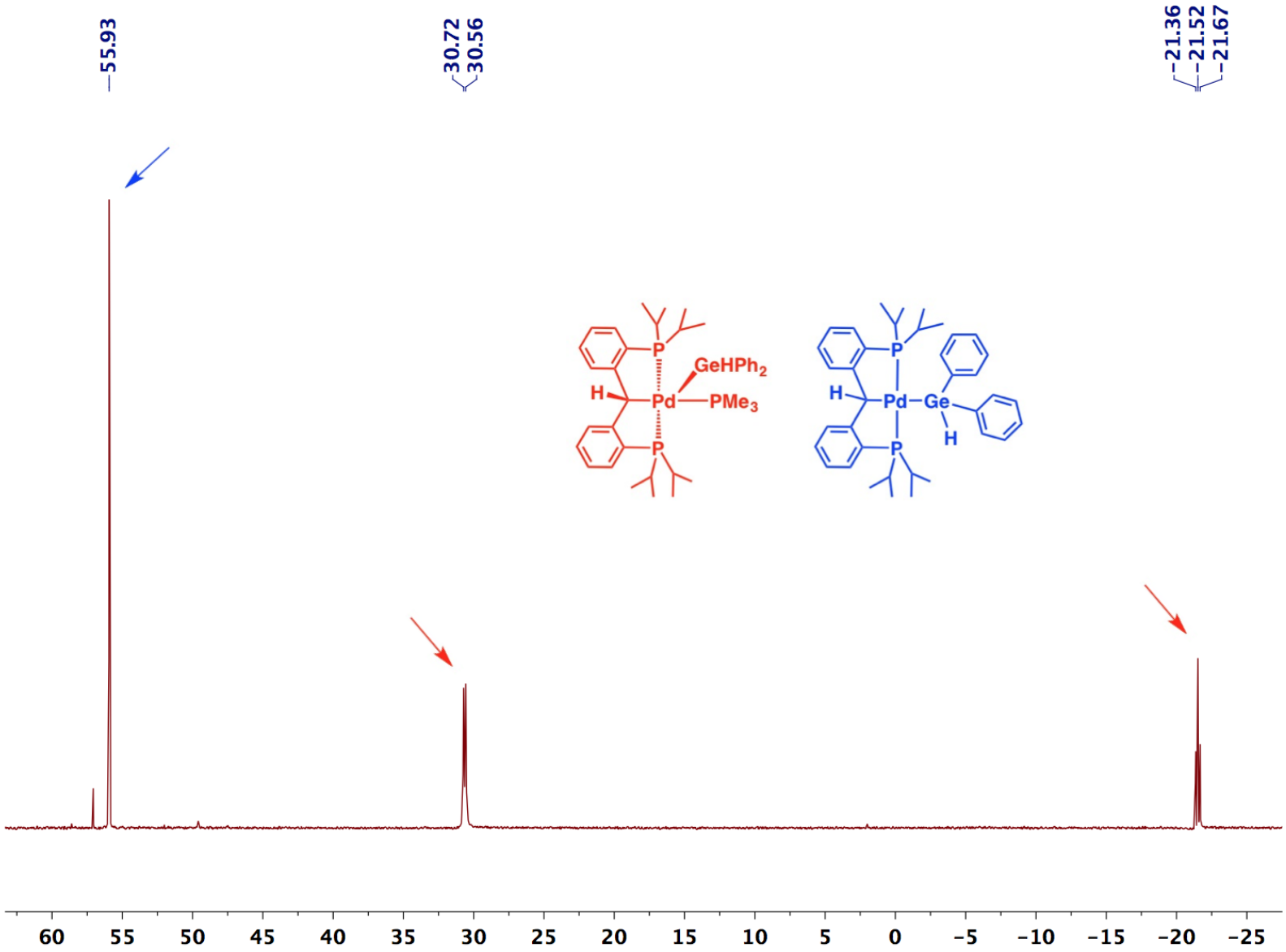


Figure S54. $^{31}P\{^{1}H\}$ NMR spectrum for the mixture of [PC(H)P]Pd(PMe_3)($GeHPh_2$) (**13**) and [PC(H)P]Pd($GeHPh_2$) (**11**).

4 Crystallographic Tables

4.1 Crystal data for [PC(SiH$_2$Ph)P]PdH (3)

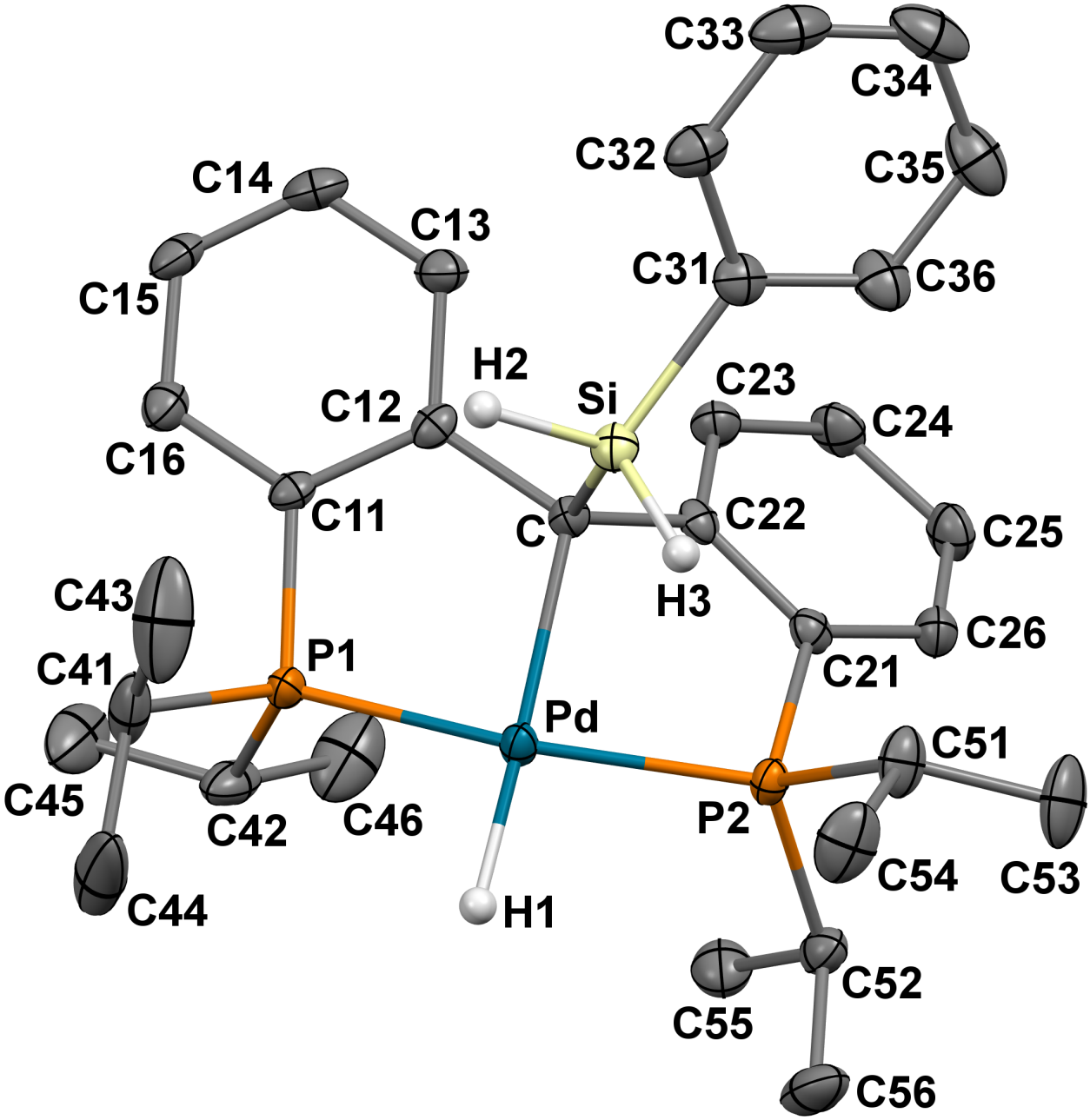


Figure S55. Thermal-ellipsoid representation of [PC(SiH$_2$Ph)P]PdH (**3**) at 50% probability. Most hydrogen atoms were omitted for clarity.

Table S1. Crystal data and structure refinement for [PC(SiH_2Ph)P]PdH (**3**).

Identification code:	cc180b	
Empirical formula:	$C_{31}H_{44}P_2PdSi$	
Formula weight:	613.09	
Temperature:	120(2) K	
Wavelength:	0.71073 Å	
Crystal system:	Orthorhombic	
Space group:	*Pbca*	
Unit cell dimensions:	a = 17.0258(7) Å	$\alpha = 90°$
	b = 18.6108(8) Å	$\beta = 90°$
	c = 19.0877(8) Å	$\gamma = 90°$
Volume:	6048.2(4) $Å^3$	
Z:	8	
Density (calculated):	1.347 $g \cdot cm^{-3}$	
Absorption coefficient (μ):	0.777 mm^{-1}	
F(000):	2560	
Crystal size:	$0.03 \times 0.02 \times 0.02$ mm^3	
θ range for data collection:	1.94 to 25.00°	
Index ranges:	$-20 \leq h \leq 20$, $-22 \leq k \leq 22$, $-22 \leq l \leq 22$	
Reflections collected:	135804	
Independent reflections:	5331 [R_{int} = 0.0258]	
Completeness to θ = 25.00°:	100.0 %	
Absorption correction:	Semi−empirical from equivalents	
Max. and min. transmission:	0.7458 and 0.6519	
Refinement method:	Full-matrix least-squares on F^2	
Data / restraints / parameters:	5331 / 0 / 336	
Goodness-of-fit on F^2:	1.194	
Final R indices [I>2σ(I)]:	R_1 = 0.0235, wR_2 = 0.0574	
R indices (all data):	R_1 = 0.0249, wR_2 = 0.0580	
Largest diff. peak and hole:	0.449 and −0.442 $e^- \cdot Å^{-3}$	

Table S2. Atomic coordinates and equivalent isotropic displacement parameters (Å^2) for [PC(SiH_2Ph)P]PdH (**3**). U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor

atom	x	y	z	U(eq)
Pd	0.76612(1)	0.17341(1)	0.60829(1)	0.016(1)
C	0.66150(12)	0.12101(11)	0.56822(11)	0.015(1)
P(1)	0.69098(3)	0.20226(3)	0.70009(3)	0.017(1)
Si	0.64397(4)	0.18335(3)	0.49250(3)	0.019(1)
P(2)	0.83150(3)	0.10459(3)	0.52793(3)	0.016(1)
C(11)	0.59369(12)	0.16927(11)	0.67716(11)	0.016(1)
C(12)	0.58896(13)	0.13009(11)	0.61458(11)	0.017(1)
C(13)	0.51360(13)	0.10732(12)	0.59337(12)	0.022(1)
C(14)	0.44772(13)	0.12073(13)	0.63390(13)	0.025(1)
C(15)	0.45400(13)	0.15858(13)	0.69620(13)	0.024(1)
C(16)	0.52652(13)	0.18366(12)	0.71722(12)	0.022(1)
C(31)	0.58580(13)	0.14491(12)	0.41717(12)	0.021(1)
C(26)	0.78074(13)	0.03744(12)	0.49826(12)	0.021(1)
C(25)	0.72971(14)	−0.09474(13)	0.50529(12)	0.025(1)
C(24)	0.65711(14)	−0.08276(13)	0.53572(13)	0.025(1)
C(23)	0.63476(13)	−0.01458(12)	0.55647(12)	0.022(1)
C(22)	0.68426(13)	0.04528(11)	0.54831(10)	0.015(1)
C(21)	0.76022(13)	0.03150(11)	0.52073(11)	0.016(1)
C(32)	0.51744(14)	0.17858(14)	0.39327(13)	0.028(1)
C(33)	0.47649(15)	0.15286(16)	0.33562(14)	0.036(1)
C(34)	0.50274(17)	0.09242(16)	0.30113(14)	0.039(1)
C(35)	0.56994(18)	0.05792(14)	0.32339(13)	0.035(1)
C(36)	0.61091(16)	0.08389(13)	0.38100(12)	0.028(1)
C(41)	0.67668(16)	0.29557(13)	0.72833(14)	0.033(1)
C(42)	0.71978(14)	0.15152(15)	0.77919(12)	0.030(1)
C(43)	0.6452(3)	0.33882(15)	0.66632(18)	0.063(1)
C(44)	0.7531(2)	0.3265(2)	0.7575(2)	0.072(1)
C(45)	0.66651(18)	0.16416(19)	0.84214(13)	0.044(1)
C(46)	0.7247(2)	0.07146(16)	0.76240(16)	0.048(1)
C(51)	0.85360(16)	0.13393(13)	0.43714(12)	0.027(1)
C(52)	0.92070(13)	0.05978(12)	0.56145(12)	0.022(1)
C(53)	0.90241(19)	0.08115(16)	0.39383(14)	0.042(1)
C(54)	0.88819(17)	0.20995(14)	0.43551(15)	0.038(1)
C(55)	0.90424(15)	0.03167(14)	0.63509(13)	0.031(1)
C(56)	0.99116(14)	0.11027(15)	0.56324(16)	0.036(1)
H(1)	0.8391(18)	0.2116(17)	0.6388(16)	0.051(9)
H(2)	0.6029(15)	0.2427(14)	0.5170(13)	0.029(7)
H(3)	0.7124(15)	0.2092(14)	0.4637(13)	0.026(7)
H(13)	0.5079	0.0822	0.5503	0.026
H(14)	0.3978	0.1038	0.6189	0.031

Continued on next page

Table S2. – continued from previous page

atom	x	y	x	U(eq)
H(15)	0.4088	0.1672	0.7241	0.029
H(16)	0.5310	0.2109	0.7591	0.026
H(26)	0.8309	−0.0451	0.4777	0.025
H(25)	0.7442	−0.1413	0.4896	0.029
H(24)	0.6221	−0.1219	0.5424	0.030
H(23)	0.5844	−0.0080	0.5769	0.026
H(32)	0.4986	0.2200	0.4170	0.033
H(33)	0.4305	0.1769	0.3200	0.044
H(34)	0.4745	0.0745	0.2619	0.046
H(35)	0.5882	0.0165	0.2993	0.042
H(36)	0.6570	0.0596	0.3961	0.034
H(41)	0.6363	0.2962	0.7664	0.039
H(42)	0.7737	0.1678	0.7926	0.035
H(43A)	0.6844	0.3392	0.6287	0.095
H(43B)	0.6346	0.3882	0.6813	0.095
H(43C)	0.5966	0.3168	0.6492	0.095
H(44A)	0.7937	0.3250	0.7212	0.108
H(44B)	0.7700	0.2979	0.7979	0.108
H(44C)	0.7444	0.3764	0.7721	0.108
H(45A)	0.6651	0.2156	0.8531	0.066
H(45B)	0.6869	0.1376	0.8826	0.066
H(45C)	0.6133	0.1474	0.8312	0.066
H(46A)	0.6720	0.0530	0.7521	0.072
H(46B)	0.7466	0.0457	0.8027	0.072
H(46C)	0.7587	0.0642	0.7216	0.072
H(51)	0.8017	0.1374	0.4129	0.033
H(52)	0.9334	0.0181	0.5303	0.027
H(53A)	0.8769	0.0340	0.3939	0.062
H(53B)	0.9550	0.0769	0.4142	0.062
H(53C)	0.9066	0.0987	0.3456	0.062
H(54A)	0.8896	0.2273	0.3871	0.057
H(54B)	0.9416	0.2090	0.4546	0.057
H(54C)	0.8555	0.2421	0.4638	0.057
H(55A)	0.8576	0.0008	0.6342	0.046
H(55B)	0.8950	0.0722	0.6668	0.046
H(55C)	0.9495	0.0039	0.6516	0.046
H(56A)	1.0040	0.1255	0.5154	0.054
H(56B)	1.0363	0.0852	0.5837	0.054
H(56C)	0.9785	0.1525	0.5917	0.054

Table S3. Anisotropic displacement parameters ($Å^2$) for [PC(SiH_2Ph)P]PdH (**3**). The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11} + ...+ 2hka^*b^*U_{12}]$.

atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Pd	0.0152(1)	0.0154(1)	0.0159(1)	−0.0025(1)	0.0038(1)	−0.0018(1)
C	0.0144(10)	0.0171(10)	0.0149(10)	−0.0010(8)	0.0002(8)	−0.0005(8)
P(1)	0.0141(3)	0.0203(3)	0.0154(3)	−0.0033(2)	0.0026(2)	−0.0015(2)
Si	0.0205(3)	0.0180(3)	0.0181(3)	0.0015(2)	−0.0005(2)	0.0025(2)
P(2)	0.0160(3)	0.0153(3)	0.0161(3)	−0.0008(2)	0.0042(2)	−0.0004(2)
C(11)	0.0127(10)	0.0178(11)	0.0175(11)	0.0034(8)	−0.0007(8)	0.0023(8)
C(12)	0.0160(10)	0.0158(10)	0.0190(11)	0.0037(8)	0.0016(9)	0.0029(8)
C(13)	0.0173(11)	0.0236(12)	0.0244(12)	−0.0010(9)	−0.0033(9)	0.0000(9)
C(14)	0.0134(11)	0.0291(13)	0.0341(13)	0.0045(11)	−0.0026(10)	0.0000(10)
C(15)	0.0133(11)	0.0332(13)	0.0266(12)	0.0050(10)	0.0025(9)	0.0055(10)
C(16)	0.0201(11)	0.0261(12)	0.0184(11)	0.0016(9)	0.0010(9)	0.0047(9)
C(31)	0.0226(12)	0.0239(12)	0.0169(11)	0.0059(9)	0.0008(9)	−0.0017(10)
C(26)	0.0209(11)	0.0214(12)	0.0204(11)	−0.0046(9)	0.0024(9)	0.0009(9)
C(25)	0.0297(13)	0.0179(11)	0.0262(12)	−0.0060(9)	0.0006(10)	−0.0007(10)
C(24)	0.0268(12)	0.0209(12)	0.0277(13)	−0.0032(10)	−0.0003(10)	−0.0074(10)
C(23)	0.0184(11)	0.0236(12)	0.0226(11)	−0.0028(9)	0.0013(9)	−0.0032(9)
C(22)	0.0194(11)	0.0167(10)	0.0102(9)	0.0003(8)	−0.0024(8)	0.0004(9)
C(21)	0.0185(11)	0.0180(11)	0.0118(10)	0.0004(8)	0.0003(8)	−0.0020(9)
C(32)	0.0223(12)	0.0330(14)	0.0274(13)	0.0082(11)	0.0010(10)	0.0003(10)
C(33)	0.0218(13)	0.0533(17)	0.0345(15)	0.0185(13)	−0.0052(11)	−0.0038(12)
C(34)	0.0449(17)	0.0472(17)	0.0238(13)	0.0078(12)	−0.0117(12)	−0.0179(14)
C(35)	0.0553(18)	0.0291(13)	0.0213(12)	0.0018(11)	−0.0033(12)	−0.0059(13)
C(36)	0.0360(14)	0.0273(13)	0.0210(12)	0.0033(10)	−0.0043(10)	0.0026(11)
C(41)	0.0363(15)	0.0243(12)	0.0374(15)	−0.0132(11)	0.0201(12)	−0.0072(11)
C(42)	0.0174(11)	0.0522(16)	0.0189(12)	0.0051(11)	−0.0022(10)	0.0036(11)
C(43)	0.114(3)	0.0206(14)	0.055(2)	0.0076(14)	0.040(2)	0.0129(17)
C(44)	0.0435(19)	0.067(2)	0.106(3)	−0.065(2)	0.036(2)	−0.0294(17)
C(45)	0.0385(16)	0.076(2)	0.0174(13)	0.0099(13)	0.0014(12)	0.0152(15)
C(46)	0.0549(19)	0.0495(18)	0.0396(17)	0.0228(14)	0.0130(15)	0.0205(15)
C(51)	0.0369(14)	0.0243(12)	0.0210(12)	0.0039(10)	0.0113(11)	0.0030(11)
C(52)	0.0174(11)	0.0201(11)	0.0288(12)	−0.0042(10)	0.0012(10)	0.0019(9)
C(53)	0.0606(19)	0.0382(16)	0.0261(14)	0.0019(12)	0.0230(14)	0.0095(14)
C(54)	0.0437(16)	0.0298(14)	0.0403(15)	0.0109(12)	0.0189(13)	−0.0025(12)
C(55)	0.0307(14)	0.0335(14)	0.0287(13)	0.0012(11)	−0.0049(11)	0.0077(11)
C(56)	0.0170(12)	0.0324(14)	0.0586(18)	−0.0076(13)	0.0009(12)	−0.0031(11)

Table S4. Distances [Å] for [PC(SiH_2Ph)P]PdH (**3**).

atom – atom	distance	atom – atom	distance
Pd – C	2.170(2)	Pd – P(1)	2.2350(6)
Pd – P(2)	2.2876(6)	Pd – Si	3.0404(6)
Pd – H(1)	1.54(3)	C – C(22)	1.510(3)
C – C(12)	1.529(3)	C – Si	1.877(2)
P(1) – C(11)	1.820(2)	P(1) – C(41)	1.835(2)
P(1) – C(42)	1.847(2)	Si – C(31)	1.887(2)
Si – H(2)	1.39(3)	Si – H(3)	1.37(3)
P(2) – C(21)	1.828(2)	P(2) – C(52)	1.847(2)
P(2) – C(51)	1.855(2)	C(11) – C(16)	1.402(3)
C(11) – C(12)	1.402(3)	C(12) – C(13)	1.411(3)
C(13) – C(14)	1.385(3)	C(13) – H(13)	0.9500
C(14) – C(15)	1.386(4)	C(14) – H(14)	0.9500
C(15) – C(16)	1.380(3)	C(15) – H(15)	0.9500
C(16) – H(16)	0.9500	C(31) – C(36)	1.396(3)
C(31) – C(32)	1.398(3)	C(26) – C(25)	1.382(3)
C(26) – C(21)	1.397(3)	C(26) – H(26)	0.9500
C(25) – C(24)	1.384(3)	C(25) – H(25)	0.9500
C(24) – C(23)	1.383(3)	C(24) – H(24)	0.9500
C(23) – C(22)	1.406(3)	C(23) – H(23)	0.9500
C(22) – C(21)	1.420(3)	C(32) – C(33)	1.388(4)
C(32) – H(32)	0.9500	C(33) – C(34)	1.378(4)
C(33) – H(33)	0.9500	C(34) – C(35)	1.379(4)
C(34) – H(34)	0.9500	C(35) – C(36)	1.389(4)
C(35) – H(35)	0.9500	C(36) – H(36)	0.9500
C(41) – C(44)	1.527(4)	C(41) – C(43)	1.528(4)
C(41) – H(41)	1.0000	C(42) – C(45)	1.524(3)
C(42) – C(46)	1.526(4)	C(42) – H(42)	1.0000
C(43) – H(43A)	0.9800	C(43) – H(43B)	0.9800
C(43) – H(43C)	0.9800	C(44) – H(44A)	0.9800
C(45) – H(45A)	0.9800	C(45) – H(45B)	0.9800
C(45) – H(45C)	0.9800	C(46) – H(46A)	0.9800
C(46) – H(46B)	0.9800	C(46) – H(46C)	0.9800
C(51) – C(53)	1.529(3)	C(51) – C(54)	1.533(4)
C(51) – H(51)	1.0000	C(52) – C(56)	1.524(3)
C(52) – C(55)	1.526(3)	C(52) – H(52)	1.0000
C(53) – H(53A)	0.9800	C(53) – H(53B)	0.9800
C(53) – H(53C)	0.9800	C(54) – H(54A)	0.9800
C(54) – H(54B)	0.9800	C(54) – H(54C)	0.9800
C(55) – H(55A)	0.9800	C(55) – H(55B)	0.9800
C(55) – H(55C)	0.9800	C(56) – H(56A)	0.9800
C(56) – H(56B)	0.9800	C(56) – H(56C)	0.9800

Table S5. Angles [°] for [PC(SiH_2Ph)P]PdH (**3**).

atom – atom – atom	angle	atom – atom – atom	angle
C – Pd – P(1)	85.10(6)	C – Pd – P(2)	84.92(6)
P(1) – Pd – P(2)	159.85(2)	C – Pd – Si	37.78(6)
P(1) – Pd – Si	99.43(2)	P(2) – Pd – Si	83.079(19)
C – Pd – H(1)	178.2(12)	P(1) – Pd – H(1)	93.1(12)
P(2) – Pd – H(1)	96.8(12)	Si – Pd – H(1)	142.8(12)
C(22) – C – C(12)	117.14(18)	C(22) – C – Si	115.08(14)
C(12) – C – Si	104.41(14)	C(22) – C – Pd	107.30(14)
C(12) – C – Pd	114.17(14)	Si – C – Pd	97.13(9)
C(11) – P(1) – C(41)	105.62(11)	C(11) – P(1) – C(42)	105.41(11)
C(41) – P(1) – C(42)	106.20(13)	C(11) – P(1) – Pd	104.55(7)
C(41) – P(1) – Pd	122.25(8)	C(42) – P(1) – Pd	111.48(8)
C – Si – C(31)	115.84(10)	C – Si – Pd	45.09(6)
C(31) – Si – Pd	152.86(8)	C – Si – H(2)	108.2(11)
C(31) – Si – H(2)	107.1(10)	Pd – Si – H(2)	98.5(10)
C – Si – H(3)	112.9(11)	C(31) – Si – H(3)	105.8(10)
Pd – Si – H(3)	74.5(10)	H(2) – Si – H(3)	106.5(15)
C(21) – P(2) – C(52)	103.65(10)	C(21) – P(2) – C(51)	106.46(11)
C(52) – P(2) – C(51)	106.84(11)	C(21) – P(2) – Pd	98.28(7)
C(52) – P(2) – Pd	114.87(8)	C(51) – P(2) – Pd	124.07(8)
C(16) – C(11) – C(12)	121.2(2)	C(16) – C(11) – P(1)	123.15(17)
C(12) – C(11) – P(1)	115.64(16)	C(11) – C(12) – C(13)	116.9(2)
C(11) – C(12) – C	120.29(19)	C(13) – C(12) – C	122.38(19)
C(14) – C(13) – C(12)	121.5(2)	C(14) – C(13) – H(13)	119.3
C(12) – C(13) – H(13)	119.3	C(13) – C(14) – C(15)	120.5(2)
C(13) – C(14) – H(14)	119.7	C(15) – C(14) – H(14)	119.7
C(16) – C(15) – C(14)	119.4(2)	C(16) – C(15) – H(15)	120.3
C(14) – C(15) – H(15)	120.3	C(15) – C(16) – C(11)	120.5(2)
C(15) – C(16) – H(16)	119.8	C(11) – C(16) – H(16)	119.8
C(36) – C(31) – C(32)	117.3(2)	C(36) – C(31) – Si	121.63(18)
C(32) – C(31) – Si	121.04(19)	C(25) – C(26) – C(21)	121.4(2)
C(25) – C(26) – H(26)	119.3	C(21) – C(26) – H(26)	119.3
C(26) – C(25) – C(24)	118.6(2)	C(26) – C(25) – H(25)	120.7
C(24) – C(25) – H(25)	120.7	C(23) – C(24) – C(25)	120.9(2)
C(23) – C(24) – H(24)	119.5	C(25) – C(24) – H(24)	119.5
C(24) – C(23) – C(22)	122.0(2)	C(24) – C(23) – H(23)	119.0
C(22) – C(23) – H(23)	119.0	C(23) – C(22) – C(21)	116.37(19)
C(23) – C(22) – C	123.91(19)	C(21) – C(22) – C	119.71(19)
C(26) – C(21) – C(22)	120.5(2)	C(26) – C(21) – P(2)	122.71(17)
C(22) – C(21) – P(2)	116.26(16)	C(33) – C(32) – C(31)	121.5(3)
C(33) – C(32) – H(32)	119.3	C(31) – C(32) – H(32)	119.3
C(34) – C(33) – C(32)	119.8(2)	C(34) – C(33) – H(33)	120.1

Continued on next page

Table S5. – continued from previous page

atom – atom – atom	angle	atom – atom – atom	angle
C(32) – C(33) – H(33)	120.1	C(33) – C(34) – C(35)	120.1(2)
C(33) – C(34) – H(34)	119.9	C(35) – C(34) – H(34)	119.9
C(34) – C(35) – C(36)	119.9(3)	C(34) – C(35) – H(35)	120.0
C(36) – C(35) – H(35)	120.0	C(35) – C(36) – C(31)	121.4(2)
C(35) – C(36) – H(36)	119.3	C(31) – C(36) – H(36)	119.3
C(44) – C(41) – C(43)	112.5(3)	C(44) – C(41) – P(1)	110.5(2)
C(43) – C(41) – P(1)	108.51(19)	C(44) – C(41) – H(41)	108.4
C(43) – C(41) – H(41)	108.4	P(1) – C(41) – H(41)	108.4
C(45) – C(42) – C(46)	110.4(2)	C(45) – C(42) – P(1)	114.06(18)
C(46) – C(42) – P(1)	109.99(18)	C(45) – C(42) – H(42)	107.4
C(46) – C(42) – H(42)	107.4	P(1) – C(42) – H(42)	107.4
C(41) – C(43) – H(43A)	109.5	C(41) – C(43) – H(43B)	109.5
H(43A) – C(43) – H(43B)	109.5	C(41) – C(43) – H(43C)	109.5
H(43A) – C(43) – H(43C)	109.5	H(43B) – C(43) – H(43C)	109.5
C(41) – C(44) – H(44A)	109.5	C(41) – C(44) – H(44B)	109.5
H(44A) – C(44) – H(44B)	109.5	C(41) – C(44) – H(44C)	109.5
H(44A) – C(44) – H(44C)	109.5	H(44B) – C(44) – H(44C)	109.5
C(42) – C(45) – H(45A)	109.5	C(42) – C(45) – H(45B)	109.5
H(45A) – C(45) – H(45B)	109.5	C(42) – C(45) – H(45C)	109.5
H(45A) – C(45) – H(45C)	109.5	H(45B) – C(45) – H(45C)	109.5
C(42) – C(46) – H(46A)	109.5	C(42) – C(46) – H(46B)	109.5
H(46A) – C(46) – H(46B)	109.5	C(42) – C(46) – H(46C)	109.5
H(46A) – C(46) – H(46C)	109.5	H(46B) – C(46) – H(46C)	109.5
C(53) – C(51) – C(54)	111.9(2)	C(53) – C(51) – P(2)	115.21(17)
C(54) – C(51) – P(2)	111.62(18)	C(53) – C(51) – H(51)	105.8
C(54) – C(51) – H(51)	105.8	P(2) – C(51) – H(51)	105.8
C(56) – C(52) – C(55)	109.6(2)	C(56) – C(52) – P(2)	112.12(17)
C(55) – C(52) – P(2)	108.84(16)	C(56) – C(52) – H(52)	108.7
C(55) – C(52) – H(52)	108.7	P(2) – C(52) – H(52)	108.7
C(51) – C(53) – H(53A)	109.5	C(51) – C(53) – H(53B)	109.5
H(53A) – C(53) – H(53B)	109.5	C(51) – C(53) – H(53C)	109.5
H(53A) – C(53) – H(53C)	109.5	H(53B) – C(53) – H(53C)	109.5
C(51) – C(54) – H(54A)	109.5	C(51) – C(54) – H(54B)	109.5
H(54A) – C(54) – H(54B)	109.5	C(51) – C(54) – H(54C)	109.5
H(54A) – C(54) – H(54C)	109.5	H(54B) – C(54) – H(54C)	109.5
C(52) – C(55) – H(55A)	109.5	C(52) – C(55) – H(55B)	109.5
H(55A) – C(55) – H(55B)	109.5	C(52) – C(55) – H(55C)	109.5
H(55A) – C(55) – H(55C)	109.5	H(55B) – C(55) – H(55C)	109.5
C(52) – C(56) – H(56A)	109.5	C(52) – C(56) – H(56B)	109.5
H(56A) – C(56) – H(56B)	109.5	C(52) – C(56) – H(56C)	109.5
H(56A) – C(56) – H(56C)	109.5	H(56B) – C(56) – H(56C)	109.5

4.2 Crystal data for [PC(SiHPh$_2$)P]PdH (4)

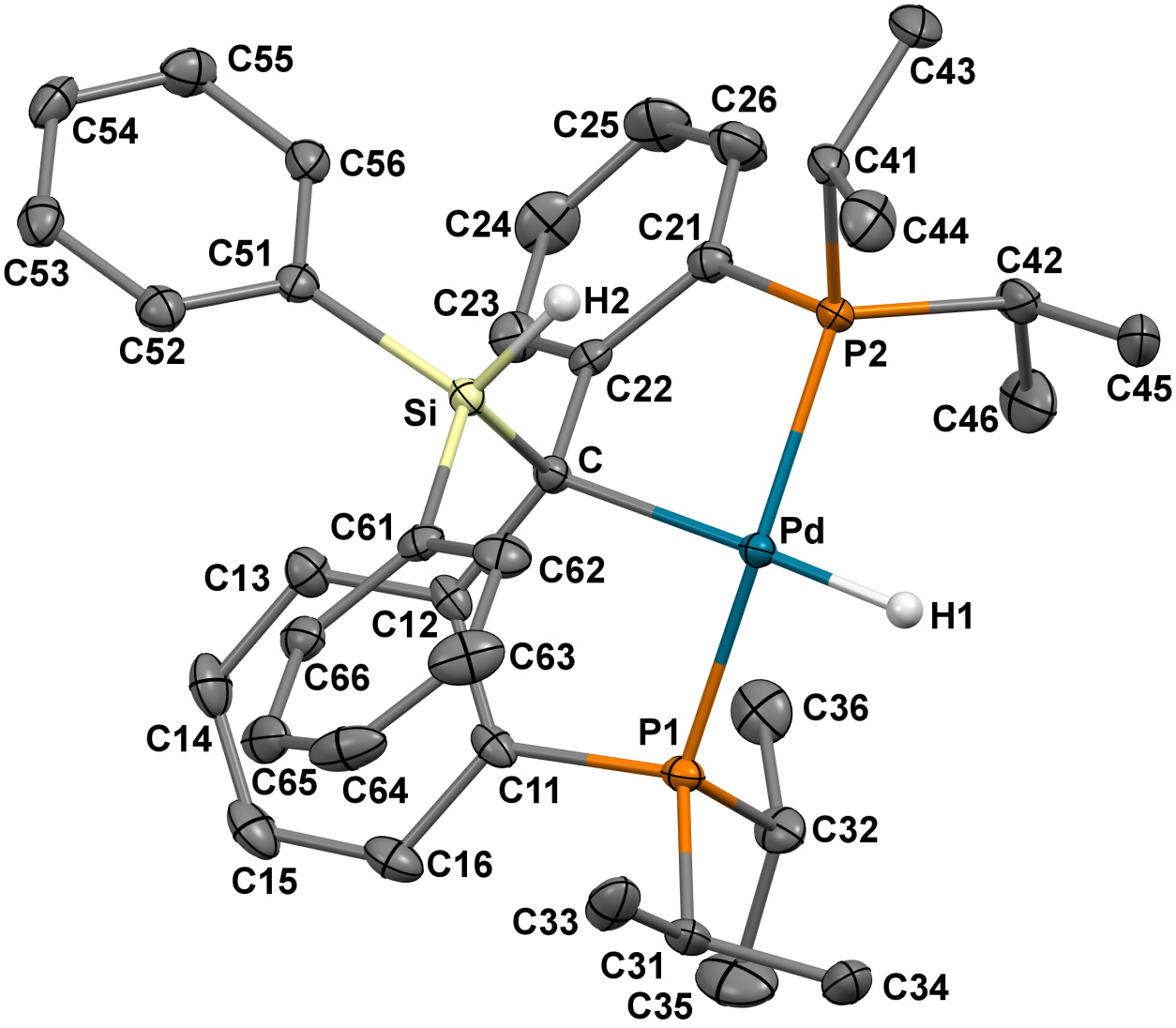


Figure S56. Thermal-ellipsoid representation of [PC(SiHPh$_2$)P]PdH (**4**) at 50% probability. Most hydrogen atoms were omitted for clarity.

Table S6. Crystal data and structure refinement for [PC(SiHPh$_2$)P]PdH (**4**).

Identification code:	cc170b	
Empirical formula:	$C_{37}H_{48}P_2PdSi$	
Formula weight:	689.18	
Temperature:	120(2) K	
Wavelength:	0.71073 Å	
Crystal system:	Monoclinic	
Space group:	$P2_1/n$	
Unit cell dimensions:	a = 9.402(3) Å	$\alpha = 90°$
	b = 19.186(5) Å	$\beta = 93.284(5)°$
	c = 19.053(5) Å	$\gamma = 90°$
Volume:	3431.3(16) Å^3	
Z:	4	
Density (calculated):	1.334 g·cm^{-3}	
Absorption coefficient (μ):	0.693 mm^{-1}	
F(000):	1440	
Crystal size:	0.23 × 0.16 × 0.10 mm^3	
θ range for data collection:	1.51 to 25.00°	
Index ranges:	$-11 \le h \le 9$, $-22 \le k \le 22$, $-22 \le l \le 22$	
Reflections collected:	37894	
Independent reflections:	6047 [R_{int} = 0.0665]	
Completeness to θ = 25.00°:	100.0 %	
Absorption correction:	Semi−empirical from equivalents	
Max. and min. transmission:	0.7454 and 0.6944	
Refinement method:	Full-matrix least-squares on F^2	
Data / restraints / parameters:	6047 / 0 / 386	
Goodness-of-fit on F^2:	1.026	
Final R indices [I>2σ(I)]:	R_1 = 0.0316, wR_2 = 0.0656	
R indices (all data):	R_1 = 0.0495, wR_2 = 0.0694	
Largest diff. peak and hole:	0.411 and −0.400 e$^-$·Å^{-3}	

Table S7. Atomic coordinates and equivalent isotropic displacement parameters (Å^2) for [PC(SiHPh$_2$)P]PdH (**4**). U(eq) is defined as one third of the trace of the orthogonalized U$_{ij}$ tensor

atom	x	y	z	U(eq)
Pd	0.26540(2)	0.84763(1)	0.22427(1)	0.012(1)
P(1)	0.28267(8)	0.80114(4)	0.33229(4)	0.015(1)
P(2)	0.16878(8)	0.86909(4)	0.11370(4)	0.014(1)
C	0.0811(3)	0.90247(14)	0.26035(14)	0.013(1)
C(11)	0.1538(3)	0.85018(15)	0.37998(14)	0.016(1)
C(12)	0.0582(3)	0.89195(14)	0.33844(14)	0.014(1)
C(13)	−0.0467(3)	0.92831(15)	0.37303(15)	0.019(1)
C(14)	−0.0552(3)	0.92503(16)	0.44530(16)	0.025(1)
C(15)	0.0412(4)	0.88512(16)	0.48549(16)	0.027(1)
C(16)	0.1444(3)	0.84799(16)	0.45323(15)	0.024(1)
C(21)	−0.0169(3)	0.87844(14)	0.13588(15)	0.016(1)
C(22)	−0.0419(3)	0.88591(14)	0.20847(14)	0.014(1)
C(23)	−0.1835(3)	0.87702(15)	0.22702(16)	0.021(1)
C(24)	−0.2947(3)	0.86612(16)	0.17730(17)	0.027(1)
C(25)	−0.2693(4)	0.86384(17)	0.10647(18)	0.031(1)
C(26)	−0.1310(3)	0.86945(17)	0.08682(17)	0.027(1)
C(31)	0.4488(3)	0.79580(15)	0.38836(15)	0.020(1)
C(32)	0.2126(3)	0.71068(15)	0.32865(16)	0.022(1)
C(33)	0.5176(3)	0.86714(16)	0.39439(18)	0.028(1)
Si	0.14726(8)	0.99462(4)	0.25230(4)	0.013(1)
C(34)	0.5514(3)	0.74417(16)	0.35678(17)	0.027(1)
C(35)	0.2147(4)	0.67306(17)	0.39917(19)	0.041(1)
C(36)	0.0627(3)	0.71033(16)	0.29339(18)	0.029(1)
C(41)	0.2078(3)	0.94387(15)	0.05609(15)	0.018(1)
C(42)	0.1680(3)	0.79170(15)	0.05613(16)	0.022(1)
C(43)	0.1510(4)	0.93784(17)	−0.02069(15)	0.031(1)
C(44)	0.3671(3)	0.96207(17)	0.06112(17)	0.031(1)
C(45)	0.3166(4)	0.77619(17)	0.03171(17)	0.032(1)
C(46)	0.1101(4)	0.72806(16)	0.09406(18)	0.037(1)
C(51)	0.0044(3)	1.06303(14)	0.26150(15)	0.016(1)
C(52)	0.0134(3)	1.11776(15)	0.31060(15)	0.020(1)
C(53)	−0.0938(3)	1.16647(15)	0.31482(16)	0.022(1)
C(54)	−0.2137(3)	1.16330(15)	0.26908(16)	0.023(1)
C(55)	−0.2246(3)	1.11057(16)	0.21922(16)	0.023(1)
C(56)	−0.1178(3)	1.06115(15)	0.21592(15)	0.020(1)
C(61)	0.3008(3)	1.01432(14)	0.31671(15)	0.015(1)
C(62)	0.4381(3)	1.02243(15)	0.29368(16)	0.023(1)
C(63)	0.5525(3)	1.04038(16)	0.33945(18)	0.030(1)
C(64)	0.5316(4)	1.05087(16)	0.40946(19)	0.031(1)
C(65)	0.3973(4)	1.04246(15)	0.43418(17)	0.025(1)

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Table S7. – continued from previous page

atom	x	y	x	U(eq)
C(66)	0.2840(3)	1.02418(14)	0.38859(15)	0.019(1)
H(13)	−0.1137	0.9559	0.3462	0.023
H(14)	−0.1273	0.9502	0.4673	0.030
H(15)	0.0362	0.8834	0.5351	0.032
H(16)	0.2102	0.8205	0.4809	0.029
H(23)	−0.2036	0.8785	0.2753	0.025
H(24)	−0.3889	0.8602	0.1919	0.033
H(25)	−0.3457	0.8585	0.0721	0.037
H(26)	−0.1129	0.8671	0.0383	0.033
H(31)	0.4261	0.7794	0.4363	0.023
H(32)	0.2746	0.6834	0.2977	0.027
H(33A)	0.5386	0.8838	0.3475	0.042
H(33B)	0.6064	0.8640	0.4238	0.042
H(33C)	0.4525	0.8997	0.4158	0.042
H(2)	0.196(3)	1.0058(14)	0.1866(15)	0.020(8)
H(1)	0.390(3)	0.8037(15)	0.2010(15)	0.024(8)
H(34A)	0.5709	0.7590	0.3090	0.041
H(34B)	0.5083	0.6976	0.3552	0.041
H(34C)	0.6407	0.7428	0.3859	0.041
H(35A)	0.1740	0.6263	0.3925	0.062
H(35B)	0.1583	0.6995	0.4317	0.062
H(35C)	0.3132	0.6692	0.4186	0.062
H(36A)	0.0624	0.7365	0.2492	0.043
H(36B)	−0.0035	0.7321	0.3247	0.043
H(36C)	0.0330	0.6622	0.2836	0.043
H(41)	0.1580	0.9849	0.0758	0.022
H(42)	0.1035	0.8014	0.0137	0.027
H(43A)	0.1707	0.9812	−0.0456	0.046
H(43B)	0.0480	0.9296	−0.0224	0.046
H(43C)	0.1981	0.8989	−0.0432	0.046
H(44A)	0.4206	0.9254	0.0385	0.046
H(44B)	0.4003	0.9658	0.1107	0.046
H(44C)	0.3819	1.0066	0.0374	0.046
H(45A)	0.3147	0.7323	0.0053	0.048
H(45B)	0.3840	0.7721	0.0727	0.048
H(45C)	0.3466	0.8141	0.0014	0.048
H(46A)	0.1070	0.6879	0.0623	0.056
H(46B)	0.0138	0.7381	0.1084	0.056
H(46C)	0.1723	0.7175	0.1357	0.056
H(52)	0.0957	1.1213	0.3418	0.024
H(53)	−0.0854	1.2023	0.3492	0.027
H(54)	−0.2875	1.1968	0.2718	0.028

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Table S7. – continued from previous page

atom	x	y	x	U(eq)
H(55)	−0.3058	1.1083	0.1872	0.028
H(56)	−0.1276	1.0251	0.1819	0.024
H(62)	0.4538	1.0155	0.2454	0.028
H(63)	0.6450	1.0454	0.3224	0.036
H(64)	0.6093	1.0639	0.4408	0.038
H(65)	0.3829	1.0493	0.4826	0.031
H(66)	0.1925	1.0181	0.4064	0.023

Table S8. Anisotropic displacement parameters (Å^2) for [PC(SiHPh$_2$)P]PdH (**4**). The anisotropic displacement factor exponent takes the form: $-2\pi^2$[h^{2}a*^{2}U$_{11}$ + ...+ 2hka*b*U$_{12}$].

atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Pd	0.0125(1)	0.0137(1)	0.0106(1)	0.0009(1)	−0.0001(1)	0.0007(1)
P(1)	0.0181(4)	0.0134(4)	0.0120(4)	0.0018(3)	−0.0017(3)	−0.0004(3)
P(2)	0.0169(4)	0.0143(4)	0.0101(4)	−0.0002(3)	−0.0004(3)	0.0030(3)
C	0.0126(15)	0.0151(14)	0.0113(14)	0.0002(12)	0.0000(11)	0.0002(12)
C(11)	0.0225(16)	0.0143(14)	0.0115(15)	0.0001(12)	0.0025(12)	−0.0070(13)
C(12)	0.0175(16)	0.0135(15)	0.0113(15)	−0.0015(11)	0.0031(12)	−0.0075(12)
C(13)	0.0169(16)	0.0222(16)	0.0182(16)	−0.0006(13)	0.0028(13)	−0.0021(13)
C(14)	0.0271(19)	0.0284(18)	0.0219(18)	−0.0045(14)	0.0131(14)	−0.0025(15)
C(15)	0.036(2)	0.0302(18)	0.0154(17)	0.0001(14)	0.0092(14)	−0.0082(16)
C(16)	0.0289(18)	0.0269(17)	0.0152(16)	0.0049(14)	−0.0002(13)	−0.0062(15)
C(21)	0.0165(16)	0.0144(14)	0.0168(16)	0.0009(12)	−0.0003(12)	−0.0005(12)
C(22)	0.0139(15)	0.0114(14)	0.0168(16)	0.0021(12)	−0.0004(12)	0.0018(12)
C(23)	0.0180(16)	0.0228(16)	0.0224(17)	0.0023(13)	0.0032(13)	−0.0015(13)
C(24)	0.0119(16)	0.0306(19)	0.040(2)	0.0002(15)	0.0002(14)	−0.0070(14)
C(25)	0.0200(18)	0.039(2)	0.031(2)	−0.0017(15)	−0.0100(15)	−0.0023(15)
C(26)	0.0269(19)	0.0349(19)	0.0189(17)	−0.0007(14)	−0.0049(14)	0.0002(15)
C(31)	0.0231(17)	0.0221(16)	0.0129(16)	−0.0005(12)	−0.0051(13)	0.0053(14)
C(32)	0.034(2)	0.0119(15)	0.0212(17)	0.0012(12)	−0.0017(14)	−0.0033(14)
C(33)	0.0219(18)	0.0274(18)	0.033(2)	−0.0086(14)	−0.0114(15)	0.0064(14)
Si	0.0152(4)	0.0136(4)	0.0108(4)	−0.0004(3)	0.0014(3)	−0.0004(3)
C(34)	0.0290(19)	0.0268(18)	0.0245(18)	−0.0024(14)	−0.0061(15)	0.0118(15)
C(35)	0.063(3)	0.0251(19)	0.035(2)	0.0134(16)	−0.0056(19)	−0.0125(18)
C(36)	0.032(2)	0.0217(17)	0.033(2)	−0.0018(14)	0.0020(15)	−0.0115(15)
C(41)	0.0258(17)	0.0167(15)	0.0131(16)	0.0011(12)	0.0044(13)	0.0027(13)
C(42)	0.0318(19)	0.0176(16)	0.0165(17)	−0.0049(13)	−0.0067(14)	0.0024(14)
C(43)	0.050(2)	0.0280(18)	0.0143(17)	0.0048(14)	0.0033(15)	0.0103(17)
C(44)	0.030(2)	0.0319(19)	0.031(2)	0.0048(15)	0.0126(15)	−0.0006(16)
C(45)	0.042(2)	0.0318(19)	0.0220(19)	−0.0084(15)	−0.0034(16)	0.0185(17)
C(46)	0.063(3)	0.0163(17)	0.032(2)	−0.0059(15)	−0.0028(19)	−0.0016(17)
C(51)	0.0186(16)	0.0159(15)	0.0143(15)	0.0033(12)	0.0038(12)	0.0010(13)
C(52)	0.0243(18)	0.0177(16)	0.0183(17)	0.0013(13)	0.0021(13)	−0.0016(14)
C(53)	0.0284(18)	0.0159(16)	0.0227(17)	0.0009(13)	0.0065(14)	0.0014(14)
C(54)	0.0203(16)	0.0191(17)	0.0319(19)	0.0047(14)	0.0083(14)	0.0070(14)
C(55)	0.0160(16)	0.0299(18)	0.0238(17)	0.0041(14)	0.0009(13)	0.0007(15)
C(56)	0.0248(18)	0.0192(16)	0.0162(16)	0.0009(13)	0.0042(13)	0.0028(14)
C(61)	0.0165(16)	0.0107(14)	0.0186(16)	0.0028(12)	−0.0013(12)	0.0006(12)
C(62)	0.0268(19)	0.0217(17)	0.0205(17)	0.0070(13)	0.0020(14)	−0.0027(14)
C(63)	0.0191(18)	0.0282(18)	0.042(2)	0.0138(16)	−0.0014(16)	−0.0073(15)
C(64)	0.030(2)	0.0194(17)	0.042(2)	0.0062(15)	−0.0201(17)	−0.0064(15)
C(65)	0.038(2)	0.0144(16)	0.0232(18)	−0.0054(13)	−0.0100(15)	0.0037(15)

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Table S8. – continued from previous page

atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C(66)	0.0231(17)	0.0139(15)	0.0194(17)	−0.0007(12)	−0.0018(13)	0.0011(13)

Table S9. Distances [Å] for [PC(SiHPh$_2$)P]PdH (**4**).

atom – atom	distance	atom – atom	distance
Pd – C	2.173(3)	Pd – P(1)	2.2402(9)
Pd – P(2)	2.2834(9)	Pd – H(1)	1.53(3)
P(1) – C(11)	1.818(3)	P(1) – C(31)	1.844(3)
P(1) – C(32)	1.856(3)	P(2) – C(21)	1.828(3)
P(2) – C(42)	1.846(3)	P(2) – C(41)	1.856(3)
C – C(22)	1.511(4)	C – C(12)	1.529(4)
C – Si	1.884(3)	C(11) – C(16)	1.404(4)
C(11) – C(12)	1.412(4)	C(12) – C(13)	1.403(4)
C(13) – C(14)	1.385(4)	C(13) – H(13)	0.9500
C(14) – C(15)	1.384(4)	C(14) – H(14)	0.9500
C(15) – C(16)	1.377(4)	C(15) – H(15)	0.9500
C(16) – H(16)	0.9500	C(21) – C(26)	1.392(4)
C(21) – C(22)	1.423(4)	C(22) – C(23)	1.407(4)
C(23) – C(24)	1.386(4)	C(23) – H(23)	0.9500
C(24) – C(25)	1.385(5)	C(24) – H(24)	0.9500
C(25) – C(26)	1.378(5)	C(25) – H(25)	0.9500
C(26) – H(26)	0.9500	C(31) – C(33)	1.515(4)
C(31) – C(34)	1.530(4)	C(31) – H(31)	1.0000
C(32) – C(35)	1.524(4)	C(32) – C(36)	1.526(4)
C(32) – H(32)	1.0000	C(33) – H(33A)	0.9800
C(33) – H(33B)	0.9800	C(33) – H(33C)	0.9800
Si – C(61)	1.879(3)	Si – C(51)	1.893(3)
Si – H(2)	1.38(3)	C(34) – H(34A)	0.9800
C(34) – H(34B)	0.9800	C(34) – H(34C)	0.9800
C(35) – H(35A)	0.9800	C(35) – H(35B)	0.9800
C(35) – H(35C)	0.9800	C(36) – H(36A)	0.9800
C(36) – H(36B)	0.9800	C(36) – H(36C)	0.9800
C(41) – C(43)	1.533(4)	C(41) – C(44)	1.535(4)
C(41) – H(41)	1.0000	C(42) – C(45)	1.527(5)
C(42) – C(46)	1.535(4)	C(42) – H(42)	1.0000
C(43) – H(43A)	0.9800	C(43) – H(43B)	0.9800
C(43) – H(43C)	0.9800	C(44) – H(44A)	0.9800
C(44) – H(44B)	0.9800	C(44) – H(44C)	0.9800
C(45) – H(45A)	0.9800	C(45) – H(45B)	0.9800
C(45) – H(45C)	0.9800	C(46) – H(46A)	0.9800
C(46) – H(46B)	0.9800	C(46) – H(46C)	0.9800
C(51) – C(56)	1.400(4)	C(51) – C(52)	1.406(4)
C(52) – C(53)	1.380(4)	C(52) – H(52)	0.9500
C(53) – C(54)	1.386(4)	C(53) – H(53)	0.9500
C(54) – C(55)	1.388(4)	C(54) – H(54)	0.9500
C(55) – C(56)	1.386(4)	C(55) – H(55)	0.9500

Continued on next page

Table S9. – continued from previous page

atom – atom	distance	atom – atom	distance
C(56) – H(56)	0.9500	C(61) – C(62)	1.396(4)
C(61) – C(66)	1.400(4)	C(62) – C(63)	1.388(4)
C(62) – H(62)	0.9500	C(63) – C(64)	1.374(5)
C(63) – H(63)	0.9500	C(64) – C(65)	1.382(5)
C(64) – H(64)	0.9500	C(65) – C(66)	1.380(4)
C(65) – H(65)	0.9500	C(66) – H(66)	0.9500

Table S10. Angles [°] for [PC(SiHPh$_2$)P]PdH (**4**).

atom – atom – atom	angle	atom – atom – atom	angle
C – Pd – P(1)	85.37(7)	C – Pd – P(2)	85.53(7)
P(1) – Pd – P(2)	157.43(3)	C – Pd – H(1)	175.5(11)
P(1) – Pd – H(1)	91.8(10)	P(2) – Pd – H(1)	95.9(10)
C(11) – P(1) – C(31)	107.81(13)	C(11) – P(1) – C(32)	104.91(14)
C(31) – P(1) – C(32)	104.88(13)	C(11) – P(1) – Pd	103.76(9)
C(31) – P(1) – Pd	124.66(11)	C(32) – P(1) – Pd	109.33(10)
C(21) – P(2) – C(42)	104.19(14)	C(21) – P(2) – C(41)	106.54(13)
C(42) – P(2) – C(41)	105.34(14)	C(21) – P(2) – Pd	98.00(9)
C(42) – P(2) – Pd	113.02(10)	C(41) – P(2) – Pd	127.11(10)
C(22) – C – C(12)	117.6(2)	C(22) – C – Si	112.83(18)
C(12) – C – Si	105.58(18)	C(22) – C – Pd	106.61(18)
C(12) – C – Pd	113.77(18)	Si – C – Pd	98.94(12)
C(16) – C(11) – C(12)	120.0(3)	C(16) – C(11) – P(1)	124.3(2)
C(12) – C(11) – P(1)	115.8(2)	C(13) – C(12) – C(11)	117.5(3)
C(13) – C(12) – C	122.2(3)	C(11) – C(12) – C	120.0(2)
C(14) – C(13) – C(12)	121.8(3)	C(14) – C(13) – H(13)	119.1
C(12) – C(13) – H(13)	119.1	C(15) – C(14) – C(13)	120.1(3)
C(15) – C(14) – H(14)	119.9	C(13) – C(14) – H(14)	119.9
C(16) – C(15) – C(14)	119.7(3)	C(16) – C(15) – H(15)	120.2
C(14) – C(15) – H(15)	120.2	C(15) – C(16) – C(11)	121.0(3)
C(15) – C(16) – H(16)	119.5	C(11) – C(16) – H(16)	119.5
C(26) – C(21) – C(22)	120.1(3)	C(26) – C(21) – P(2)	122.8(2)
C(22) – C(21) – P(2)	116.6(2)	C(23) – C(22) – C(21)	116.3(3)
C(23) – C(22) – C	124.1(3)	C(21) – C(22) – C	119.6(2)
C(24) – C(23) – C(22)	122.3(3)	C(24) – C(23) – H(23)	118.9
C(22) – C(23) – H(23)	118.9	C(25) – C(24) – C(23)	120.4(3)
C(25) – C(24) – H(24)	119.8	C(23) – C(24) – H(24)	119.8
C(26) – C(25) – C(24)	118.7(3)	C(26) – C(25) – H(25)	120.6
C(24) – C(25) – H(25)	120.6	C(25) – C(26) – C(21)	122.0(3)
C(25) – C(26) – H(26)	119.0	C(21) – C(26) – H(26)	119.0
C(33) – C(31) – C(34)	109.8(3)	C(33) – C(31) – P(1)	109.7(2)
C(34) – C(31) – P(1)	109.9(2)	C(33) – C(31) – H(31)	109.1
C(34) – C(31) – H(31)	109.1	P(1) – C(31) – H(31)	109.1
C(35) – C(32) – C(36)	110.6(3)	C(35) – C(32) – P(1)	115.0(2)
C(36) – C(32) – P(1)	109.7(2)	C(35) – C(32) – H(32)	107.0
C(36) – C(32) – H(32)	107.0	P(1) – C(32) – H(32)	107.0
C(31) – C(33) – H(33A)	109.5	C(31) – C(33) – H(33B)	109.5
H(33A) – C(33) – H(33B)	109.5	C(31) – C(33) – H(33C)	109.5
H(33A) – C(33) – H(33C)	109.5	H(33B) – C(33) – H(33C)	109.5
C(61) – Si – C	112.39(12)	C(61) – Si – C(51)	108.82(13)
C – Si – C(51)	113.80(13)	C(61) – Si – H(2)	106.1(12)

Continued on next page

Table S10. – continued from previous page

atom – atom – atom	angle	atom – atom – atom	angle
C – Si – H(2)	110.5(11)	C(51) – Si – H(2)	104.7(11)
C(31) – C(34) – H(34A)	109.5	C(31) – C(34) – H(34B)	109.5
H(34A) – C(34) – H(34B)	109.5	C(31) – C(34) – H(34C)	109.5
H(34A) – C(34) – H(34C)	109.5	H(34B) – C(34) – H(34C)	109.5
C(32) – C(35) – H(35A)	109.5	C(32) – C(35) – H(35B)	109.5
H(35A) – C(35) – H(35B)	109.5	C(32) – C(35) – H(35C)	109.5
H(35A) – C(35) – H(35C)	109.5	H(35B) – C(35) – H(35C)	109.5
C(32) – C(36) – H(36A)	109.5	C(32) – C(36) – H(36B)	109.5
H(36A) – C(36) – H(36B)	109.5	C(32) – C(36) – H(36C)	109.5
H(36A) – C(36) – H(36C)	109.5	H(36B) – C(36) – H(36C)	109.5
C(43) – C(41) – C(44)	111.2(3)	C(43) – C(41) – P(2)	115.9(2)
C(44) – C(41) – P(2)	111.4(2)	C(43) – C(41) – H(41)	105.9
C(44) – C(41) – H(41)	105.9	P(2) – C(41) – H(41)	105.9
C(45) – C(42) – C(46)	110.1(3)	C(45) – C(42) – P(2)	111.4(2)
C(46) – C(42) – P(2)	110.5(2)	C(45) – C(42) – H(42)	108.2
C(46) – C(42) – H(42)	108.2	P(2) – C(42) – H(42)	108.2
C(41) – C(43) – H(43A)	109.5	C(41) – C(43) – H(43B)	109.5
H(43A) – C(43) – H(43B)	109.5	C(41) – C(43) – H(43C)	109.5
H(43A) – C(43) – H(43C)	109.5	H(43B) – C(43) – H(43C)	109.5
C(41) – C(44) – H(44A)	109.5	C(41) – C(44) – H(44B)	109.5
H(44A) – C(44) – H(44B)	109.5	C(41) – C(44) – H(44C)	109.5
H(44A) – C(44) – H(44C)	109.5	H(44B) – C(44) – H(44C)	109.5
C(42) – C(45) – H(45A)	109.5	C(42) – C(45) – H(45B)	109.5
H(45A) – C(45) – H(45B)	109.5	C(42) – C(45) – H(45C)	109.5
H(45A) – C(45) – H(45C)	109.5	H(45B) – C(45) – H(45C)	109.5
C(42) – C(46) – H(46A)	109.5	C(42) – C(46) – H(46B)	109.5
H(46A) – C(46) – H(46B)	109.5	C(42) – C(46) – H(46C)	109.5
H(46A) – C(46) – H(46C)	109.5	H(46B) – C(46) – H(46C)	109.5
C(56) – C(51) – C(52)	116.6(3)	C(56) – C(51) – Si	119.1(2)
C(52) – C(51) – Si	124.3(2)	C(53) – C(52) – C(51)	121.9(3)
C(53) – C(52) – H(52)	119.1	C(51) – C(52) – H(52)	119.1
C(52) – C(53) – C(54)	120.3(3)	C(52) – C(53) – H(53)	119.9
C(54) – C(53) – H(53)	119.9	C(53) – C(54) – C(55)	119.2(3)
C(53) – C(54) – H(54)	120.4	C(55) – C(54) – H(54)	120.4
C(56) – C(55) – C(54)	120.3(3)	C(56) – C(55) – H(55)	119.9
C(54) – C(55) – H(55)	119.9	C(55) – C(56) – C(51)	121.7(3)
C(55) – C(56) – H(56)	119.1	C(51) – C(56) – H(56)	119.1
C(62) – C(61) – C(66)	116.8(3)	C(62) – C(61) – Si	120.5(2)
C(66) – C(61) – Si	122.7(2)	C(63) – C(62) – C(61)	121.8(3)
C(63) – C(62) – H(62)	119.1	C(61) – C(62) – H(62)	119.1
C(64) – C(63) – C(62)	119.8(3)	C(64) – C(63) – H(63)	120.1
C(62) – C(63) – H(63)	120.1	C(63) – C(64) – C(65)	119.9(3)

Continued on next page

Table S10. – continued from previous page

atom – atom – atom	angle	atom – atom – atom	angle
C(63) – C(64) – H(64)	120.1	C(65) – C(64) – H(64)	120.1
C(66) – C(65) – C(64)	120.1(3)	C(66) – C(65) – H(65)	119.9
C(64) – C(65) – H(65)	119.9	C(65) – C(66) – C(61)	121.6(3)
C(65) – C(66) – H(66)	119.2	C(61) – C(66) – H(66)	119.2

4.3 Crystal data for [PC(SiPh$_3$)P]PdH (5)

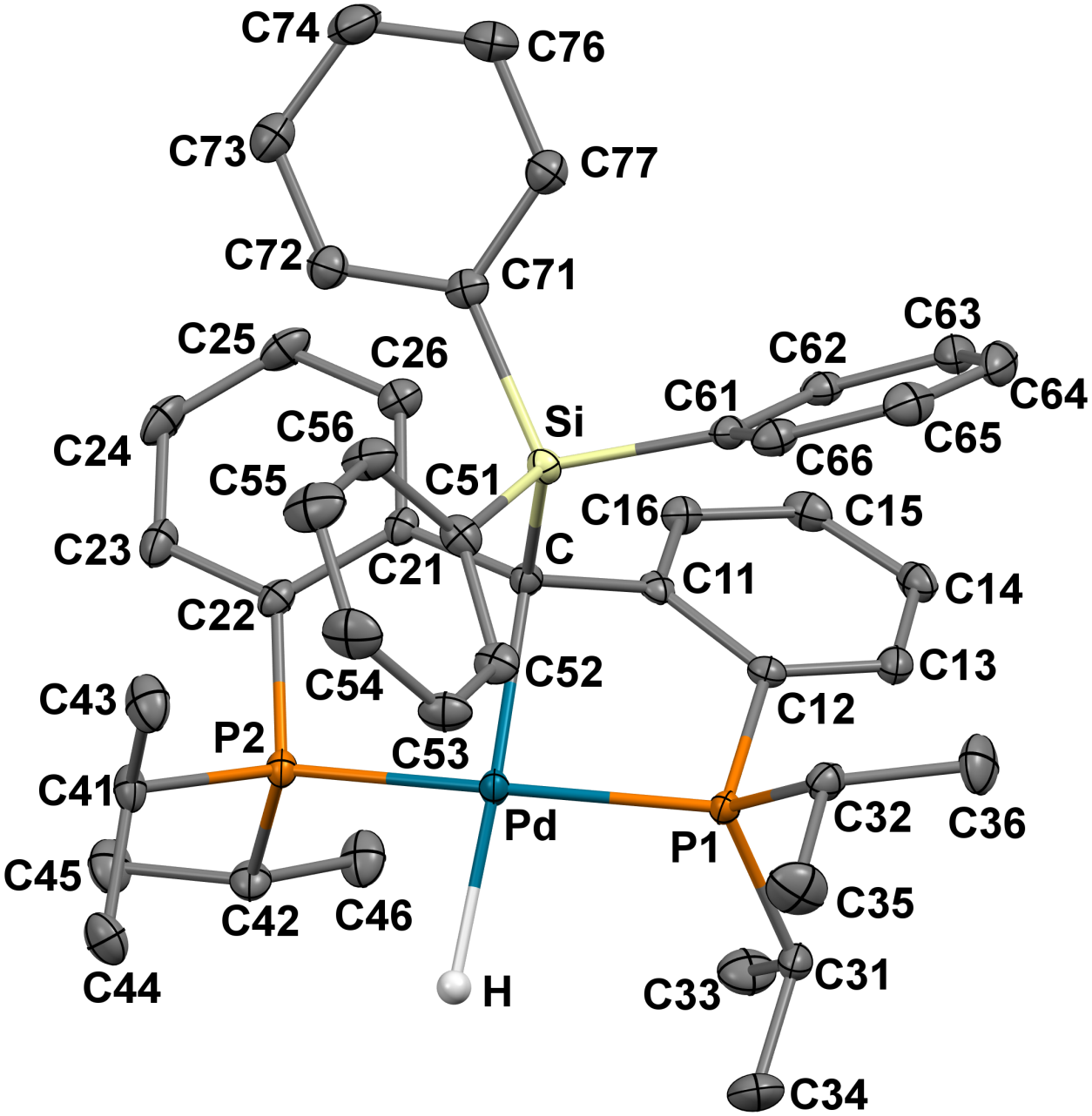

Figure S57. Thermal-ellipsoid representation of [PC(SiPh$_3$)P]PdH (**5**) at 50% probability. Most hydrogen atoms were omitted for clarity.

Table S11. Crystal data and structure refinement for [PC($SiPh_3$)P]PdH (**5**).

Identification code:	cc231	
Empirical formula:	$C_{43}H_{52}P_2PdSi$	
Formula weight:	765.28	
Temperature:	120(2) K	
Wavelength:	0.71073 Å	
Crystal system:	Triclinic	
Space group:	$P\bar{1}$	
Unit cell dimensions:	a = 9.5894(6) Å	α = 78.851(3)°
	b = 10.6642(7) Å	β = 76.192(3)°
	c = 19.5486(13) Å	γ = 76.697(2)°
Volume:	1868.9(2) $Å^3$	
Z:	2	
Density (calculated):	1.360 $g \cdot cm^{-3}$	
Absorption coefficient (μ):	0.644 mm^{-1}	
F(000):	800	
Crystal size:	$0.12 \times 0.10 \times 0.09$ mm^3	
θ range for data collection:	1.98 to 28.45°	
Index ranges:	$-12 \leq h \leq 12$, $-14 \leq k \leq 14$, $-26 \leq l \leq 26$	
Reflections collected:	56344	
Independent reflections:	9370 [R_{int} = 0.0469]	
Completeness to θ = 25.00°:	100.0 %	
Absorption correction:	Semi−empirical from equivalents	
Max. and min. transmission:	0.7457 and 0.6829	
Refinement method:	Full-matrix least-squares on F^2	
Data / restraints / parameters:	9370 / 0 / 435	
Goodness-of-fit on F^2:	1.049	
Final R indices [I>2σ(I)]:	R_1 = 0.0333, wR_2 = 0.0732	
R indices (all data):	R_1 = 0.0443, wR_2 = 0.0772	
Largest diff. peak and hole:	1.946 and −1.739 $e^- \cdot Å^{-3}$	

Table S12. Atomic coordinates and equivalent isotropic displacement parameters (Å^2) for [PC(SiPh$_3$)P]PdH (**5**). U(eq) is defined as one third of the trace of the orthogonalized U$_{ij}$ tensor

atom	x	y	z	U(eq)
Pd	0.26115(2)	0.07611(2)	0.32212(1)	0.012(1)
P(1)	0.31475(6)	0.27875(5)	0.28653(3)	0.012(1)
C(21)	0.5405(2)	−0.1405(2)	0.30667(11)	0.013(1)
C(22)	0.4397(2)	−0.2145(2)	0.35149(11)	0.014(1)
C(23)	0.4836(3)	−0.3474(2)	0.37531(12)	0.020(1)
C(24)	0.6285(3)	−0.4082(2)	0.35847(13)	0.022(1)
C(25)	0.7295(3)	−0.3374(2)	0.31549(13)	0.021(1)
C(26)	0.6856(2)	−0.2079(2)	0.28869(12)	0.016(1)
C(31)	0.2590(2)	0.3873(2)	0.35633(11)	0.017(1)
C(32)	0.2741(2)	0.3816(2)	0.20287(12)	0.016(1)
C(33)	0.3237(3)	0.3232(3)	0.42174(13)	0.027(1)
C(34)	0.0922(3)	0.4234(3)	0.37895(14)	0.028(1)
C(35)	0.1100(3)	0.4228(3)	0.20342(15)	0.030(1)
C(36)	0.3494(3)	0.4988(2)	0.17817(13)	0.026(1)
C(41)	0.1272(2)	−0.2233(2)	0.37531(12)	0.017(1)
C(42)	0.2432(3)	−0.1316(2)	0.47842(11)	0.017(1)
C(43)	0.1262(3)	−0.2204(2)	0.29691(13)	0.026(1)
C(44)	−0.0266(3)	−0.1733(2)	0.41666(13)	0.024(1)
C(45)	0.2502(3)	−0.2675(2)	0.52236(12)	0.024(1)
C(46)	0.3602(3)	−0.0665(2)	0.49020(13)	0.024(1)
C(51)	0.3137(2)	−0.0127(2)	0.15517(11)	0.016(1)
C(52)	0.1877(2)	0.0811(2)	0.17219(12)	0.018(1)
C(53)	0.0574(2)	0.0812(2)	0.15265(12)	0.020(1)
C(54)	0.0496(3)	−0.0159(3)	0.11656(14)	0.026(1)
C(55)	0.1723(3)	−0.1102(3)	0.09901(15)	0.030(1)
C(56)	0.3026(3)	−0.1073(2)	0.11742(13)	0.023(1)
C(61)	0.5537(2)	0.1468(2)	0.11557(11)	0.014(1)
C(62)	0.6791(2)	0.1878(2)	0.12060(11)	0.015(1)
C(63)	0.7299(3)	0.2908(2)	0.07377(12)	0.019(1)
C(64)	0.6559(3)	0.3564(2)	0.02083(12)	0.023(1)
C(65)	0.5332(3)	0.3167(2)	0.01336(12)	0.022(1)
C(66)	0.4832(2)	0.2124(2)	0.05997(12)	0.018(1)
C(71)	0.6274(2)	−0.1450(2)	0.13600(11)	0.015(1)
C(72)	0.6159(2)	−0.2754(2)	0.16224(12)	0.019(1)
C(73)	0.7111(3)	−0.3782(2)	0.13158(13)	0.023(1)
C(74)	0.8205(3)	−0.3538(2)	0.07291(14)	0.027(1)
C(76)	0.8332(3)	−0.2267(2)	0.04468(14)	0.027(1)
C(77)	0.7376(2)	−0.1239(2)	0.07577(12)	0.019(1)
P(2)	0.25695(6)	−0.12495(5)	0.38185(3)	0.013(1)

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Table S12. – continued from previous page

atom	x	y	x	U(eq)
Si	0.49393(6)	−0.00202(5)	0.17528(3)	0.012(1)
C	0.4899(2)	0.00090(19)	0.27439(11)	0.012(1)
C(11)	0.5743(2)	0.0987(2)	0.28454(10)	0.011(1)
C(12)	0.5124(2)	0.2344(2)	0.27727(11)	0.012(1)
C(13)	0.5959(2)	0.3270(2)	0.27533(11)	0.016(1)
C(14)	0.7391(2)	0.2901(2)	0.28428(12)	0.017(1)
C(15)	0.7958(2)	0.1584(2)	0.29963(11)	0.018(1)
C(16)	0.7150(2)	0.0658(2)	0.30034(11)	0.015(1)
H(23)	0.4130	−0.3961	0.4033	0.024
H(24)	0.6585	−0.4974	0.3762	0.027
H(25)	0.8296	−0.3780	0.3043	0.025
H(26)	0.7560	−0.1629	0.2570	0.020
H(31)	0.2974	0.4693	0.3363	0.020
H(32)	0.3144	0.3244	0.1650	0.019
H(33A)	0.2816	0.2461	0.4442	0.040
H(33B)	0.3010	0.3851	0.4558	0.040
H(33C)	0.4301	0.2971	0.4072	0.040
H	0.065(3)	0.132(3)	0.3851(16)	0.040
H(34A)	0.0515	0.4764	0.3388	0.042
H(34B)	0.0669	0.4731	0.4189	0.042
H(34C)	0.0515	0.3437	0.3936	0.042
H(35A)	0.0948	0.4435	0.1543	0.045
H(35B)	0.0699	0.4999	0.2274	0.045
H(35C)	0.0604	0.3515	0.2289	0.045
H(36A)	0.3157	0.5507	0.1359	0.039
H(36B)	0.4556	0.4685	0.1663	0.039
H(36C)	0.3253	0.5525	0.2163	0.039
H(41)	0.1609	−0.3154	0.3964	0.020
H(42)	0.1460	−0.0782	0.4971	0.020
H(43A)	0.0895	−0.1312	0.2760	0.038
H(43B)	0.0626	−0.2777	0.2932	0.038
H(43C)	0.2259	−0.2505	0.2713	0.038
H(44A)	−0.0581	−0.0811	0.3988	0.035
H(44B)	−0.0250	−0.1831	0.4674	0.035
H(44C)	−0.0949	−0.2236	0.4102	0.035
H(45A)	0.1802	−0.3109	0.5114	0.036
H(45B)	0.2255	−0.2598	0.5732	0.036
H(45C)	0.3492	−0.3189	0.5107	0.036
H(46A)	0.4573	−0.1195	0.4756	0.036
H(46B)	0.3438	−0.0585	0.5407	0.036
H(46C)	0.3546	0.0203	0.4618	0.036
H(52)	0.1911	0.1469	0.1979	0.021

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Table S12. – continued from previous page

atom	x	y	x	U(eq)
H(53)	−0.0258	0.1475	0.1640	0.024
H(54)	−0.0396	−0.0176	0.1039	0.031
H(55)	0.1675	−0.1770	0.0743	0.036
H(56)	0.3866	−0.1715	0.1039	0.027
H(62)	0.7307	0.1440	0.1570	0.018
H(63)	0.8157	0.3162	0.0782	0.023
H(64)	0.6890	0.4285	−0.0104	0.027
H(65)	0.4832	0.3607	−0.0236	0.026
H(66)	0.3997	0.1853	0.0540	0.021
H(72)	0.5408	−0.2937	0.2021	0.023
H(73)	0.7013	−0.4654	0.1508	0.027
H(74)	0.8865	−0.4241	0.0522	0.032
H(76)	0.9072	−0.2094	0.0040	0.032
H(77)	0.7473	−0.0371	0.0556	0.023
H(13)	0.5534	0.4170	0.2677	0.019
H(14)	0.7973	0.3534	0.2800	0.021
H(15)	0.8912	0.1314	0.3098	0.021
H(16)	0.7563	−0.0236	0.3120	0.018

Table S13. Anisotropic displacement parameters (Å^2) for [PC(SiPh$_3$)P]PdH (**5**). The anisotropic displacement factor exponent takes the form: $-2\pi^2$[h^{2}a*^{2}U$_{11}$ + ...+ 2hka*b*U$_{12}$].

atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Pd	0.0116(1)	0.0094(1)	0.0153(1)	−0.0002(1)	−0.0025(1)	−0.0030(1)
P(1)	0.0113(2)	0.0089(2)	0.0144(3)	−0.0011(2)	−0.0020(2)	−0.0019(2)
C(21)	0.0158(10)	0.0116(9)	0.0115(10)	−0.0020(7)	−0.0044(8)	−0.0028(8)
C(22)	0.0171(10)	0.0121(9)	0.0129(10)	−0.0029(8)	−0.0054(8)	−0.0012(8)
C(23)	0.0289(13)	0.0123(10)	0.0182(11)	−0.0005(8)	−0.0061(10)	−0.0046(9)
C(24)	0.0317(13)	0.0110(10)	0.0232(12)	−0.0017(9)	−0.0122(10)	0.0033(9)
C(25)	0.0201(11)	0.0165(11)	0.0261(12)	−0.0069(9)	−0.0107(10)	0.0053(9)
C(26)	0.0165(10)	0.0168(10)	0.0167(11)	−0.0037(8)	−0.0054(9)	−0.0013(8)
C(31)	0.0209(11)	0.0120(10)	0.0154(10)	−0.0023(8)	0.0004(9)	−0.0044(8)
C(32)	0.0179(11)	0.0133(10)	0.0155(10)	−0.0016(8)	−0.0031(8)	−0.0007(8)
C(33)	0.0300(14)	0.0321(14)	0.0169(12)	−0.0064(10)	−0.0032(10)	−0.0035(11)
C(34)	0.0218(12)	0.0259(13)	0.0309(14)	−0.0111(11)	0.0026(10)	0.0020(10)
C(35)	0.0217(13)	0.0329(14)	0.0312(14)	0.0014(11)	−0.0099(11)	0.0031(11)
C(36)	0.0387(15)	0.0200(12)	0.0200(12)	0.0059(9)	−0.0076(11)	−0.0119(11)
C(41)	0.0220(11)	0.0144(10)	0.0168(11)	−0.0002(8)	−0.0055(9)	−0.0091(9)
C(42)	0.0222(11)	0.0175(10)	0.0121(10)	−0.0034(8)	−0.0027(9)	−0.0055(9)
C(43)	0.0324(14)	0.0282(13)	0.0220(12)	−0.0035(10)	−0.0077(10)	−0.0152(11
C(44)	0.0188(11)	0.0275(12)	0.0265(13)	−0.0013(10)	−0.0043(10)	−0.0108(10)
C(45)	0.0351(14)	0.0231(12)	0.0148(11)	0.0012(9)	−0.0056(10)	−0.0104(10)
C(46)	0.0336(14)	0.0240(12)	0.0197(12)	−0.0030(9)	−0.0101(10)	−0.0113(10)
C(51)	0.0152(10)	0.0198(11)	0.0128(10)	−0.0010(8)	−0.0041(8)	−0.0054(8)
C(52)	0.0181(11)	0.0211(11)	0.0154(11)	−0.0049(9)	−0.0048(9)	−0.0045(9)
C(53)	0.0141(11)	0.0263(12)	0.0201(12)	−0.0063(9)	−0.0044(9)	0.0003(9)
C(54)	0.0145(11)	0.0383(14)	0.0304(14)	−0.0106(11)	−0.0091(10)	−0.0054(10)
C(55)	0.0252(13)	0.0356(14)	0.0354(15)	−0.0201(12)	−0.0101(11)	−0.0041(11)
C(56)	0.0174(11)	0.0275(12)	0.0261(13)	−0.0127(10)	−0.0064(10)	−0.0009(9)
C(61)	0.0144(10)	0.0135(10)	0.0123(10)	−0.0024(8)	−0.0005(8)	−0.0003(8)
C(62)	0.0162(10)	0.0153(10)	0.0117(10)	−0.0031(8)	−0.0018(8)	0.0002(8)
C(63)	0.0222(11)	0.0177(11)	0.0176(11)	−0.0049(9)	0.0009(9)	−0.0059(9)
C(64)	0.0325(13)	0.0145(11)	0.0162(11)	0.0008(9)	0.0016(10)	−0.0050(9)
C(65)	0.0268(12)	0.0214(12)	0.0139(11)	−0.0008(9)	−0.0049(9)	0.0017(9)
C(66)	0.0190(11)	0.0183(11)	0.0153(11)	−0.0044(8)	−0.0042(9)	0.0001(9)
C(71)	0.0137(10)	0.0175(10)	0.0153(10)	−0.0049(8)	−0.0054(8)	−0.0019(8)
C(72)	0.0189(11)	0.0192(11)	0.0193(11)	−0.0042(9)	−0.0038(9)	−0.0049(9)
C(73)	0.0274(13)	0.0167(11)	0.0248(12)	−0.0048(9)	−0.0068(10)	−0.0030(9)
C(74)	0.0260(13)	0.0222(12)	0.0308(14)	−0.0124(10)	−0.0023(11)	0.0018(10)
C(76)	0.0232(13)	0.0286(13)	0.0244(13)	−0.0080(10)	0.0039(10)	−0.0035(10)
C(77)	0.0197(11)	0.0191(11)	0.0197(11)	−0.0036(9)	−0.0036(9)	−0.0041(9)
P(2)	0.0155(3)	0.0104(2)	0.0126(3)	−0.0004(2)	−0.0030(2)	−0.0048(2)
Si	0.0111(3)	0.0130(3)	0.0129(3)	−0.0015(2)	−0.0029(2)	−0.0027(2)

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Table S13. – continued from previous page

atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C	0.0123(10)	0.0100(9)	0.0133(10)	−0.0008(7)	−0.0025(8)	−0.0021(7)
C(11)	0.0134(10)	0.0138(10)	0.0067(9)	−0.0012(7)	−0.0006(7)	−0.0039(8)
C(12)	0.0116(10)	0.0148(10)	0.0102(9)	−0.0023(8)	−0.0011(8)	−0.0021(8)
C(13)	0.0180(11)	0.0143(10)	0.0150(10)	−0.0029(8)	−0.0009(8)	−0.0051(8)
C(14)	0.0161(11)	0.0216(11)	0.0169(11)	−0.0063(9)	−0.0003(9)	−0.0088(9)
C(15)	0.0132(10)	0.0261(12)	0.0153(11)	−0.0058(9)	−0.0032(8)	−0.0047(9)
C(16)	0.0145(10)	0.0155(10)	0.0132(10)	−0.0018(8)	−0.0034(8)	−0.0013(8)

Table S14. Distances [Å] for [PC($SiPh_3$)P]PdH (**5**).

atom – atom	distance	atom – atom	distance
Pd – C	2.198(2)	Pd – P(2)	2.2386(5)
Pd – P(1)	2.2753(5)	Pd – H	2.02(3)
P(1) – C(12)	1.819(2)	P(1) – C(32)	1.856(2)
P(1) – C(31)	1.862(2)	C(21) – C(26)	1.407(3)
C(21) – C(22)	1.416(3)	C(21) – C	1.533(3)
C(22) – C(23)	1.402(3)	C(22) – P(2)	1.813(2)
C(23) – C(24)	1.382(3)	C(23) – H(23)	0.9500
C(24) – C(25)	1.384(3)	C(24) – H(24)	0.9500
C(25) – C(26)	1.385(3)	C(25) – H(25)	0.9500
C(26) – H(26)	0.9500	C(31) – C(33)	1.528(3)
C(31) – C(34)	1.532(3)	C(31) – H(31)	1.0000
C(32) – C(36)	1.528(3)	C(32) – C(35)	1.531(3)
C(32) – H(32)	1.0000	C(33) – H(33A)	0.9800
C(33) – H(33B)	0.9800	C(33) – H(33C)	0.9800
C(34) – H(34A)	0.9800	C(34) – H(34B)	0.9800
C(34) – H(34C)	0.9800	C(35) – H(35A)	0.9800
C(35) – H(35B)	0.9800	C(35) – H(35C)	0.9800
C(36) – H(36A)	0.9800	C(36) – H(36B)	0.9800
C(36) – H(36C)	0.9800	C(41) – C(43)	1.529(3)
C(41) – C(44)	1.532(3)	C(41) – P(2)	1.842(2)
C(41) – H(41)	1.0000	C(42) – C(46)	1.529(3)
C(42) – C(45)	1.531(3)	C(42) – P(2)	1.849(2)
C(42) – H(42)	1.0000	C(43) – H(43A)	0.9800
C(43) – H(43B)	0.9800	C(43) – H(43C)	0.9800
C(44) – H(44A)	0.9800	C(44) – H(44B)	0.9800
C(44) – H(44C)	0.9800	C(45) – H(45A)	0.9800
C(45) – H(45B)	0.9800	C(45) – H(45C)	0.9800
C(46) – H(46A)	0.9800	C(46) – H(46B)	0.9800
C(46) – H(46C)	0.9800	C(51) – C(56)	1.395(3)
C(51) – C(52)	1.397(3)	C(51) – Si	1.894(2)
C(52) – C(53)	1.390(3)	C(52) – H(52)	0.9500
C(53) – C(54)	1.385(3)	C(53) – H(53)	0.9500
C(54) – C(55)	1.382(4)	C(54) – H(54)	0.9500
C(55) – C(56)	1.388(3)	C(55) – H(55)	0.9500
C(56) – H(56)	0.9500	C(61) – C(62)	1.401(3)
C(61) – C(66)	1.403(3)	C(61) – Si	1.895(2)
C(62) – C(63)	1.388(3)	C(62) – H(62)	0.9500
C(63) – C(64)	1.380(3)	C(63) – H(63)	0.9500
C(64) – C(65)	1.385(3)	C(64) – H(64)	0.9500
C(65) – C(66)	1.394(3)	C(65) – H(65)	0.9500
C(66) – H(66)	0.9500	C(71) – C(77)	1.402(3)

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Table S14. – continued from previous page

atom – atom	distance	atom – atom	distance
C(71) – C(72)	1.407(3)	C(71) – Si	1.907(2)
C(72) – C(73)	1.388(3)	C(72) – H(72)	0.9500
C(73) – C(74)	1.385(4)	C(73) – H(73)	0.9500
C(74) – C(76)	1.383(4)	C(74) – H(74)	0.9500
C(76) – C(77)	1.393(3)	C(76) – H(76)	0.9500
C(77) – H(77)	0.9500	Si – C	1.935(2)
C – C(11)	1.526(3)	C(11) – C(16)	1.406(3)
C(11) – C(12)	1.425(3)	C(12) – C(13)	1.397(3)
C(13) – C(14)	1.383(3)	C(13) – H(13)	0.9500
C(14) – C(15)	1.386(3)	C(14) – H(14)	0.9500
C(15) – C(16)	1.385(3)	C(15) – H(15)	0.9500
C(16) – H(16)	0.9500		

Table S15. Angles [°] for [PC(SiPh$_3$)P]PdH (**5**).

atom – atom – atom	angle	atom – atom – atom	angle
C – Pd – P(2)	86.58(5)	C – Pd – P(1)	86.80(5)
P(2) – Pd – P(1)	160.92(2)	C – Pd – H	168.1(8)
P(2) – Pd – H	87.0(8)	P(1) – Pd – H	96.2(8)
C(12) – P(1) – C(32)	108.19(10)	C(12) – P(1) – C(31)	103.15(10)
C(32) – P(1) – C(31)	106.59(10)	C(12) – P(1) – Pd	98.55(7)
C(32) – P(1) – Pd	122.63(7)	C(31) – P(1) – Pd	115.44(7)
C(26) – C(21) – C(22)	116.06(19)	C(26) – C(21) – C	122.45(18)
C(22) – C(21) – C	121.24(18)	C(23) – C(22) – C(21)	121.2(2)
C(23) – C(22) – P(2)	122.42(17)	C(21) – C(22) – P(2)	116.21(15)
C(24) – C(23) – C(22)	120.7(2)	C(24) – C(23) – H(23)	119.7
C(22) – C(23) – H(23)	119.7	C(23) – C(24) – C(25)	119.2(2)
C(23) – C(24) – H(24)	120.4	C(25) – C(24) – H(24)	120.4
C(24) – C(25) – C(26)	120.5(2)	C(24) – C(25) – H(25)	119.7
C(26) – C(25) – H(25)	119.7	C(25) – C(26) – C(21)	122.3(2)
C(25) – C(26) – H(26)	118.8	C(21) – C(26) – H(26)	118.8
C(33) – C(31) – C(34)	109.20(19)	C(33) – C(31) – P(1)	110.90(16)
C(34) – C(31) – P(1)	111.67(16)	C(33) – C(31) – H(31)	108.3
C(34) – C(31) – H(31)	108.3	P(1) – C(31) – H(31)	108.3
C(36) – C(32) – C(35)	110.7(2)	C(36) – C(32) – P(1)	115.37(16)
C(35) – C(32) – P(1)	113.18(16)	C(36) – C(32) – H(32)	105.5
C(35) – C(32) – H(32)	105.5	P(1) – C(32) – H(32)	105.5
C(31) – C(33) – H(33A)	109.5	C(31) – C(33) – H(33B)	109.5
H(33A) – C(33) – H(33B)	109.5	C(31) – C(33) – H(33C)	109.5
H(33A) – C(33) – H(33C)	109.5	H(33B) – C(33) – H(33C)	109.5
C(31) – C(34) – H(34A)	109.5	C(31) – C(34) – H(34B)	109.5
H(34A) – C(34) – H(34B)	109.5	C(31) – C(34) – H(34C)	109.5
H(34A) – C(34) – H(34C)	109.5	H(34B) – C(34) – H(34C)	109.5
C(32) – C(35) – H(35A)	109.5	C(32) – C(35) – H(35B)	109.5
H(35A) – C(35) – H(35B)	109.5	C(32) – C(35) – H(35C)	109.5
H(35A) – C(35) – H(35C)	109.5	H(35B) – C(35) – H(35C)	109.5
C(32) – C(36) – H(36A)	109.5	C(32) – C(36) – H(36B)	109.5
H(36A) – C(36) – H(36B)	109.5	C(32) – C(36) – H(36C)	109.5
H(36A) – C(36) – H(36C)	109.5	H(36B) – C(36) – H(36C)	109.5
C(43) – C(41) – C(44)	110.9(2)	C(43) – C(41) – P(2)	109.36(15)
C(44) – C(41) – P(2)	110.79(15)	C(43) – C(41) – H(41)	108.6
C(44) – C(41) – H(41)	108.6	P(2) – C(41) – H(41)	108.6
C(46) – C(42) – C(45)	110.32(19)	C(46) – C(42) – P(2)	109.55(15)
C(45) – C(42) – P(2)	115.53(15)	C(46) – C(42) – H(42)	107.0
C(45) – C(42) – H(42)	107.0	P(2) – C(42) – H(42)	107.0
C(41) – C(43) – H(43A)	109.5	C(41) – C(43) – H(43B)	109.5
H(43A) – C(43) – H(43B)	109.5	C(41) – C(43) – H(43C)	109.5

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Table S15. – continued from previous page

atom – atom – atom	angle	atom – atom – atom	angle
H(43A) – C(43) – H(43C)	109.5	H(43B) – C(43) – H(43C)	109.5
C(41) – C(44) – H(44A)	109.5	C(41) – C(44) – H(44B)	109.5
H(44A) – C(44) – H(44B)	109.5	C(41) – C(44) – H(44C)	109.5
H(44A) – C(44) – H(44C)	109.5	H(44B) – C(44) – H(44C)	109.5
C(42) – C(45) – H(45A)	109.5	C(42) – C(45) – H(45B)	109.5
H(45A) – C(45) – H(45B)	109.5	C(42) – C(45) – H(45C)	109.5
H(45A) – C(45) – H(45C)	109.5	H(45B) – C(45) – H(45C)	109.5
C(42) – C(46) – H(46A)	109.5	C(42) – C(46) – H(46B)	109.5
H(46A) – C(46) – H(46B)	109.5	C(42) – C(46) – H(46C)	109.5
H(46A) – C(46) – H(46C)	109.5	H(46B) – C(46) – H(46C)	109.5
C(56) – C(51) – C(52)	116.6(2)	C(56) – C(51) – Si	122.00(17)
C(52) – C(51) – Si	121.18(16)	C(53) – C(52) – C(51)	122.1(2)
C(53) – C(52) – H(52)	118.9	C(51) – C(52) – H(52)	118.9
C(54) – C(53) – C(52)	119.7(2)	C(54) – C(53) – H(53)	120.2
C(52) – C(53) – H(53)	120.2	C(55) – C(54) – C(53)	119.6(2)
C(55) – C(54) – H(54)	120.2	C(53) – C(54) – H(54)	120.2
C(54) – C(55) – C(56)	120.1(2)	C(54) – C(55) – H(55)	120.0
C(56) – C(55) – H(55)	120.0	C(55) – C(56) – C(51)	121.9(2)
C(55) – C(56) – H(56)	119.0	C(51) – C(56) – H(56)	119.0
C(62) – C(61) – C(66)	117.07(19)	C(62) – C(61) – Si	121.21(16)
C(66) – C(61) – Si	121.42(16)	C(63) – C(62) – C(61)	121.7(2)
C(63) – C(62) – H(62)	119.2	C(61) – C(62) – H(62)	119.2
C(64) – C(63) – C(62)	120.1(2)	C(64) – C(63) – H(63)	120.0
C(62) – C(63) – H(63)	120.0	C(63) – C(64) – C(65)	119.8(2)
C(63) – C(64) – H(64)	120.1	C(65) – C(64) – H(64)	120.1
C(64) – C(65) – C(66)	120.1(2)	C(64) – C(65) – H(65)	120.0
C(66) – C(65) – H(65)	120.0	C(65) – C(66) – C(61)	121.2(2)
C(65) – C(66) – H(66)	119.4	C(61) – C(66) – H(66)	119.4
C(77) – C(71) – C(72)	116.4(2)	C(77) – C(71) – Si	120.82(16)
C(72) – C(71) – Si	122.65(17)	C(73) – C(72) – C(71)	121.9(2)
C(73) – C(72) – H(72)	119.0	C(71) – C(72) – H(72)	119.0
C(74) – C(73) – C(72)	120.1(2)	C(74) – C(73) – H(73)	120.0
C(72) – C(73) – H(73)	120.0	C(76) – C(74) – C(73)	119.7(2)
C(76) – C(74) – H(74)	120.2	C(73) – C(74) – H(74)	120.2
C(74) – C(76) – C(77)	120.0(2)	C(74) – C(76) – H(76)	120.0
C(77) – C(76) – H(76)	120.0	C(76) – C(77) – C(71)	121.9(2)
C(76) – C(77) – H(77)	119.1	C(71) – C(77) – H(77)	119.1
C(22) – P(2) – C(41)	107.16(10)	C(22) – P(2) – C(42)	104.08(10)
C(41) – P(2) – C(42)	105.11(10)	C(22) – P(2) – Pd	103.58(7)
C(41) – P(2) – Pd	122.97(7)	C(42) – P(2) – Pd	112.35(7)
C(51) – Si – C(61)	106.62(9)	C(51) – Si – C(71)	103.35(9)
C(61) – Si – C(71)	104.03(9)	C(51) – Si – C	115.04(9)

Continued on next page

Table S15. – continued from previous page

atom – atom – atom	angle	atom – atom – atom	angle
C(61) – Si – C	112.12(9)	C(71) – Si – C	114.64(9)
C(11) – C – C(21)	115.47(17)	C(11) – C – Si	112.86(13)
C(21) – C – Si	106.28(13)	C(11) – C – Pd	104.43(13)
C(21) – C – Pd	111.43(13)	Si – C – Pd	106.06(9)
C(16) – C(11) – C(12)	115.08(18)	C(16) – C(11) – C	124.56(18)
C(12) – C(11) – C	120.36(18)	C(13) – C(12) – C(11)	121.19(19)
C(13) – C(12) – P(1)	121.23(16)	C(11) – C(12) – P(1)	116.71(15)
C(14) – C(13) – C(12)	121.2(2)	C(14) – C(13) – H(13)	119.4
C(12) – C(13) – H(13)	119.4	C(13) – C(14) – C(15)	118.3(2)
C(13) – C(14) – H(14)	120.8	C(15) – C(14) – H(14)	120.8
C(16) – C(15) – C(14)	120.8(2)	C(16) – C(15) – H(15)	119.6
C(14) – C(15) – H(15)	119.6	C(15) – C(16) – C(11)	122.6(2)
C(15) – C(16) – H(16)	118.7	C(11) – C(16) – H(16)	118.7

4.4 Crystal data for [PC(H)P]Pd(SiPh$_3$)·C$_5$H$_{12}$ (**8**·C$_5$H$_{12}$)

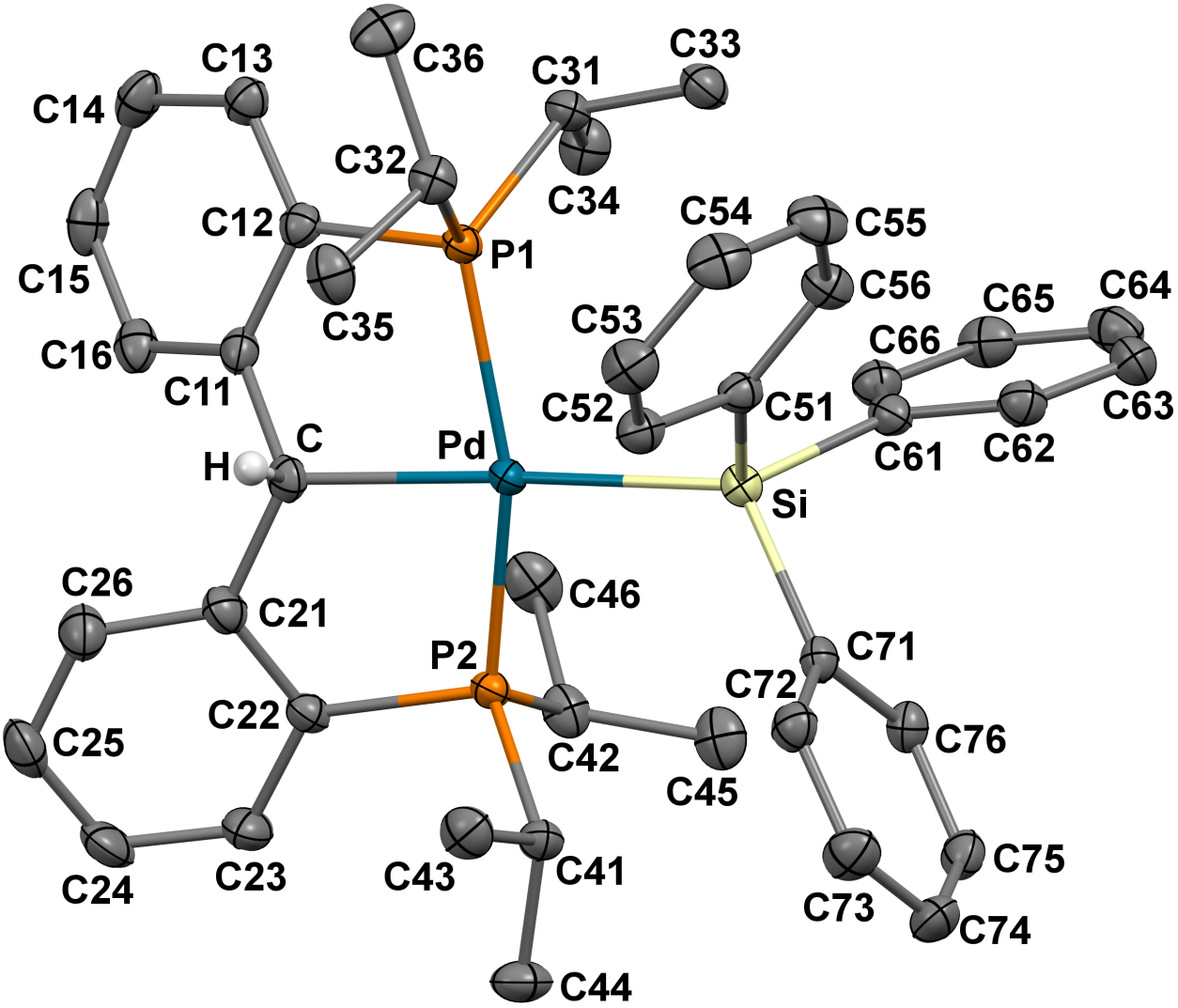

Figure S58. Thermal-ellipsoid representation of [PC(H)P]Pd(SiPh$_3$)·C$_5$H$_{12}$ (**8**·**C$_5$H$_{12}$**) at 50% probability. Most hydrogen atoms and the solvent were omitted for clarity.

Table S16. Crystal data and structure refinement for [PC(H)P]Pd($SiPh_3$)·C_5H_{12} (**8·C_5H_{12}**).

Identification code:	cc243	
Empirical formula:	$C_{48}H_{64}P_2PdSi$	
Formula weight:	837.42	
Temperature:	120(2) K	
Wavelength:	0.71073 Å	
Crystal system:	Monoclinic	
Space group:	$P2_1/c$	
Unit cell dimensions:	a = 11.401(2) Å	α = 90°
	b = 12.592(2) Å	β = 97.666(3)°
	c = 30.423(5) Å	γ = 90°
Volume:	4328.5(13) Å^3	
Z:	4	
Density (calculated):	1.285 g·cm^{-3}	
Absorption coefficient (μ):	0.562 mm^{-1}	
F(000):	1768	
Crystal size:	0.11 × 0.10 × 0.09 mm^3	
θ range for data collection:	1.35 to 28.37°	
Index ranges:	$-15 \le h \le 15$, $-16 \le k \le 16$, $-40 \le l \le 40$	
Reflections collected:	126183	
Independent reflections:	10820 [R_{int} = 0.0937]	
Completeness to θ = 25.00°:	100.0 %	
Absorption correction:	Semi−empirical from equivalents	
Max. and min. transmission:	0.7457 and 0.6854	
Refinement method:	Full-matrix least-squares on F^2	
Data / restraints / parameters:	10820 / 60 / 527	
Goodness-of-fit on F^2:	1.066	
Final R indices [I>2σ(I)]:	R_1 = 0.0412, wR_2 = 0.0852	
R indices (all data):	R_1 = 0.0684, wR_2 = 0.0983	
Largest diff. peak and hole:	1.455 and −0.960 e$^-$·Å^{-3}	

Table S17. Atomic coordinates and equivalent isotropic displacement parameters (Å^2) for [PC(H)P]Pd(SiPh$_3$)·C$_5$H$_{12}$ (**8·C$_5$H$_{12}$**). U(eq) is defined as one third of the trace of the orthogonalized U$_{ij}$ tensor

atom	x	y	z	U(eq)
C	1.0992(2)	0.6051(2)	0.39512(9)	0.020(1)
Pd	0.93031(2)	0.53825(2)	0.36794(1)	0.016(1)
Si	0.75463(7)	0.42896(6)	0.35192(2)	0.017(1)
C(21)	1.0950(3)	0.6955(2)	0.42711(10)	0.023(1)
C(22)	0.9875(2)	0.7440(2)	0.43210(9)	0.018(1)
C(23)	0.9867(3)	0.8354(2)	0.45866(10)	0.027(1)
C(24)	1.0902(3)	0.8736(3)	0.48146(10)	0.032(1)
C(25)	1.1954(3)	0.8201(3)	0.47963(10)	0.031(1)
C(26)	1.1982(3)	0.7332(3)	0.45269(10)	0.029(1)
C(31)	1.0080(2)	0.4418(2)	0.26257(9)	0.020(1)
C(32)	1.1178(2)	0.3217(2)	0.34024(9)	0.021(1)
C(33)	0.9184(3)	0.3548(2)	0.24965(10)	0.025(1)
C(81)	0.2131(10)	0.0087(9)	0.3894(4)	0.055(3)
C(83)	0.3965(11)	0.0651(10)	0.4316(4)	0.085(4)
C(85)	0.6173(10)	0.0540(10)	0.4139(4)	0.077(3)
C(84)	0.5284(9)	0.0470(9)	0.4459(4)	0.078(3)
C(82)	0.3512(7)	−0.0094(7)	0.3944(3)	0.048(2)
C(91)	0.2253(9)	0.0030(8)	0.3774(3)	0.038(2)
C(92)	0.3348(15)	0.0233(14)	0.4117(6)	0.105(5)
C(93)	0.4256(10)	0.0919(10)	0.4032(4)	0.077(4)
C(94)	0.5526(14)	0.0989(13)	0.4138(5)	0.104(5)
C(95)	0.6095(10)	−0.0002(9)	0.4324(4)	0.064(3)
C(34)	0.9649(3)	0.5501(2)	0.24422(10)	0.026(1)
C(35)	1.1716(3)	0.3263(2)	0.38907(10)	0.028(1)
C(36)	1.2105(3)	0.2825(2)	0.31182(11)	0.031(1)
C(41)	0.7763(2)	0.6379(2)	0.45357(9)	0.019(1)
C(42)	0.7718(3)	0.7746(2)	0.37395(10)	0.023(1)
C(43)	0.8521(3)	0.5611(2)	0.48422(10)	0.028(1)
C(44)	0.7339(3)	0.7310(3)	0.47981(10)	0.030(1)
C(45)	0.6423(3)	0.7437(2)	0.36029(10)	0.028(1)
C(46)	0.8332(3)	0.7994(3)	0.33322(10)	0.031(1)
C(51)	0.8078(2)	0.2854(2)	0.35759(9)	0.019(1)
C(52)	0.8829(2)	0.2563(2)	0.39621(10)	0.023(1)
C(53)	0.9278(3)	0.1545(2)	0.40246(10)	0.028(1)
C(54)	0.9000(3)	0.0775(2)	0.37038(11)	0.030(1)
C(55)	0.8274(3)	0.1038(2)	0.33195(11)	0.030(1)
C(56)	0.7821(3)	0.2062(2)	0.32586(9)	0.023(1)
C(61)	0.6518(2)	0.4422(2)	0.29727(9)	0.021(1)
C(62)	0.5595(2)	0.3703(2)	0.28566(9)	0.023(1)

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Table S17. – continued from previous page

atom	x	y	x	U(eq)
C(63)	0.4796(3)	0.3825(3)	0.24755(10)	0.027(1)
C(64)	0.4884(3)	0.4688(3)	0.22012(10)	0.030(1)
C(65)	0.5774(3)	0.5420(3)	0.23074(10)	0.028(1)
C(66)	0.6578(3)	0.5285(2)	0.26888(9)	0.023(1)
C(71)	0.6376(2)	0.4325(2)	0.39180(9)	0.018(1)
C(72)	0.6472(3)	0.3766(2)	0.43181(9)	0.023(1)
C(73)	0.5607(3)	0.3829(3)	0.45988(10)	0.030(1)
C(74)	0.4626(3)	0.4464(3)	0.44901(10)	0.029(1)
C(75)	0.4495(3)	0.5017(2)	0.40955(10)	0.024(1)
C(76)	0.5349(2)	0.4937(2)	0.38133(9)	0.021(1)
P(1)	1.05226(6)	0.45229(6)	0.32326(2)	0.016(1)
P(2)	0.85747(6)	0.67189(6)	0.40682(2)	0.016(1)
C(11)	1.1729(2)	0.6267(2)	0.35802(9)	0.020(1)
C(12)	1.1744(2)	0.5472(2)	0.32543(9)	0.019(1)
C(13)	1.2555(2)	0.5515(2)	0.29512(9)	0.022(1)
C(14)	1.3296(3)	0.6392(3)	0.29408(10)	0.026(1)
C(15)	1.3200(3)	0.7223(2)	0.32294(10)	0.026(1)
C(16)	1.2441(2)	0.7159(2)	0.35478(10)	0.024(1)
H	1.1415	0.5466	0.4130	0.023
H(23)	0.9142	0.8709	0.4608	0.033
H(24)	1.0896	0.9367	0.4985	0.039
H(25)	1.2659	0.8437	0.4971	0.037
H(26)	1.2712	0.6979	0.4513	0.035
H(31)	1.0807	0.4237	0.2490	0.024
H(32)	1.0522	0.2685	0.3376	0.025
H(33A)	0.8438	0.3725	0.2606	0.038
H(33B)	0.9486	0.2874	0.2627	0.038
H(33C)	0.9048	0.3482	0.2173	0.038
H(81A)	0.1949	0.0818	0.3797	0.083
H(81B)	0.1851	−0.0033	0.4181	0.083
H(81C)	0.1737	−0.0410	0.3675	0.083
H(83A)	0.3527	0.0530	0.4572	0.102
H(83B)	0.3831	0.1395	0.4217	0.102
H(85A)	0.6974	0.0503	0.4301	0.116
H(85B)	0.6073	0.1214	0.3977	0.116
H(85C)	0.6053	−0.0051	0.3928	0.116
H(84A)	0.5535	0.0985	0.4700	0.093
H(84B)	0.5366	−0.0245	0.4595	0.093
H(82A)	0.3718	−0.0840	0.4022	0.058
H(82B)	0.3833	0.0093	0.3667	0.058
H(91A)	0.1702	−0.0437	0.3903	0.057
H(91B)	0.2498	−0.0308	0.3511	0.057

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Table S17. – continued from previous page

atom	x	y	x	U(eq)
H(91C)	0.1861	0.0707	0.3690	0.057
H(92A)	0.3055	0.0497	0.4389	0.126
H(92B)	0.3717	−0.0467	0.4192	0.126
H(93A)	0.3987	0.1613	0.4134	0.092
H(93B)	0.4139	0.0964	0.3704	0.092
H(94A)	0.5718	0.1570	0.4356	0.125
H(94B)	0.5866	0.1179	0.3866	0.125
H(95A)	0.6019	−0.0554	0.4095	0.076
H(95B)	0.5708	−0.0239	0.4576	0.076
H(95C)	0.6935	0.0132	0.4424	0.076
H(34A)	1.0294	0.6018	0.2497	0.039
H(34B)	0.8980	0.5735	0.2590	0.039
H(34C)	0.9396	0.5442	0.2122	0.039
H(35A)	1.1948	0.2547	0.3994	0.041
H(35B)	1.1130	0.3547	0.4068	0.041
H(35C)	1.2414	0.3725	0.3923	0.041
H(36A)	1.2378	0.2116	0.3218	0.046
H(36B)	1.2778	0.3317	0.3148	0.046
H(36C)	1.1751	0.2792	0.2807	0.046
H(41)	0.7040	0.5978	0.4408	0.023
H(42)	0.7734	0.8404	0.3924	0.027
H(43A)	0.8069	0.5362	0.5074	0.041
H(43B)	0.9237	0.5976	0.4979	0.041
H(43C)	0.8743	0.5003	0.4670	0.041
H(44A)	0.8019	0.7638	0.4979	0.044
H(44B)	0.6780	0.7049	0.4992	0.044
H(44C)	0.6946	0.7837	0.4592	0.044
H(45A)	0.6048	0.7296	0.3869	0.042
H(45B)	0.6384	0.6798	0.3418	0.042
H(45C)	0.6008	0.8020	0.3435	0.042
H(46A)	0.9160	0.8183	0.3428	0.046
H(46B)	0.7929	0.8590	0.3169	0.046
H(46C)	0.8298	0.7368	0.3140	0.046
H(52)	0.9034	0.3081	0.4186	0.027
H(53)	0.9780	0.1374	0.4290	0.034
H(54)	0.9305	0.0076	0.3747	0.036
H(55)	0.8082	0.0518	0.3095	0.036
H(56)	0.7321	0.2225	0.2992	0.028
H(62)	0.5513	0.3114	0.3045	0.028
H(63)	0.4187	0.3316	0.2402	0.032
H(64)	0.4334	0.4775	0.1940	0.036
H(65)	0.5837	0.6016	0.2121	0.034

Continued on next page

Table S17. – continued from previous page

atom	x	y	x	U(eq)
H(66)	0.7188	0.5797	0.2758	0.028
H(72)	0.7148	0.3332	0.4401	0.028
H(73)	0.5692	0.3433	0.4867	0.036
H(74)	0.4045	0.4520	0.4686	0.035
H(75)	0.3819	0.5453	0.4017	0.029
H(76)	0.5235	0.5309	0.3539	0.025
H(13)	1.2604	0.4943	0.2751	0.026
H(14)	1.3859	0.6418	0.2737	0.032
H(15)	1.3661	0.7846	0.3210	0.031
H(16)	1.2404	0.7733	0.3748	0.029

Table S18. Anisotropic displacement parameters (Å^2) for [PC(H)P]Pd(SiPh$_3$)·C$_5$H$_{12}$ (**8·C$_5$H$_{12}$**). The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11} + ...+ 2hka^*b^*U_{12}]$.

atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C	0.0171(13)	0.0220(14)	0.0181(13)	0.0004(11)	−0.0020(10)	0.0012(11)
Pd	0.0155(1)	0.0162(1)	0.0157(1)	−0.0040(1)	0.0030(1)	−0.0013(1)
Si	0.0178(4)	0.0164(4)	0.0164(4)	−0.0003(3)	0.0011(3)	−0.0005(3)
C(21)	0.0249(15)	0.0204(14)	0.0240(15)	−0.0047(12)	0.0034(12)	−0.0052(12)
C(22)	0.0223(14)	0.0168(13)	0.0162(13)	−0.0024(11)	0.0034(11)	−0.0025(11)
C(23)	0.0273(16)	0.0266(16)	0.0291(16)	−0.0110(13)	0.0083(13)	−0.0026(13)
C(24)	0.0399(19)	0.0321(18)	0.0251(16)	−0.0147(14)	0.0065(14)	−0.0097(14)
C(25)	0.0322(17)	0.0365(19)	0.0221(15)	−0.0045(13)	−0.0053(13)	−0.0103(14)
C(26)	0.0233(15)	0.0280(17)	0.0345(17)	−0.0040(14)	−0.0008(13)	−0.0002(13)
C(31)	0.0210(13)	0.0225(15)	0.0166(13)	−0.0029(11)	0.0031(11)	0.0004(11)
C(32)	0.0221(14)	0.0188(14)	0.0226(14)	0.0019(11)	0.0027(11)	0.0005(11)
C(33)	0.0282(16)	0.0256(16)	0.0212(14)	−0.0053(12)	0.0028(12)	−0.0035(12)
C(81)	0.056(3)	0.055(3)	0.056(3)	0.0004(10)	0.0073(11)	0.0005(10)
C(83)	0.085(4)	0.085(4)	0.084(4)	−0.0007(10)	0.0112(11)	0.0004(10)
C(85)	0.077(3)	0.078(3)	0.077(3)	−0.0013(10)	0.0108(11)	−0.0004(10)
C(84)	0.077(4)	0.079(4)	0.078(4)	−0.0005(10)	0.0096(11)	−0.0004(10)
C(82)	0.049(2)	0.048(2)	0.048(2)	−0.0007(10)	0.0064(10)	−0.0009(10)
C(91)	0.038(3)	0.038(3)	0.038(3)	0.0005(10)	0.0047(10)	0.0007(10)
C(92)	0.105(5)	0.105(5)	0.105(5)	0.0000(10)	0.0139(12)	−0.0002(10)
C(93)	0.077(4)	0.077(4)	0.077(4)	0.0008(10)	0.0099(11)	0.0000(10)
C(94)	0.104(5)	0.104(5)	0.105(5)	0.0000(10)	0.0130(12)	0.0002(10)
C(95)	0.064(3)	0.063(3)	0.064(3)	−0.0010(10)	0.0077(11)	0.0003(10)
C(34)	0.0256(15)	0.0255(16)	0.0272(15)	0.0063(13)	0.0016(12)	−0.0006(12)
C(35)	0.0297(16)	0.0251(16)	0.0262(16)	0.0041(13)	−0.0031(13)	−0.0025(13)
C(36)	0.0330(17)	0.0207(16)	0.0400(19)	0.0029(13)	0.0105(14)	0.0080(13)
C(41)	0.0196(14)	0.0222(14)	0.0166(13)	−0.0003(11)	0.0039(11)	0.0001(11)
C(42)	0.0263(15)	0.0158(14)	0.0249(15)	0.0019(11)	−0.0001(12)	−0.0011(11)
C(43)	0.0285(16)	0.0332(18)	0.0203(14)	0.0055(12)	0.0010(12)	0.0028(13)
C(44)	0.0361(18)	0.0285(17)	0.0269(16)	−0.0059(13)	0.0143(13)	0.0011(14)
C(45)	0.0295(16)	0.0231(16)	0.0303(16)	0.0063(13)	−0.0035(13)	0.0022(13)
C(46)	0.0411(19)	0.0246(16)	0.0252(16)	0.0060(13)	0.0016(14)	−0.0072(14)
C(51)	0.0194(14)	0.0175(14)	0.0208(14)	−0.0007(11)	0.0061(11)	−0.0011(11)
C(52)	0.0230(15)	0.0221(15)	0.0233(15)	−0.0004(12)	0.0054(11)	0.0003(12)
C(53)	0.0295(16)	0.0286(17)	0.0266(16)	0.0064(13)	0.0040(13)	0.0035(13)
C(54)	0.0376(18)	0.0165(14)	0.0373(18)	0.0043(13)	0.0093(15)	0.0037(13)
C(55)	0.0400(18)	0.0183(15)	0.0321(17)	−0.0055(13)	0.0103(14)	−0.0040(13)
C(56)	0.0280(16)	0.0210(15)	0.0206(14)	0.0009(11)	0.0040(12)	−0.0014(12)
C(61)	0.0206(14)	0.0224(15)	0.0179(13)	−0.0024(11)	0.0009(11)	0.0032(11)
C(62)	0.0232(14)	0.0263(16)	0.0210(14)	0.0005(12)	0.0039(11)	0.0002(12)
C(63)	0.0237(15)	0.0337(17)	0.0221(14)	−0.0056(13)	0.0011(12)	−0.0033(13)

Continued on next page

Table S18. – continued from previous page

atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C(64)	0.0313(16)	0.0375(18)	0.0199(14)	−0.0030(14)	−0.0014(12)	0.0093(15)
C(65)	0.0316(16)	0.0280(16)	0.0245(15)	0.0040(13)	0.0048(12)	0.0074(14)
C(66)	0.0232(14)	0.0238(15)	0.0221(14)	0.0006(12)	0.0039(11)	−0.0004(12)
C(71)	0.0169(13)	0.0170(13)	0.0202(13)	−0.0010(10)	0.0001(10)	−0.0023(10)
C(72)	0.0202(14)	0.0270(16)	0.0220(14)	0.0017(12)	0.0010(11)	0.0015(12)
C(73)	0.0289(16)	0.0408(19)	0.0218(15)	0.0069(14)	0.0050(12)	0.0028(14)
C(74)	0.0199(14)	0.041(2)	0.0272(15)	−0.0022(14)	0.0078(12)	−0.0010(13)
C(75)	0.0167(14)	0.0269(15)	0.0283(15)	−0.0015(12)	0.0009(12)	0.0011(11)
C(76)	0.0182(13)	0.0207(14)	0.0228(14)	0.0017(11)	0.0005(11)	−0.0023(11)
P(1)	0.0177(3)	0.0155(3)	0.0165(3)	−0.0024(3)	0.0035(3)	−0.0011(3)
P(2)	0.0177(3)	0.0164(3)	0.0146(3)	−0.0021(3)	0.0026(3)	−0.0005(3)
C(11)	0.0145(13)	0.0189(14)	0.0257(15)	−0.0023(11)	0.0005(11)	−0.0007(11)
C(12)	0.0169(12)	0.0177(13)	0.0210(13)	0.0002(11)	0.0024(10)	0.0010(11)
C(13)	0.0195(13)	0.0256(16)	0.0201(13)	0.0026(12)	0.0019(11)	−0.0001(12)
C(14)	0.0184(14)	0.0361(18)	0.0250(15)	0.0103(13)	0.0034(12)	−0.0012(12)
C(15)	0.0207(14)	0.0225(15)	0.0329(17)	0.0105(13)	−0.0043(12)	−0.0052(12)
C(16)	0.0193(14)	0.0204(15)	0.0313(16)	−0.0012(12)	−0.0021(12)	0.0019(11)

Table S19. Distances [Å] for [PC(H)P]Pd(SiPh$_3$)·C$_5$H$_{12}$ (**8·C$_5$H$_{12}$**).

atom – atom	distance	atom – atom	distance
C – C(21)	1.502(4)	C – C(11)	1.519(4)
C – Pd	2.162(3)	C – H	1.0000
Pd – P(2)	2.2765(7)	Pd – P(1)	2.3360(7)
Pd – Si	2.4253(8)	Si – C(51)	1.907(3)
Si – C(61)	1.910(3)	Si – C(71)	1.920(3)
C(21) – C(22)	1.396(4)	C(21) – C(26)	1.404(4)
C(22) – C(23)	1.407(4)	C(22) – P(2)	1.820(3)
C(23) – C(24)	1.373(4)	C(23) – H(23)	0.9500
C(24) – C(25)	1.383(5)	C(24) – H(24)	0.9500
C(25) – C(26)	1.370(4)	C(25) – H(25)	0.9500
C(26) – H(26)	0.9500	C(31) – C(33)	1.514(4)
C(31) – C(34)	1.529(4)	C(31) – P(1)	1.853(3)
C(31) – H(31)	1.0000	C(32) – C(35)	1.531(4)
C(32) – C(36)	1.534(4)	C(32) – P(1)	1.851(3)
C(32) – H(32)	1.0000	C(33) – H(33A)	0.9800
C(33) – H(33B)	0.9800	C(33) – H(33C)	0.9800
C(81) – C(82)	1.577(14)	C(81) – H(81A)	0.9800
C(81) – H(81B)	0.9800	C(81) – H(81C)	0.9800
C(83) – C(82)	1.510(16)	C(83) – C(84)	1.526(15)
C(83) – H(83A)	0.9900	C(83) – H(83B)	0.9900
C(85) – C(84)	1.500(17)	C(85) – H(85A)	0.9800
C(85) – H(85B)	0.9800	C(85) – H(85C)	0.9800
C(84) – H(84A)	0.9900	C(84) – H(84B)	0.9900
C(82) – H(82A)	0.9900	C(82) – H(82B)	0.9900
C(91) – C(92)	1.538(19)	C(91) – H(91A)	0.9800
C(91) – H(91B)	0.9800	C(91) – H(91C)	0.9800
C(92) – C(93)	1.399(19)	C(92) – H(92A)	0.9900
C(92) – H(92B)	0.9900	C(93) – C(94)	1.443(17)
C(93) – H(93A)	0.9900	C(93) – H(93B)	0.9900
C(94) – C(95)	1.48(2)	C(94) – H(94A)	0.9900
C(94) – H(94B)	0.9900	C(95) – H(95A)	0.9800
C(95) – H(95B)	0.9800	C(95) – H(95C)	0.9800
C(34) – H(34A)	0.9800	C(34) – H(34B)	0.9800
C(34) – H(34C)	0.9800	C(35) – H(35A)	0.9800
C(35) – H(35B)	0.9800	C(35) – H(35C)	0.9800
C(36) – H(36A)	0.9800	C(36) – H(36B)	0.9800
C(36) – H(36C)	0.9800	C(41) – C(43)	1.528(4)
C(41) – C(44)	1.532(4)	C(41) – P(2)	1.848(3)
C(41) – H(41)	1.0000	C(42) – C(45)	1.529(4)
C(42) – C(46)	1.534(4)	C(42) – P(2)	1.834(3)
C(42) – H(42)	1.0000	C(43) – H(43A)	0.9800

Continued on next page

Table S19. – continued from previous page

atom – atom	distance	atom – atom	distance
C(43) – H(43B)	0.9800	C(43) – H(43C)	0.9800
C(44) – H(44A)	0.9800	C(44) – H(44B)	0.9800
C(44) – H(44C)	0.9800	C(45) – H(45A)	0.9800
C(45) – H(45B)	0.9800	C(45) – H(45C)	0.9800
C(46) – H(46A)	0.9800	C(46) – H(46B)	0.9800
C(46) – H(46C)	0.9800	C(51) – C(56)	1.392(4)
C(51) – C(52)	1.407(4)	C(52) – C(53)	1.384(4)
C(52) – H(52)	0.9500	C(53) – C(54)	1.382(4)
C(53) – H(53)	0.9500	C(54) – C(55)	1.380(5)
C(54) – H(54)	0.9500	C(55) – C(56)	1.392(4)
C(55) – H(55)	0.9500	C(56) – H(56)	0.9500
C(61) – C(66)	1.396(4)	C(61) – C(62)	1.397(4)
C(62) – C(63)	1.384(4)	C(62) – H(62)	0.9500
C(63) – C(64)	1.381(4)	C(63) – H(63)	0.9500
C(64) – C(65)	1.377(5)	C(64) – H(64)	0.9500
C(65) – C(66)	1.390(4)	C(65) – H(65)	0.9500
C(66) – H(66)	0.9500	C(71) – C(72)	1.397(4)
C(71) – C(76)	1.403(4)	C(72) – C(73)	1.391(4)
C(72) – H(72)	0.9500	C(73) – C(74)	1.378(4)
C(73) – H(73)	0.9500	C(74) – C(75)	1.379(4)
C(74) – H(74)	0.9500	C(75) – C(76)	1.385(4)
C(75) – H(75)	0.9500	C(76) – H(76)	0.9500
P(1) – C(12)	1.829(3)	C(11) – C(16)	1.397(4)
C(11) – C(12)	1.411(4)	C(12) – C(13)	1.392(4)
C(13) – C(14)	1.394(4)	C(13) – H(13)	0.9500
C(14) – C(15)	1.379(4)	C(14) – H(14)	0.9500
C(15) – C(16)	1.385(4)	C(15) – H(15)	0.9500
C(16) – H(16)	0.9500		

Table S20. Angles [°] for [PC(H)P]Pd($SiPh_3$)·C_5H_{12} (**8·C_5H_{12}**).

atom – atom – atom	angle	atom – atom – atom	angle
C(21) – C – C(11)	114.5(2)	C(21) – C – Pd	116.05(19)
C(11) – C – Pd	109.77(18)	C(21) – C – H	105.1
C(11) – C – H	105.1	Pd – C – H	105.1
C – Pd – P(2)	83.19(8)	C – Pd – P(1)	80.46(7)
P(2) – Pd – P(1)	158.68(3)	C – Pd – Si	165.27(8)
P(2) – Pd – Si	100.08(3)	P(1) – Pd – Si	99.20(3)
C(51) – Si – C(61)	108.17(12)	C(51) – Si – C(71)	101.76(12)
C(61) – Si – C(71)	98.65(12)	C(51) – Si – Pd	106.01(9)
C(61) – Si – Pd	121.34(9)	C(71) – Si – Pd	119.01(9)
C(22) – C(21) – C(26)	118.3(3)	C(22) – C(21) – C	120.4(2)
C(26) – C(21) – C	121.3(3)	C(21) – C(22) – C(23)	119.6(3)
C(21) – C(22) – P(2)	114.4(2)	C(23) – C(22) – P(2)	125.7(2)
C(24) – C(23) – C(22)	120.4(3)	C(24) – C(23) – H(23)	119.8
C(22) – C(23) – H(23)	119.8	C(23) – C(24) – C(25)	120.0(3)
C(23) – C(24) – H(24)	120.0	C(25) – C(24) – H(24)	120.0
C(26) – C(25) – C(24)	120.1(3)	C(26) – C(25) – H(25)	119.9
C(24) – C(25) – H(25)	119.9	C(25) – C(26) – C(21)	121.2(3)
C(25) – C(26) – H(26)	119.4	C(21) – C(26) – H(26)	119.4
C(33) – C(31) – C(34)	112.2(2)	C(33) – C(31) – P(1)	113.29(19)
C(34) – C(31) – P(1)	109.37(19)	C(33) – C(31) – H(31)	107.2
C(34) – C(31) – H(31)	107.2	P(1) – C(31) – H(31)	107.2
C(35) – C(32) – C(36)	110.0(2)	C(35) – C(32) – P(1)	109.4(2)
C(36) – C(32) – P(1)	114.3(2)	C(35) – C(32) – H(32)	107.6
C(36) – C(32) – H(32)	107.6	P(1) – C(32) – H(32)	107.6
C(31) – C(33) – H(33A)	109.5	C(31) – C(33) – H(33B)	109.5
H(33A) – C(33) – H(33B)	109.5	C(31) – C(33) – H(33C)	109.5
H(33A) – C(33) – H(33C)	109.5	H(33B) – C(33) – H(33C)	109.5
C(82) – C(81) – H(81A)	109.5	C(82) – C(81) – H(81B)	109.5
H(81A) – C(81) – H(81B)	109.5	C(82) – C(81) – H(81C)	109.5
H(81A) – C(81) – H(81C)	109.5	H(81B) – C(81) – H(81C)	109.5
C(82) – C(83) – C(84)	110.3(9)	C(82) – C(83) – H(83A)	109.6
C(84) – C(83) – H(83A)	109.6	C(82) – C(83) – H(83B)	109.6
C(84) – C(83) – H(83B)	109.6	H(83A) – C(83) – H(83B)	108.1
C(84) – C(85) – H(85A)	109.5	C(84) – C(85) – H(85B)	109.5
H(85A) – C(85) – H(85B)	109.5	C(84) – C(85) – H(85C)	109.5
H(85A) – C(85) – H(85C)	109.5	H(85B) – C(85) – H(85C)	109.5
C(85) – C(84) – C(83)	122.1(10)	C(85) – C(84) – H(84A)	106.8
C(83) – C(84) – H(84A)	106.8	C(85) – C(84) – H(84B)	106.8
C(83) – C(84) – H(84B)	106.8	H(84A) – C(84) – H(84B)	106.7
C(83) – C(82) – C(81)	102.6(9)	C(83) – C(82) – H(82A)	111.2
C(81) – C(82) – H(82A)	111.2	C(83) – C(82) – H(82B)	111.2

Continued on next page

Table S20. – continued from previous page

atom – atom – atom	angle	atom – atom – atom	angle
C(81) – C(82) – H(82B)	111.2	H(82A) – C(82) – H(82B)	109.2
C(93) – C(92) – C(91)	122.0(14)	C(93) – C(92) – H(92A)	106.8
C(91) – C(92) – H(92A)	106.8	C(93) – C(92) – H(92B)	106.8
C(91) – C(92) – H(92B)	106.8	H(92A) – C(92) – H(92B)	106.7
C(92) – C(93) – C(94)	137.9(13)	C(92) – C(93) – H(93A)	102.6
C(94) – C(93) – H(93A)	102.6	C(92) – C(93) – H(93B)	102.6
C(94) – C(93) – H(93B)	102.6	H(93A) – C(93) – H(93B)	105.0
C(93) – C(94) – C(95)	114.1(12)	C(93) – C(94) – H(94A)	108.7
C(95) – C(94) – H(94A)	108.7	C(93) – C(94) – H(94B)	108.7
C(95) – C(94) – H(94B)	108.7	H(94A) – C(94) – H(94B)	107.6
C(31) – C(34) – H(34A)	109.5	C(31) – C(34) – H(34B)	109.5
H(34A) – C(34) – H(34B)	109.5	C(31) – C(34) – H(34C)	109.5
H(34A) – C(34) – H(34C)	109.5	H(34B) – C(34) – H(34C)	109.5
C(32) – C(35) – H(35A)	109.5	C(32) – C(35) – H(35B)	109.5
H(35A) – C(35) – H(35B)	109.5	C(32) – C(35) – H(35C)	109.5
H(35A) – C(35) – H(35C)	109.5	H(35B) – C(35) – H(35C)	109.5
C(32) – C(36) – H(36A)	109.5	C(32) – C(36) – H(36B)	109.5
H(36A) – C(36) – H(36B)	109.5	C(32) – C(36) – H(36C)	109.5
H(36A) – C(36) – H(36C)	109.5	H(36B) – C(36) – H(36C)	109.5
C(43) – C(41) – C(44)	111.0(2)	C(43) – C(41) – P(2)	108.40(19)
C(44) – C(41) – P(2)	116.7(2)	C(43) – C(41) – H(41)	106.7
C(44) – C(41) – H(41)	106.7	P(2) – C(41) – H(41)	106.7
C(45) – C(42) – C(46)	111.1(3)	C(45) – C(42) – P(2)	113.2(2)
C(46) – C(42) – P(2)	108.5(2)	C(45) – C(42) – H(42)	108.0
C(46) – C(42) – H(42)	108.0	P(2) – C(42) – H(42)	108.0
C(41) – C(43) – H(43A)	109.5	C(41) – C(43) – H(43B)	109.5
H(43A) – C(43) – H(43B)	109.5	C(41) – C(43) – H(43C)	109.5
H(43A) – C(43) – H(43C)	109.5	H(43B) – C(43) – H(43C)	109.5
C(41) – C(44) – H(44A)	109.5	C(41) – C(44) – H(44B)	109.5
H(44A) – C(44) – H(44B)	109.5	C(41) – C(44) – H(44C)	109.5
H(44A) – C(44) – H(44C)	109.5	H(44B) – C(44) – H(44C)	109.5
C(42) – C(45) – H(45A)	109.5	C(42) – C(45) – H(45B)	109.5
H(45A) – C(45) – H(45B)	109.5	C(42) – C(45) – H(45C)	109.5
H(45A) – C(45) – H(45C)	109.5	H(45B) – C(45) – H(45C)	109.5
C(42) – C(46) – H(46A)	109.5	C(42) – C(46) – H(46B)	109.5
H(46A) – C(46) – H(46B)	109.5	C(42) – C(46) – H(46C)	109.5
H(46A) – C(46) – H(46C)	109.5	H(46B) – C(46) – H(46C)	109.5
C(56) – C(51) – C(52)	116.1(3)	C(56) – C(51) – Si	125.6(2)
C(52) – C(51) – Si	118.2(2)	C(53) – C(52) – C(51)	121.9(3)
C(53) – C(52) – H(52)	119.0	C(51) – C(52) – H(52)	119.0
C(54) – C(53) – C(52)	120.5(3)	C(54) – C(53) – H(53)	119.8
C(52) – C(53) – H(53)	119.8	C(55) – C(54) – C(53)	119.0(3)

Continued on next page

Table S20. – continued from previous page

atom – atom – atom	angle	atom – atom – atom	angle
C(55) – C(54) – H(54)	120.5	C(53) – C(54) – H(54)	120.5
C(54) – C(55) – C(56)	120.3(3)	C(54) – C(55) – H(55)	119.8
C(56) – C(55) – H(55)	119.8	C(55) – C(56) – C(51)	122.1(3)
C(55) – C(56) – H(56)	118.9	C(51) – C(56) – H(56)	118.9
C(66) – C(61) – C(62)	116.5(3)	C(66) – C(61) – Si	122.1(2)
C(62) – C(61) – Si	121.2(2)	C(63) – C(62) – C(61)	122.0(3)
C(63) – C(62) – H(62)	119.0	C(61) – C(62) – H(62)	119.0
C(64) – C(63) – C(62)	120.0(3)	C(64) – C(63) – H(63)	120.0
C(62) – C(63) – H(63)	120.0	C(65) – C(64) – C(63)	119.7(3)
C(65) – C(64) – H(64)	120.1	C(63) – C(64) – H(64)	120.1
C(64) – C(65) – C(66)	119.8(3)	C(64) – C(65) – H(65)	120.1
C(66) – C(65) – H(65)	120.1	C(65) – C(66) – C(61)	122.0(3)
C(65) – C(66) – H(66)	119.0	C(61) – C(66) – H(66)	119.0
C(72) – C(71) – C(76)	116.1(3)	C(72) – C(71) – Si	123.9(2)
C(76) – C(71) – Si	119.9(2)	C(73) – C(72) – C(71)	121.8(3)
C(73) – C(72) – H(72)	119.1	C(71) – C(72) – H(72)	119.1
C(74) – C(73) – C(72)	120.3(3)	C(74) – C(73) – H(73)	119.8
C(72) – C(73) – H(73)	119.8	C(73) – C(74) – C(75)	119.5(3)
C(73) – C(74) – H(74)	120.2	C(75) – C(74) – H(74)	120.2
C(74) – C(75) – C(76)	119.9(3)	C(74) – C(75) – H(75)	120.0
C(76) – C(75) – H(75)	120.0	C(75) – C(76) – C(71)	122.3(3)
C(75) – C(76) – H(76)	118.9	C(71) – C(76) – H(76)	118.9
C(12) – P(1) – C(32)	107.04(13)	C(12) – P(1) – C(31)	100.82(12)
C(32) – P(1) – C(31)	105.13(13)	C(12) – P(1) – Pd	100.69(9)
C(32) – P(1) – Pd	119.91(9)	C(31) – P(1) – Pd	120.58(9)
C(22) – P(2) – C(42)	102.90(13)	C(22) – P(2) – C(41)	104.70(12)
C(42) – P(2) – C(41)	107.33(13)	C(22) – P(2) – Pd	104.80(9)
C(42) – P(2) – Pd	116.26(10)	C(41) – P(2) – Pd	118.93(9)
C(16) – C(11) – C(12)	117.3(3)	C(16) – C(11) – C	125.5(3)
C(12) – C(11) – C	117.0(2)	C(13) – C(12) – C(11)	120.6(3)
C(13) – C(12) – P(1)	124.8(2)	C(11) – C(12) – P(1)	114.12(19)
C(12) – C(13) – C(14)	120.3(3)	C(12) – C(13) – H(13)	119.9
C(14) – C(13) – H(13)	119.9	C(15) – C(14) – C(13)	119.2(3)
C(15) – C(14) – H(14)	120.4	C(13) – C(14) – H(14)	120.4
C(14) – C(15) – C(16)	120.7(3)	C(14) – C(15) – H(15)	119.6
C(16) – C(15) – H(15)	119.6	C(15) – C(16) – C(11)	121.3(3)
C(15) – C(16) – H(16)	119.3	C(11) – C(16) – H(16)	119.3

4.5 Crystal data for [PC(Bpin)P]PdH (9)

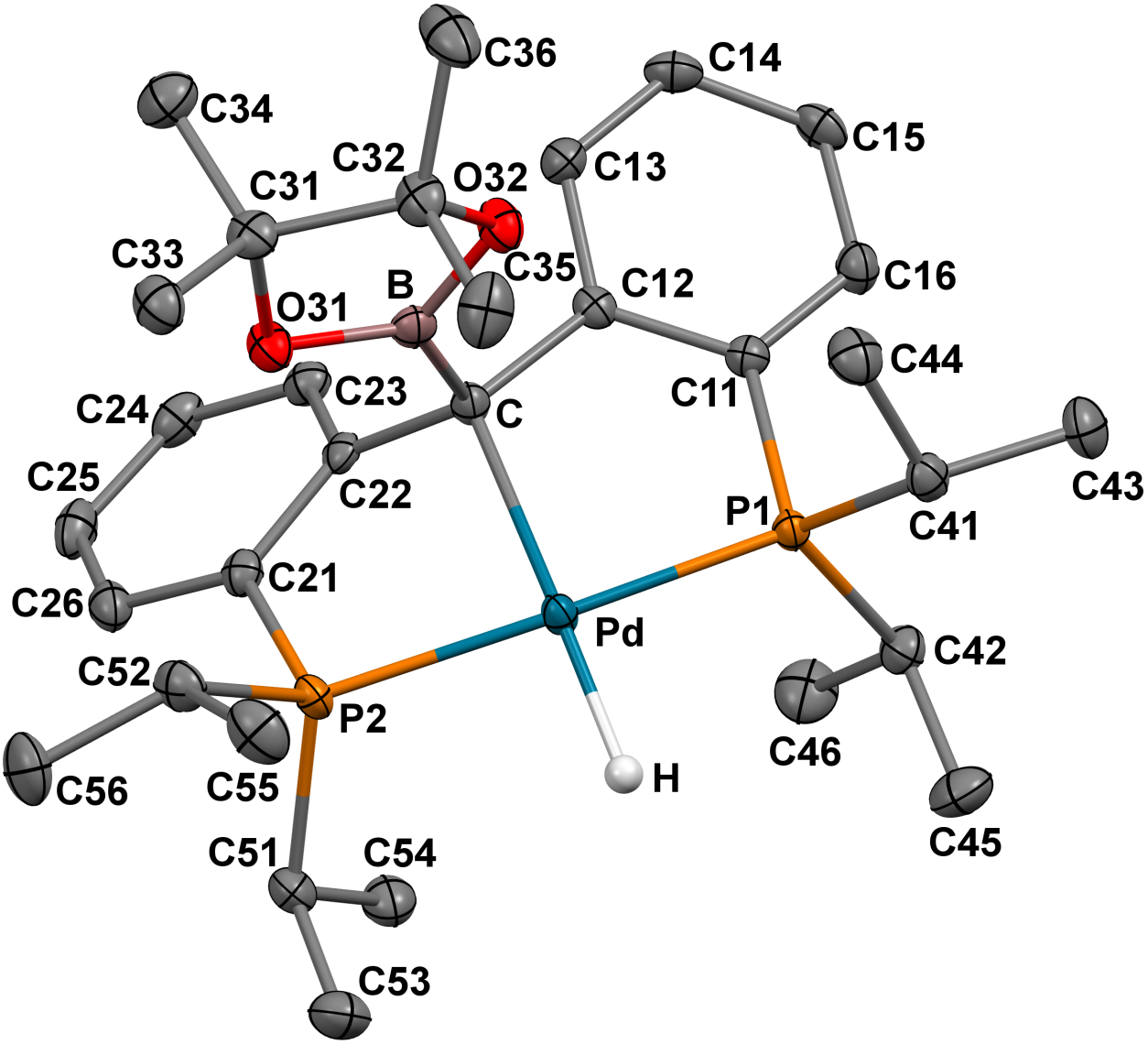

Figure S59. Thermal-ellipsoid representation of [PC(Bpin)P]PdH (**9**) at 50% probability. Most hydrogen atoms were omitted for clarity.

Table S21. Crystal data and structure refinement for [PC(Bpin)P]PdH (**9**).

Identification code:	cc181a	
Empirical formula:	$C_{31}H_{49}BO_2P_2Pd$	
Formula weight:	632.85	
Temperature:	120(2) K	
Wavelength:	0.71073 Å	
Crystal system:	Monoclinic	
Space group:	$P2_1/c$	
Unit cell dimensions:	a = 17.3966(10) Å	$\alpha = 90°$
	b = 10.0819(6) Å	$\beta = 115.8960(18)°$
	c = 19.8141(11) Å	$\gamma = 90°$
Volume:	3126.3(3) Å^3	
Z:	4	
Density (calculated):	1.345 g·cm^{-3}	
Absorption coefficient (μ):	0.721 mm^{-1}	
F(000):	1328	
Crystal size:	0.03 × 0.02 × 0.02 mm^3	
θ range for data collection:	1.30 to 25.00°	
Index ranges:	$-20 \le h \le 20$, $-11 \le k \le 11$, $-23 \le l \le 23$	
Reflections collected:	71734	
Independent reflections:	5509 [R_{int} = 0.0279]	
Completeness to θ = 25.00°:	100.0 %	
Absorption correction:	Semi−empirical from equivalents	
Max. and min. transmission:	0.7458 and 0.6655	
Refinement method:	Full-matrix least-squares on F^2	
Data / restraints / parameters:	5509 / 0 / 350	
Goodness-of-fit on F^2:	1.065	
Final R indices [I>2σ(I)]:	R_1 = 0.0203, wR_2 = 0.0513	
R indices (all data):	R_1 = 0.0237, wR_2 = 0.0528	
Largest diff. peak and hole:	0.781 and −0.667 e$^-$·Å^{-3}	

Table S22. Atomic coordinates and equivalent isotropic displacement parameters (Å^2) for [PC(Bpin)P]PdH (**9**). U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor

atom	x	y	z	U(eq)
Pd	0.67571(1)	0.50861(1)	0.27417(1)	0.013(1)
B	0.82663(12)	0.65902(19)	0.35972(11)	0.016(1)
C	0.80525(10)	0.51143(16)	0.36439(9)	0.014(1)
P(1)	0.63274(3)	0.46931(4)	0.36433(2)	0.013(1)
P(2)	0.73929(3)	0.48864(4)	0.19578(2)	0.015(1)
C(21)	0.84049(10)	0.41650(16)	0.26252(9)	0.015(1)
C(16)	0.73781(11)	0.41854(17)	0.51905(10)	0.019(1)
C(15)	0.81471(11)	0.42228(17)	0.58264(9)	0.020(1)
C(14)	0.88772(11)	0.46203(17)	0.57652(10)	0.020(1)
C(13)	0.88350(11)	0.49106(16)	0.50663(10)	0.018(1)
C(12)	0.80730(11)	0.48171(15)	0.44053(9)	0.014(1)
C(11)	0.73283(10)	0.45121(16)	0.44856(9)	0.014(1)
C(22)	0.85567(10)	0.41832(16)	0.33891(9)	0.014(1)
C(23)	0.92059(10)	0.33429(16)	0.38734(10)	0.017(1)
C(24)	0.97223(11)	0.26208(17)	0.36381(10)	0.021(1)
C(25)	0.96078(11)	0.26947(17)	0.29016(10)	0.022(1)
C(26)	0.89418(11)	0.34549(17)	0.23982(10)	0.019(1)
O(31)	0.86186(8)	0.70894(11)	0.31424(7)	0.019(1)
C(31)	0.88600(11)	0.84627(17)	0.33615(10)	0.020(1)
O(32)	0.81480(8)	0.75777(12)	0.40274(7)	0.020(1)
C(33)	0.87166(12)	0.92697(18)	0.26680(10)	0.024(1)
C(34)	0.98066(12)	0.8445(2)	0.39001(11)	0.027(1)
C(35)	0.74001(12)	0.9329(2)	0.31776(12)	0.030(1)
C(36)	0.86618(15)	0.98158(19)	0.43829(12)	0.032(1)
C(41)	0.57146(11)	0.60208(17)	0.38368(9)	0.017(1)
C(42)	0.57194(11)	0.31656(17)	0.35790(10)	0.019(1)
C(43)	0.53990(12)	0.57012(19)	0.44247(11)	0.025(1)
C(44)	0.62376(12)	0.72993(18)	0.40306(11)	0.024(1)
C(45)	0.48215(12)	0.3272(2)	0.29398(11)	0.029(1)
C(46)	0.61953(13)	0.19601(19)	0.34826(12)	0.030(1)
C(51)	0.69203(11)	0.35461(18)	0.12545(9)	0.020(1)
C(52)	0.76273(12)	0.62836(18)	0.14690(10)	0.021(1)
C(53)	0.60712(12)	0.3972(2)	0.06107(10)	0.028(1)
C(54)	0.67952(12)	0.23130(18)	0.16460(10)	0.024(1)
C(55)	0.68801(13)	0.7259(2)	0.11497(11)	0.029(1)
C(56)	0.79422(14)	0.5892(2)	0.08850(11)	0.031(1)
C(32)	0.82732(12)	0.88456(17)	0.37363(10)	0.021(1)
H(16)	0.6874	0.3934	0.5232	0.023
H(15)	0.8176	0.3979	0.6300	0.024

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Table S22. – continued from previous page

atom	x	y	x	U(eq)
H(14)	0.9405	0.4693	0.6201	0.024
H(13)	0.9341	0.5183	0.5034	0.021
H(23)	0.9295	0.3266	0.4380	0.020
H(24)	1.0159	0.2070	0.3985	0.025
H(25)	0.9979	0.2233	0.2746	0.026
H(26)	0.8848	0.3495	0.1889	0.023
H(33A)	0.9110	0.8966	0.2466	0.036
H(33B)	0.8822	1.0210	0.2803	0.036
H(33C)	0.8126	0.9154	0.2288	0.036
H	0.5830(18)	0.489(2)	0.2091(16)	0.062(8)
H(34A)	1.0125	0.7999	0.3662	0.041
H(34B)	0.9891	0.7968	0.4358	0.041
H(34C)	1.0014	0.9358	0.4027	0.041
H(35A)	0.7459	1.0189	0.2974	0.045
H(35B)	0.7028	0.9426	0.3430	0.045
H(35C)	0.7149	0.8685	0.2768	0.045
H(36A)	0.8810	1.0640	0.4205	0.048
H(36B)	0.9178	0.9427	0.4779	0.048
H(36C)	0.8248	1.0007	0.4583	0.048
H(41)	0.5196	0.6189	0.3356	0.021
H(42)	0.5667	0.3059	0.4059	0.023
H(43A)	0.5056	0.6442	0.4463	0.037
H(43B)	0.5890	0.5560	0.4911	0.037
H(43C)	0.5048	0.4896	0.4278	0.037
H(44A)	0.6440	0.7474	0.3649	0.036
H(44B)	0.6728	0.7206	0.4522	0.036
H(44C)	0.5880	0.8039	0.4045	0.036
H(45A)	0.4859	0.3447	0.2469	0.044
H(45B)	0.4515	0.4000	0.3043	0.044
H(45C)	0.4514	0.2439	0.2897	0.044
H(46A)	0.5881	0.1150	0.3478	0.045
H(46B)	0.6769	0.1922	0.3900	0.045
H(46C)	0.6241	0.2035	0.3008	0.045
H(51)	0.7330	0.3323	0.1041	0.024
H(52)	0.8109	0.6783	0.1867	0.025
H(53A)	0.6170	0.4719	0.0342	0.042
H(53B)	0.5673	0.4241	0.0814	0.042
H(53C)	0.5828	0.3227	0.0264	0.042
H(54A)	0.6596	0.1576	0.1288	0.036
H(54B)	0.6370	0.2500	0.1833	0.036
H(54C)	0.7339	0.2073	0.2067	0.036
H(55A)	0.7060	0.8063	0.0979	0.044

Continued on next page

Table S22. – continued from previous page

atom	x	y	x	U(eq)
H(55B)	0.6700	0.7491	0.1540	0.044
H(55C)	0.6401	0.6848	0.0725	0.044
H(56A)	0.7487	0.5418	0.0471	0.046
H(56B)	0.8444	0.5317	0.1119	0.046
H(56C)	0.8096	0.6693	0.0691	0.046

Table S23. Anisotropic displacement parameters (Å^2) for [PC(Bpin)P]PdH (**9**). The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11} + ...+ 2hka^*b^*U_{12}]$.

atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Pd	0.0133(1)	0.0165(1)	0.0107(1)	0.0014(1)	0.0061(1)	0.0022(1)
B	0.0128(9)	0.0201(10)	0.0137(9)	0.0014(8)	0.0037(8)	0.0007(8)
C	0.0131(8)	0.0167(8)	0.0131(8)	0.0015(6)	0.0065(7)	0.0012(6)
P(1)	0.0123(2)	0.0167(2)	0.0120(2)	0.0008(2)	0.0062(2)	0.0004(2)
P(2)	0.0173(2)	0.0167(2)	0.0116(2)	0.0005(2)	0.0080(2)	0.0009(2)
C(21)	0.0161(8)	0.0129(8)	0.0183(8)	0.0009(7)	0.0090(7)	−0.0015(6)
C(16)	0.0195(9)	0.0215(9)	0.0187(9)	0.0027(7)	0.0111(7)	0.0000(7)
C(15)	0.0263(10)	0.0203(9)	0.0124(8)	0.0030(7)	0.0085(7)	0.0014(7)
C(14)	0.0206(9)	0.0195(9)	0.0143(8)	−0.0002(7)	0.0027(7)	0.0001(7)
C(13)	0.0163(9)	0.0191(9)	0.0182(9)	−0.0011(7)	0.0075(7)	−0.0026(7)
C(12)	0.0169(8)	0.0107(8)	0.0142(8)	0.0004(6)	0.0075(7)	0.0008(6)
C(11)	0.0150(8)	0.0134(8)	0.0137(8)	0.0001(6)	0.0058(7)	−0.0001(6)
C(22)	0.0120(8)	0.0127(8)	0.0176(8)	−0.0008(6)	0.0074(7)	−0.0039(6)
C(23)	0.0164(8)	0.0160(8)	0.0175(9)	0.0012(7)	0.0067(7)	−0.0023(7)
C(24)	0.0154(9)	0.0160(8)	0.0278(10)	0.0033(7)	0.0075(8)	0.0015(7)
C(25)	0.0196(9)	0.0170(9)	0.0342(11)	−0.0028(8)	0.0170(8)	0.0001(7)
C(26)	0.0220(9)	0.0189(9)	0.0218(9)	−0.0022(7)	0.0139(8)	−0.0031(7)
O(31)	0.0248(6)	0.0152(6)	0.0200(6)	−0.0004(5)	0.0130(5)	−0.0024(5)
C(31)	0.0242(9)	0.0139(8)	0.0212(9)	0.0001(7)	0.0106(8)	−0.0028(7)
O(32)	0.0259(7)	0.0158(6)	0.0211(6)	0.0011(5)	0.0140(5)	−0.0008(5)
C(33)	0.0308(10)	0.0209(9)	0.0245(10)	0.0021(8)	0.0156(8)	−0.0024(8)
C(34)	0.0242(10)	0.0262(10)	0.0303(11)	0.0012(8)	0.0104(9)	−0.0042(8)
C(35)	0.0297(11)	0.0222(10)	0.0436(12)	0.0091(9)	0.0213(10)	0.0060(8)
C(36)	0.0509(13)	0.0228(10)	0.0325(11)	−0.0068(8)	0.0273(11)	−0.0098(9)
C(41)	0.0154(8)	0.0202(9)	0.0167(8)	0.0009(7)	0.0074(7)	0.0036(7)
C(42)	0.0204(9)	0.0187(9)	0.0203(9)	−0.0003(7)	0.0104(8)	−0.0032(7)
C(43)	0.0256(10)	0.0284(10)	0.0271(10)	−0.0005(8)	0.0174(8)	0.0038(8)
C(44)	0.0286(10)	0.0197(9)	0.0269(10)	−0.0011(8)	0.0144(8)	0.0010(8)
C(45)	0.0219(10)	0.0294(10)	0.0308(11)	−0.0033(8)	0.0065(9)	−0.0085(8)
C(46)	0.0338(11)	0.0190(10)	0.0394(12)	−0.0020(8)	0.0183(10)	−0.0002(8)
C(51)	0.0215(9)	0.0228(9)	0.0166(9)	−0.0040(7)	0.0098(7)	−0.0015(7)
C(52)	0.0267(10)	0.0208(9)	0.0165(9)	0.0033(7)	0.0099(8)	−0.0025(7)
C(53)	0.0282(10)	0.0321(11)	0.0200(9)	−0.0051(8)	0.0069(8)	−0.0043(8)
C(54)	0.0270(10)	0.0215(9)	0.0252(10)	−0.0046(8)	0.0133(8)	−0.0049(8)
C(55)	0.0402(12)	0.0250(10)	0.0247(10)	0.0067(8)	0.0158(9)	0.0049(9)
C(56)	0.0384(12)	0.0343(11)	0.0300(11)	0.0079(9)	0.0242(10)	0.0011(9)
C(32)	0.0271(10)	0.0143(8)	0.0237(9)	0.0014(7)	0.0137(8)	−0.0025(7)

Table S24. Distances [Å] for [PC(Bpin)P]PdH (**9**).

atom – atom	distance	atom – atom	distance
Pd – C	2.1809(17)	Pd – P(1)	2.2524(4)
Pd – P(2)	2.2754(4)	Pd – H	1.58(3)
B – O(32)	1.383(2)	B – O(31)	1.387(2)
B – C	1.546(2)	C – C(22)	1.514(2)
C – C(12)	1.523(2)	P(1) – C(11)	1.8200(17)
P(1) – C(42)	1.8408(17)	P(1) – C(41)	1.8526(17)
P(2) – C(21)	1.8285(17)	P(2) – C(52)	1.8529(18)
P(2) – C(51)	1.8555(18)	C(21) – C(26)	1.398(2)
C(21) – C(22)	1.418(2)	C(16) – C(15)	1.381(2)
C(16) – C(11)	1.400(2)	C(16) – H(16)	0.9500
C(15) – C(14)	1.387(3)	C(15) – H(15)	0.9500
C(14) – C(13)	1.386(2)	C(14) – H(14)	0.9500
C(13) – C(12)	1.402(2)	C(13) – H(13)	0.9500
C(12) – C(11)	1.407(2)	C(22) – C(23)	1.403(2)
C(23) – C(24)	1.386(2)	C(23) – H(23)	0.9500
C(24) – C(25)	1.386(3)	C(24) – H(24)	0.9500
C(25) – C(26)	1.384(3)	C(25) – H(25)	0.9500
C(26) – H(26)	0.9500	O(31) – C(31)	1.457(2)
C(31) – C(33)	1.521(2)	C(31) – C(34)	1.522(3)
C(31) – C(32)	1.551(2)	O(32) – C(32)	1.457(2)
C(33) – H(33A)	0.9800	C(33) – H(33B)	0.9800
C(33) – H(33C)	0.9800	C(34) – H(34A)	0.9800
C(34) – H(34B)	0.9800	C(34) – H(34C)	0.9800
C(35) – C(32)	1.517(3)	C(35) – H(35A)	0.9800
C(35) – H(35B)	0.9800	C(35) – H(35C)	0.9800
C(36) – C(32)	1.516(3)	C(36) – H(36A)	0.9800
C(36) – H(36B)	0.9800	C(36) – H(36C)	0.9800
C(41) – C(43)	1.523(2)	C(41) – C(44)	1.527(2)
C(41) – H(41)	1.0000	C(42) – C(45)	1.526(2)
C(42) – C(46)	1.529(3)	C(42) – H(42)	1.0000
C(43) – H(43A)	0.9800	C(43) – H(43B)	0.9800
C(43) – H(43C)	0.9800	C(44) – H(44A)	0.9800
C(44) – H(44B)	0.9800	C(44) – H(44C)	0.9800
C(45) – H(45A)	0.9800	C(45) – H(45B)	0.9800
C(45) – H(45C)	0.9800	C(46) – H(46A)	0.9800
C(46) – H(46B)	0.9800	C(46) – H(46C)	0.9800
C(51) – C(54)	1.530(2)	C(51) – C(53)	1.532(3)
C(51) – H(51)	1.0000	C(52) – C(55)	1.529(3)
C(52) – C(56)	1.532(3)	C(52) – H(52)	1.0000
C(53) – H(53A)	0.9800	C(53) – H(53B)	0.9800
C(53) – H(53C)	0.9800	C(54) – H(54A)	0.9800

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Table S24. – continued from previous page

atom – atom	distance	atom – atom	distance
C(54) – H(54B)	0.9800	C(54) – H(54C)	0.9800
C(55) – H(55A)	0.9800	C(55) – H(55B)	0.9800
C(55) – H(55C)	0.9800	C(56) – H(56A)	0.9800
C(56) – H(56B)	0.9800	C(56) – H(56C)	0.9800

Table S25. Angles [°] for [PC(Bpin)P]PdH (**9**).

atom – atom – atom	angle	atom – atom – atom	angle
C – Pd – P(1)	86.23(4)	C – Pd – P(2)	85.66(4)
P(1) – Pd – P(2)	162.648(17)	C – Pd – H	173.4(9)
P(1) – Pd – H	92.9(10)	P(2) – Pd – H	93.4(10)
O(32) – B – O(31)	111.48(15)	O(32) – B – C	123.46(16)
O(31) – B – C	125.04(16)	C(22) – C – C(12)	116.23(13)
C(22) – C – B	112.77(14)	C(12) – C – B	110.26(14)
C(22) – C – Pd	105.09(10)	C(12) – C – Pd	112.22(11)
B – C – Pd	98.80(11)	C(11) – P(1) – C(42)	105.68(8)
C(11) – P(1) – C(41)	106.81(8)	C(42) – P(1) – C(41)	104.70(8)
C(11) – P(1) – Pd	103.23(5)	C(42) – P(1) – Pd	118.16(6)
C(41) – P(1) – Pd	117.21(6)	C(21) – P(2) – C(52)	108.56(8)
C(21) – P(2) – C(51)	102.96(8)	C(52) – P(2) – C(51)	106.72(8)
C(21) – P(2) – Pd	98.23(5)	C(52) – P(2) – Pd	124.97(6)
C(51) – P(2) – Pd	112.89(6)	C(26) – C(21) – C(22)	120.71(15)
C(26) – C(21) – P(2)	122.59(13)	C(22) – C(21) – P(2)	116.00(12)
C(15) – C(16) – C(11)	121.13(16)	C(15) – C(16) – H(16)	119.4
C(11) – C(16) – H(16)	119.4	C(16) – C(15) – C(14)	119.17(16)
C(16) – C(15) – H(15)	120.4	C(14) – C(15) – H(15)	120.4
C(13) – C(14) – C(15)	119.85(16)	C(13) – C(14) – H(14)	120.1
C(15) – C(14) – H(14)	120.1	C(14) – C(13) – C(12)	122.36(16)
C(14) – C(13) – H(13)	118.8	C(12) – C(13) – H(13)	118.8
C(13) – C(12) – C(11)	116.81(15)	C(13) – C(12) – C	121.05(15)
C(11) – C(12) – C	122.05(15)	C(16) – C(11) – C(12)	120.36(15)
C(16) – C(11) – P(1)	123.77(13)	C(12) – C(11) – P(1)	115.72(12)
C(23) – C(22) – C(21)	116.19(15)	C(23) – C(22) – C	123.84(15)
C(21) – C(22) – C	119.93(14)	C(24) – C(23) – C(22)	122.25(16)
C(24) – C(23) – H(23)	118.9	C(22) – C(23) – H(23)	118.9
C(23) – C(24) – C(25)	120.65(16)	C(23) – C(24) – H(24)	119.7
C(25) – C(24) – H(24)	119.7	C(26) – C(25) – C(24)	118.60(16)
C(26) – C(25) – H(25)	120.7	C(24) – C(25) – H(25)	120.7
C(25) – C(26) – C(21)	121.23(16)	C(25) – C(26) – H(26)	119.4
C(21) – C(26) – H(26)	119.4	B – O(31) – C(31)	107.63(13)
O(31) – C(31) – C(33)	109.08(14)	O(31) – C(31) – C(34)	106.31(14)
C(33) – C(31) – C(34)	109.88(15)	O(31) – C(31) – C(32)	102.41(13)
C(33) – C(31) – C(32)	114.65(15)	C(34) – C(31) – C(32)	113.83(15)
B – O(32) – C(32)	107.41(13)	C(31) – C(33) – H(33A)	109.5
C(31) – C(33) – H(33B)	109.5	H(33A) – C(33) – H(33B)	109.5
C(31) – C(33) – H(33C)	109.5	H(33A) – C(33) – H(33C)	109.5
H(33B) – C(33) – H(33C)	109.5	C(31) – C(34) – H(34A)	109.5
C(31) – C(34) – H(34B)	109.5	H(34A) – C(34) – H(34B)	109.5
C(31) – C(34) – H(34C)	109.5	H(34A) – C(34) – H(34C)	109.5

Continued on next page

Table S25. – continued from previous page

atom – atom – atom	angle	atom – atom – atom	angle
H(34B) – C(34) – H(34C)	109.5	C(32) – C(35) – H(35A)	109.5
C(32) – C(35) – H(35B)	109.5	H(35A) – C(35) – H(35B)	109.5
C(32) – C(35) – H(35C)	109.5	H(35A) – C(35) – H(35C)	109.5
H(35B) – C(35) – H(35C)	109.5	C(32) – C(36) – H(36A)	109.5
C(32) – C(36) – H(36B)	109.5	H(36A) – C(36) – H(36B)	109.5
C(32) – C(36) – H(36C)	109.5	H(36A) – C(36) – H(36C)	109.5
H(36B) – C(36) – H(36C)	109.5	C(43) – C(41) – C(44)	111.13(15)
C(43) – C(41) – P(1)	115.95(12)	C(44) – C(41) – P(1)	109.18(12)
C(43) – C(41) – H(41)	106.7	C(44) – C(41) – H(41)	106.7
P(1) – C(41) – H(41)	106.7	C(45) – C(42) – C(46)	111.50(16)
C(45) – C(42) – P(1)	110.33(12)	C(46) – C(42) – P(1)	110.34(12)
C(45) – C(42) – H(42)	108.2	C(46) – C(42) – H(42)	108.2
P(1) – C(42) – H(42)	108.2	C(41) – C(43) – H(43A)	109.5
C(41) – C(43) – H(43B)	109.5	H(43A) – C(43) – H(43B)	109.5
C(41) – C(43) – H(43C)	109.5	H(43A) – C(43) – H(43C)	109.5
H(43B) – C(43) – H(43C)	109.5	C(41) – C(44) – H(44A)	109.5
C(41) – C(44) – H(44B)	109.5	H(44A) – C(44) – H(44B)	109.5
C(41) – C(44) – H(44C)	109.5	H(44A) – C(44) – H(44C)	109.5
H(44B) – C(44) – H(44C)	109.5	C(42) – C(45) – H(45A)	109.5
C(42) – C(45) – H(45B)	109.5	H(45A) – C(45) – H(45B)	109.5
C(42) – C(45) – H(45C)	109.5	H(45A) – C(45) – H(45C)	109.5
H(45B) – C(45) – H(45C)	109.5	C(42) – C(46) – H(46A)	109.5
C(42) – C(46) – H(46B)	109.5	H(46A) – C(46) – H(46B)	109.5
C(42) – C(46) – H(46C)	109.5	H(46A) – C(46) – H(46C)	109.5
H(46B) – C(46) – H(46C)	109.5	C(54) – C(51) – C(53)	110.53(15)
C(54) – C(51) – P(2)	108.99(12)	C(53) – C(51) – P(2)	111.79(13)
C(54) – C(51) – H(51)	108.5	C(53) – C(51) – H(51)	108.5
P(2) – C(51) – H(51)	108.5	C(55) – C(52) – C(56)	111.88(15)
C(55) – C(52) – P(2)	111.34(13)	C(56) – C(52) – P(2)	115.58(13)
C(55) – C(52) – H(52)	105.7	C(56) – C(52) – H(52)	105.7
P(2) – C(52) – H(52)	105.7	C(51) – C(53) – H(53A)	109.5
C(51) – C(53) – H(53B)	109.5	H(53A) – C(53) – H(53B)	109.5
C(51) – C(53) – H(53C)	109.5	H(53A) – C(53) – H(53C)	109.5
H(53B) – C(53) – H(53C)	109.5	C(51) – C(54) – H(54A)	109.5
C(51) – C(54) – H(54B)	109.5	H(54A) – C(54) – H(54B)	109.5
C(51) – C(54) – H(54C)	109.5	H(54A) – C(54) – H(54C)	109.5
H(54B) – C(54) – H(54C)	109.5	C(52) – C(55) – H(55A)	109.5
C(52) – C(55) – H(55B)	109.5	H(55A) – C(55) – H(55B)	109.5
C(52) – C(55) – H(55C)	109.5	H(55A) – C(55) – H(55C)	109.5
H(55B) – C(55) – H(55C)	109.5	C(52) – C(56) – H(56A)	109.5
C(52) – C(56) – H(56B)	109.5	H(56A) – C(56) – H(56B)	109.5
C(52) – C(56) – H(56C)	109.5	H(56A) – C(56) – H(56C)	109.5

Continued on next page

Table S25. – continued from previous page

atom – atom – atom	angle	atom – atom – atom	angle
H(56B) – C(56) – H(56C)	109.5	O(32) – C(32) – C(36)	108.66(14)
O(32) – C(32) – C(35)	107.20(14)	C(36) – C(32) – C(35)	110.13(16)
O(32) – C(32) – C(31)	102.39(13)	C(36) – C(32) – C(31)	114.92(15)
C(35) – C(32) – C(31)	112.90(15)		

4.6 Crystal data for [PC(H)P]Pd(GeH$_2$Ph) (10)

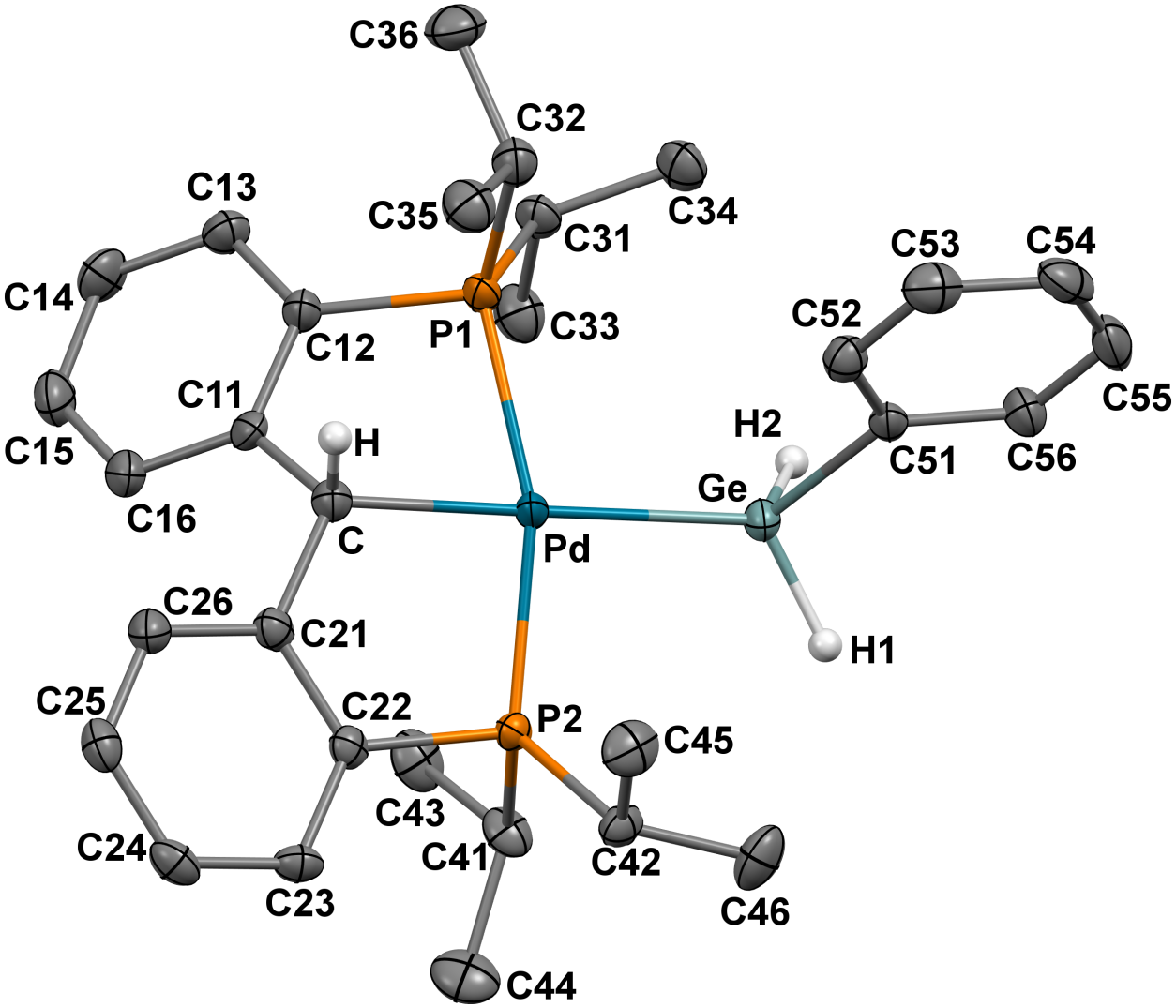

Figure S60. Thermal-ellipsoid representation of [PC(H)P]Pd(GeH$_2$Ph) (**10**) at 50% probability. Most hydrogen atoms were omitted for clarity.

Table S26. Crystal data and structure refinement for [PC(H)P]Pd(GeH_2Ph) (**10**).

Identification code:	cc293	
Empirical formula:	$C_{31}H_{44}GeP_2Pd$	
Formula weight:	657.59	
Temperature:	120(2) K	
Wavelength:	0.71073 Å	
Crystal system:	Triclinic	
Space group:	$P\bar{1}$	
Unit cell dimensions:	a = 8.3636(3) Å	α = 94.2185(11)°
	b = 10.0092(4) Å	β = 93.3363(11)°
	c = 18.4078(7) Å	γ = 100.7761(11)°
Volume:	1505.62(10) Å^3	
Z:	2	
Density (calculated):	1.451 g·cm^{-3}	
Absorption coefficient (μ):	1.719 mm^{-1}	
F(000):	676	
Crystal size:	0.09 × 0.08 × 0.07 mm^3	
θ range for data collection:	2.08 to 25.00°	
Index ranges:	$-9 \le h \le 9$, $-11 \le k \le 11$, $-21 \le l \le 21$	
Reflections collected:	32263	
Independent reflections:	5270 [R_{int} = 0.0429]	
Completeness to θ = 25.00°:	99.9 %	
Absorption correction:	Semi−empirical from equivalents	
Max. and min. transmission:	0.7457 and 0.6773	
Refinement method:	Full-matrix least-squares on F^2	
Data / restraints / parameters:	5270 / 0 / 332	
Goodness-of-fit on F^2:	1.076	
Final R indices [I>2σ(I)]:	R_1 = 0.0340, wR_2 = 0.0693	
R indices (all data):	R_1 = 0.0412, wR_2 = 0.0725	
Largest diff. peak and hole:	1.013 and −1.472 e$^-$·Å^{-3}	

Table S27. Atomic coordinates and equivalent isotropic displacement parameters (Å^2) for [PC(H)P]Pd(GeH_2Ph) (**10**). U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor

atom	x	y	z	U(eq)
Pd	0.17687(3)	0.89245(3)	0.24157(1)	0.017(1)
Ge	0.15572(5)	0.72582(4)	0.33352(2)	0.019(1)
P(1)	0.18342(12)	1.08788(9)	0.31773(5)	0.019(1)
P(2)	0.21556(11)	0.74690(9)	0.14668(5)	0.016(1)
C	0.1922(4)	1.0386(3)	0.16188(18)	0.020(1)
C(11)	0.3194(5)	1.1615(3)	0.19230(19)	0.021(1)
C(12)	0.3069(4)	1.2119(4)	0.26524(19)	0.021(1)
C(13)	0.4068(5)	1.3332(4)	0.2948(2)	0.025(1)
C(14)	0.5288(5)	1.4000(4)	0.2555(2)	0.031(1)
C(15)	0.5510(5)	1.3448(4)	0.1867(2)	0.030(1)
C(16)	0.4459(5)	1.2288(4)	0.1546(2)	0.025(1)
C(21)	0.2102(4)	0.9855(4)	0.08431(19)	0.019(1)
C(22)	0.2208(4)	0.8487(3)	0.06831(18)	0.017(1)
C(25)	0.2070(4)	1.0175(4)	−0.0442(2)	0.023(1)
C(24)	0.2185(4)	0.8827(4)	−0.06031(19)	0.023(1)
C(23)	0.2239(4)	0.7979(4)	−0.00475(18)	0.020(1)
C(26)	0.2043(4)	1.0683(4)	0.0269(2)	0.023(1)
C(31)	0.2966(5)	1.1184(4)	0.40875(19)	0.023(1)
C(32)	−0.0150(5)	1.1388(4)	0.3338(2)	0.026(1)
C(34)	0.1969(5)	1.0463(4)	0.4666(2)	0.028(1)
C(35)	−0.1238(5)	1.1253(4)	0.2630(2)	0.031(1)
C(36)	0.0016(5)	1.2807(4)	0.3718(2)	0.033(1)
C(41)	0.4172(4)	0.7003(4)	0.1568(2)	0.024(1)
C(42)	0.0729(4)	0.5879(3)	0.1122(2)	0.020(1)
C(43)	0.5425(4)	0.8292(4)	0.1841(2)	0.030(1)
C(44)	0.4670(5)	0.6284(5)	0.0884(2)	0.036(1)
C(45)	−0.0984(4)	0.6186(4)	0.1016(2)	0.030(1)
C(46)	0.0749(5)	0.4698(4)	0.1599(2)	0.034(1)
C(51)	−0.0655(4)	0.6861(3)	0.37003(18)	0.019(1)
C(52)	−0.1896(4)	0.7479(4)	0.3436(2)	0.023(1)
C(53)	−0.3448(5)	0.7226(4)	0.3693(2)	0.031(1)
C(54)	−0.3780(5)	0.6327(4)	0.4221(2)	0.033(1)
C(55)	−0.2571(5)	0.5696(4)	0.4495(2)	0.034(1)
C(56)	−0.1028(5)	0.5959(4)	0.4240(2)	0.026(1)
C(33)	0.4638(5)	1.0795(4)	0.4049(2)	0.031(1)
H(1)	0.187(5)	0.594(4)	0.315(2)	0.043(12)
H(2)	0.260(5)	0.760(4)	0.402(2)	0.038(12)
H	0.0856	1.0703	0.1606	0.024
H(13)	0.3910	1.3704	0.3423	0.030

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Table S27. – continued from previous page

atom	x	y	x	U(eq)
H(14)	0.5966	1.4829	0.2756	0.037
H(15)	0.6394	1.3869	0.1609	0.036
H(16)	0.4605	1.1947	0.1064	0.030
H(25)	0.2010	1.0753	−0.0826	0.028
H(24)	0.2227	0.8484	−0.1095	0.028
H(23)	0.2296	0.7048	−0.0159	0.025
H(26)	0.1982	1.1615	0.0373	0.028
H(31)	0.3151	1.2187	0.4231	0.028
H(32)	−0.0724	1.0734	0.3667	0.031
H(34A)	0.1001	1.0866	0.4733	0.042
H(34B)	0.2638	1.0571	0.5130	0.042
H(34C)	0.1630	0.9490	0.4507	0.042
H(35A)	−0.0769	1.1943	0.2312	0.046
H(35B)	−0.2331	1.1387	0.2743	0.046
H(35C)	−0.1313	1.0341	0.2382	0.046
H(36A)	0.0629	1.3476	0.3425	0.050
H(36B)	0.0598	1.2848	0.4200	0.050
H(36C)	−0.1071	1.3015	0.3777	0.050
H(41)	0.4134	0.6359	0.1960	0.029
H(42)	0.1059	0.5588	0.0630	0.024
H(43A)	0.6507	0.8058	0.1912	0.046
H(43B)	0.5116	0.8675	0.2305	0.046
H(43C)	0.5453	0.8966	0.1479	0.046
H(44A)	0.3826	0.5483	0.0720	0.054
H(44B)	0.5707	0.5995	0.0994	0.054
H(44C)	0.4796	0.6912	0.0498	0.054
H(45A)	−0.0966	0.6937	0.0702	0.046
H(45B)	−0.1357	0.6446	0.1491	0.046
H(45C)	−0.1729	0.5371	0.0786	0.046
H(46A)	0.0032	0.3874	0.1363	0.051
H(46B)	0.0364	0.4929	0.2077	0.051
H(46C)	0.1865	0.4532	0.1665	0.051
H(52)	−0.1681	0.8094	0.3069	0.028
H(53)	−0.4273	0.7669	0.3505	0.037
H(54)	−0.4839	0.6142	0.4396	0.039
H(55)	−0.2797	0.5079	0.4860	0.041
H(56)	−0.0206	0.5519	0.4435	0.031
H(33A)	0.4504	0.9805	0.3942	0.047
H(33B)	0.5272	1.1071	0.4518	0.047
H(33C)	0.5214	1.1260	0.3662	0.047

Table S28. Anisotropic displacement parameters (Å^2) for [PC(H)P]Pd(GeH$_2$Ph) (**10**). The anisotropic displacement factor exponent takes the form: $-2\pi^2$[h^{2}a*^{2}U$_{11}$ + ...+ 2hka*b*U$_{12}$].

atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Pd	0.0242(2)	0.0127(1)	0.0142(1)	0.0014(1)	0.0060(1)	−0.0002(1)
Ge	0.0216(2)	0.0175(2)	0.0187(2)	0.0053(2)	0.0054(2)	0.0043(2)
P(1)	0.0257(5)	0.0164(5)	0.0137(4)	0.0003(4)	0.0036(4)	0.0004(4)
P(2)	0.0156(4)	0.0143(4)	0.0163(4)	−0.0001(3)	0.0022(3)	−0.0003(3)
C	0.0231(19)	0.0178(18)	0.0187(18)	0.0027(15)	0.0036(15)	0.0027(15)
C(11)	0.033(2)	0.0132(18)	0.0202(18)	0.0037(14)	0.0063(16)	0.0077(15)
C(12)	0.027(2)	0.0166(18)	0.0193(18)	0.0025(15)	0.0054(15)	0.0010(15)
C(13)	0.033(2)	0.0185(19)	0.0228(19)	−0.0016(15)	0.0026(17)	0.0021(16)
C(14)	0.031(2)	0.019(2)	0.037(2)	−0.0023(17)	0.0010(18)	−0.0058(17)
C(15)	0.028(2)	0.027(2)	0.034(2)	0.0094(18)	0.0110(18)	0.0009(17)
C(16)	0.032(2)	0.0199(19)	0.0235(19)	0.0061(16)	0.0080(17)	0.0060(16)
C(21)	0.0186(18)	0.0192(19)	0.0184(18)	0.0004(15)	0.0034(14)	−0.0006(15)
C(22)	0.0140(17)	0.0176(18)	0.0190(18)	0.0008(14)	0.0021(14)	−0.0008(14)
C(25)	0.0190(19)	0.029(2)	0.0227(19)	0.0088(16)	0.0043(15)	0.0038(16)
C(24)	0.0216(19)	0.033(2)	0.0150(18)	−0.0011(16)	0.0011(15)	0.0040(16)
C(23)	0.0210(19)	0.0204(19)	0.0188(18)	−0.0048(15)	0.0001(15)	0.0042(15)
C(26)	0.026(2)	0.0198(19)	0.026(2)	0.0041(16)	0.0082(16)	0.0046(16)
C(31)	0.030(2)	0.0223(19)	0.0155(18)	−0.0011(15)	0.0025(15)	0.0012(16)
C(32)	0.030(2)	0.023(2)	0.023(2)	0.0033(16)	0.0039(16)	0.0024(16)
C(34)	0.035(2)	0.030(2)	0.0182(19)	0.0022(16)	0.0019(17)	0.0037(18)
C(35)	0.028(2)	0.033(2)	0.031(2)	0.0032(18)	0.0028(18)	0.0063(18)
C(36)	0.035(2)	0.027(2)	0.040(2)	−0.0039(18)	0.0070(19)	0.0112(18)
C(41)	0.0143(18)	0.033(2)	0.025(2)	0.0042(17)	0.0028(15)	0.0058(16)
C(42)	0.0193(19)	0.0152(18)	0.0251(19)	0.0003(15)	0.0013(15)	0.0010(14)
C(43)	0.0168(19)	0.041(2)	0.030(2)	0.0040(19)	0.0001(16)	−0.0019(17)
C(44)	0.022(2)	0.049(3)	0.040(2)	0.000(2)	0.0027(18)	0.0158(19)
C(45)	0.0152(19)	0.029(2)	0.044(2)	−0.0011(19)	0.0002(17)	0.0002(16)
C(46)	0.036(2)	0.019(2)	0.044(3)	0.0046(18)	−0.006(2)	−0.0035(17)
C(51)	0.026(2)	0.0149(18)	0.0150(17)	−0.0005(14)	0.0043(15)	0.0000(15)
C(52)	0.025(2)	0.0196(19)	0.0225(19)	0.0016(15)	0.0007(16)	0.0012(16)
C(53)	0.024(2)	0.031(2)	0.037(2)	−0.0052(19)	0.0020(18)	0.0035(17)
C(54)	0.027(2)	0.036(2)	0.031(2)	−0.0080(19)	0.0136(18)	−0.0032(18)
C(55)	0.044(3)	0.030(2)	0.025(2)	0.0048(18)	0.0146(19)	−0.0054(19)
C(56)	0.031(2)	0.025(2)	0.0213(19)	0.0053(16)	0.0064(16)	0.0037(17)
C(33)	0.029(2)	0.036(2)	0.028(2)	0.0071(18)	0.0015(17)	0.0055(18)

Table S29. Distances [Å] for [PC(H)P]Pd(GeH_2Ph) (**10**).

atom – atom	distance	atom – atom	distance
Pd – C	2.139(3)	Pd – P(2)	2.2685(9)
Pd – P(1)	2.3113(9)	Pd – Ge	2.4531(4)
Ge – C(51)	1.986(4)	Ge – H(1)	1.41(4)
Ge – H(2)	1.47(4)	P(1) – C(12)	1.831(4)
P(1) – C(31)	1.852(4)	P(1) – C(32)	1.858(4)
P(2) – C(22)	1.824(3)	P(2) – C(41)	1.835(4)
P(2) – C(42)	1.847(3)	C – C(21)	1.513(5)
C – C(11)	1.516(5)	C – H	1.0000
C(11) – C(16)	1.393(5)	C(11) – C(12)	1.416(5)
C(12) – C(13)	1.393(5)	C(13) – C(14)	1.384(5)
C(13) – H(13)	0.9500	C(14) – C(15)	1.380(6)
C(14) – H(14)	0.9500	C(15) – C(16)	1.389(5)
C(15) – H(15)	0.9500	C(16) – H(16)	0.9500
C(21) – C(26)	1.394(5)	C(21) – C(22)	1.400(5)
C(22) – C(23)	1.406(5)	C(25) – C(26)	1.373(5)
C(25) – C(24)	1.383(5)	C(25) – H(25)	0.9500
C(24) – C(23)	1.380(5)	C(24) – H(24)	0.9500
C(23) – H(23)	0.9500	C(26) – H(26)	0.9500
C(31) – C(33)	1.524(5)	C(31) – C(34)	1.531(5)
C(31) – H(31)	1.0000	C(32) – C(36)	1.515(5)
C(32) – C(35)	1.528(5)	C(32) – H(32)	1.0000
C(34) – H(34A)	0.9800	C(34) – H(34B)	0.9800
C(34) – H(34C)	0.9800	C(35) – H(35A)	0.9800
C(35) – H(35B)	0.9800	C(35) – H(35C)	0.9800
C(36) – H(36A)	0.9800	C(36) – H(36B)	0.9800
C(36) – H(36C)	0.9800	C(41) – C(44)	1.522(5)
C(41) – C(43)	1.534(5)	C(41) – H(41)	1.0000
C(42) – C(45)	1.525(5)	C(42) – C(46)	1.526(5)
C(42) – H(42)	1.0000	C(43) – H(43A)	0.9800
C(43) – H(43B)	0.9800	C(43) – H(43C)	0.9800
C(44) – H(44A)	0.9800	C(44) – H(44B)	0.9800
C(44) – H(44C)	0.9800	C(45) – H(45A)	0.9800
C(45) – H(45B)	0.9800	C(45) – H(45C)	0.9800
C(46) – H(46A)	0.9800	C(46) – H(46B)	0.9800
C(46) – H(46C)	0.9800	C(51) – C(52)	1.387(5)
C(51) – C(56)	1.400(5)	C(52) – C(53)	1.392(5)
C(52) – H(52)	0.9500	C(53) – C(54)	1.378(6)
C(53) – H(53)	0.9500	C(54) – C(55)	1.379(6)
C(54) – H(54)	0.9500	C(55) – C(56)	1.384(5)
C(55) – H(55)	0.9500	C(56) – H(56)	0.9500
C(33) – H(33A)	0.9800	C(33) – H(33B)	0.9800

Table S30. Angles [°] for [PC(H)P]Pd(GeH_2Ph) (**10**).

atom – atom – atom	angle	atom – atom – atom	angle
C – Pd – P(2)	84.20(10)	C – Pd – P(1)	80.63(10)
P(2) – Pd – P(1)	162.61(3)	C – Pd – Ge	179.17(10)
P(2) – Pd – Ge	96.34(3)	P(1) – Pd – Ge	98.93(3)
C(51) – Ge – Pd	112.45(10)	C(51) – Ge – H(1)	102.8(17)
Pd – Ge – H(1)	119.2(17)	C(51) – Ge – H(2)	101.9(16)
Pd – Ge – H(2)	118.7(16)	H(1) – Ge – H(2)	99(2)
C(12) – P(1) – C(31)	102.26(17)	C(12) – P(1) – C(32)	110.32(17)
C(31) – P(1) – C(32)	104.11(17)	C(12) – P(1) – Pd	99.10(12)
C(31) – P(1) – Pd	122.39(13)	C(32) – P(1) – Pd	117.20(12)
C(22) – P(2) – C(41)	105.78(16)	C(22) – P(2) – C(42)	102.62(16)
C(41) – P(2) – C(42)	105.64(17)	C(22) – P(2) – Pd	104.10(11)
C(41) – P(2) – Pd	111.36(12)	C(42) – P(2) – Pd	125.47(12)
C(21) – C – C(11)	115.5(3)	C(21) – C – Pd	116.2(2)
C(11) – C – Pd	107.1(2)	C(21) – C – H	105.7
C(11) – C – H	105.7	Pd – C – H	105.7
C(16) – C(11) – C(12)	117.7(3)	C(16) – C(11) – C	125.7(3)
C(12) – C(11) – C	116.6(3)	C(13) – C(12) – C(11)	120.4(3)
C(13) – C(12) – P(1)	125.1(3)	C(11) – C(12) – P(1)	113.3(3)
C(14) – C(13) – C(12)	120.4(3)	C(14) – C(13) – H(13)	119.8
C(12) – C(13) – H(13)	119.8	C(15) – C(14) – C(13)	119.4(4)
C(15) – C(14) – H(14)	120.3	C(13) – C(14) – H(14)	120.3
C(14) – C(15) – C(16)	120.9(4)	C(14) – C(15) – H(15)	119.5
C(16) – C(15) – H(15)	119.5	C(15) – C(16) – C(11)	120.8(3)
C(15) – C(16) – H(16)	119.6	C(11) – C(16) – H(16)	119.6
C(26) – C(21) – C(22)	118.8(3)	C(26) – C(21) – C	120.9(3)
C(22) – C(21) – C	120.2(3)	C(21) – C(22) – C(23)	119.5(3)
C(21) – C(22) – P(2)	115.2(3)	C(23) – C(22) – P(2)	125.1(3)
C(26) – C(25) – C(24)	120.3(3)	C(26) – C(25) – H(25)	119.9
C(24) – C(25) – H(25)	119.9	C(23) – C(24) – C(25)	119.9(3)
C(23) – C(24) – H(24)	120.0	C(25) – C(24) – H(24)	120.0
C(24) – C(23) – C(22)	120.3(3)	C(24) – C(23) – H(23)	119.9
C(22) – C(23) – H(23)	119.9	C(25) – C(26) – C(21)	121.2(3)
C(25) – C(26) – H(26)	119.4	C(21) – C(26) – H(26)	119.4
C(33) – C(31) – C(34)	112.6(3)	C(33) – C(31) – P(1)	110.6(3)
C(34) – C(31) – P(1)	111.5(3)	C(33) – C(31) – H(31)	107.3
C(34) – C(31) – H(31)	107.3	P(1) – C(31) – H(31)	107.3
C(36) – C(32) – C(35)	110.1(3)	C(36) – C(32) – P(1)	113.8(3)
C(35) – C(32) – P(1)	111.5(3)	C(36) – C(32) – H(32)	107.0
C(35) – C(32) – H(32)	107.0	P(1) – C(32) – H(32)	107.0
C(31) – C(34) – H(34A)	109.5	C(31) – C(34) – H(34B)	109.5
H(34A) – C(34) – H(34B)	109.5	C(31) – C(34) – H(34C)	109.5

Continued on next page

Table S30. – continued from previous page

atom – atom – atom	angle	atom – atom – atom	angle
H(34A) – C(34) – H(34C)	109.5	H(34B) – C(34) – H(34C)	109.5
C(32) – C(35) – H(35A)	109.5	C(32) – C(35) – H(35B)	109.5
H(35A) – C(35) – H(35B)	109.5	C(32) – C(35) – H(35C)	109.5
H(35A) – C(35) – H(35C)	109.5	H(35B) – C(35) – H(35C)	109.5
C(32) – C(36) – H(36A)	109.5	C(32) – C(36) – H(36B)	109.5
H(36A) – C(36) – H(36B)	109.5	C(32) – C(36) – H(36C)	109.5
H(36A) – C(36) – H(36C)	109.5	H(36B) – C(36) – H(36C)	109.5
C(44) – C(41) – C(43)	112.0(3)	C(44) – C(41) – P(2)	114.4(3)
C(43) – C(41) – P(2)	108.3(3)	C(44) – C(41) – H(41)	107.3
C(43) – C(41) – H(41)	107.3	P(2) – C(41) – H(41)	107.3
C(45) – C(42) – C(46)	111.1(3)	C(45) – C(42) – P(2)	108.9(2)
C(46) – C(42) – P(2)	114.1(3)	C(45) – C(42) – H(42)	107.5
C(46) – C(42) – H(42)	107.5	P(2) – C(42) – H(42)	107.5
C(41) – C(43) – H(43A)	109.5	C(41) – C(43) – H(43B)	109.5
H(43A) – C(43) – H(43B)	109.5	C(41) – C(43) – H(43C)	109.5
H(43A) – C(43) – H(43C)	109.5	H(43B) – C(43) – H(43C)	109.5
C(41) – C(44) – H(44A)	109.5	C(41) – C(44) – H(44B)	109.5
H(44A) – C(44) – H(44B)	109.5	C(41) – C(44) – H(44C)	109.5
H(44A) – C(44) – H(44C)	109.5	H(44B) – C(44) – H(44C)	109.5
C(42) – C(45) – H(45A)	109.5	C(42) – C(45) – H(45B)	109.5
H(45A) – C(45) – H(45B)	109.5	C(42) – C(45) – H(45C)	109.5
H(45A) – C(45) – H(45C)	109.5	H(45B) – C(45) – H(45C)	109.5
C(42) – C(46) – H(46A)	109.5	C(42) – C(46) – H(46B)	109.5
H(46A) – C(46) – H(46B)	109.5	C(42) – C(46) – H(46C)	109.5
H(46A) – C(46) – H(46C)	109.5	H(46B) – C(46) – H(46C)	109.5
C(52) – C(51) – C(56)	117.1(3)	C(52) – C(51) – Ge	121.2(3)
C(56) – C(51) – Ge	121.7(3)	C(51) – C(52) – C(53)	122.0(4)
C(51) – C(52) – H(52)	119.0	C(53) – C(52) – H(52)	119.0
C(54) – C(53) – C(52)	119.6(4)	C(54) – C(53) – H(53)	120.2
C(52) – C(53) – H(53)	120.2	C(53) – C(54) – C(55)	119.8(4)
C(53) – C(54) – H(54)	120.1	C(55) – C(54) – H(54)	120.1
C(54) – C(55) – C(56)	120.4(4)	C(54) – C(55) – H(55)	119.8
C(56) – C(55) – H(55)	119.8	C(55) – C(56) – C(51)	121.2(4)
C(55) – C(56) – H(56)	119.4	C(51) – C(56) – H(56)	119.4
C(31) – C(33) – H(33A)	109.5	C(31) – C(33) – H(33B)	109.5
H(33A) – C(33) – H(33B)	109.5	C(31) – C(33) – H(33C)	109.5
H(33A) – C(33) – H(33C)	109.5	H(33B) – C(33) – H(33C)	109.5

4.7 Crystal data for [PC(H)P]Pd(GeHPh$_2$) (11)

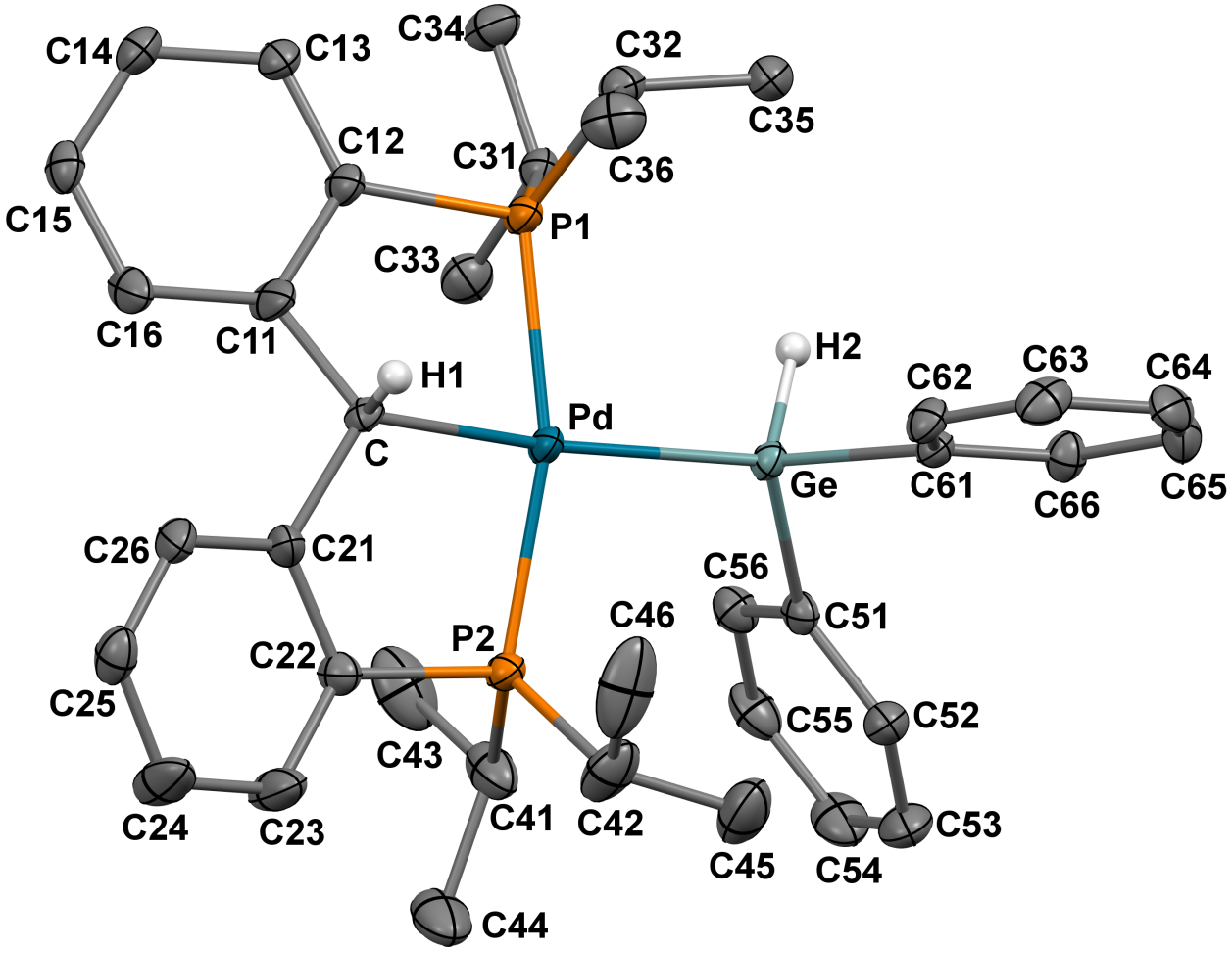

Figure S61. Thermal-ellipsoid representation of [PC(H)P]Pd(GeHPh$_2$) (**11**) at 50% probability. Most hydrogen atoms were omitted for clarity.

Table S31. Crystal data and structure refinement for [PC(H)P]Pd($GeHPh_2$) (**11**).

Identification code:	cc307	
Empirical formula:	$C_{37}H_{48}GeP_2Pd$	
Formula weight:	733.68	
Temperature:	120(2) K	
Wavelength:	0.71073 Å	
Crystal system:	Monoclinic	
Space group:	$I2/a$	
Unit cell dimensions:	a = 22.9918(15) Å	$\alpha = 90°$
	b = 12.0605(7) Å	$\beta = 105.728(4)°$
	c = 25.6249(17) Å	$\gamma = 90°$
Volume:	6839.6(7) $Å^3$	
Z:	8	
Density (calculated):	1.425 $g \cdot cm^{-3}$	
Absorption coefficient (μ):	1.522 mm^{-1}	
F(000):	3024	
Crystal size:	$0.11 \times 0.07 \times 0.05$ mm^3	
θ range for data collection:	1.65 to 25.00°	
Index ranges:	$-27 \leq h \leq 21$, $-14 \leq k \leq 14$, $-30 \leq l \leq 30$	
Reflections collected:	48072	
Independent reflections:	6020 [R_{int} = 0.0538]	
Completeness to θ = 25.00°:	100.0 %	
Absorption correction:	Semi−empirical from equivalents	
Max. and min. transmission:	0.7456 and 0.7094	
Refinement method:	Full-matrix least-squares on F^2	
Data / restraints / parameters:	6020 / 0 / 392	
Goodness-of-fit on F^2:	1.052	
Final R indices [I>2σ(I)]:	R_1 = 0.0337, wR_2 = 0.0735	
R indices (all data):	R_1 = 0.0495, wR_2 = 0.0776	
Largest diff. peak and hole:	0.744 and −0.722 $e^- \cdot Å^{-3}$	

Table S32. Atomic coordinates and equivalent isotropic displacement parameters (Å^2) for [PC(H)P]Pd(GeHPh$_2$) (**11**). U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor

atom	x	y	z	U(eq)
Pd	0.09496(1)	0.33779(2)	0.14792(1)	0.024(1)
Ge	0.02419(2)	0.18328(3)	0.13519(1)	0.021(1)
P(1)	0.06050(4)	0.41908(7)	0.21412(4)	0.027(1)
P(2)	0.15294(4)	0.27901(7)	0.09461(4)	0.025(1)
C(11)	0.16439(18)	0.5286(3)	0.21554(17)	0.042(1)
C(12)	0.11754(15)	0.5246(3)	0.24027(14)	0.028(1)
C(13)	0.11887(16)	0.5904(3)	0.28504(14)	0.029(1)
C(14)	0.16924(16)	0.6531(3)	0.30852(15)	0.034(1)
C(15)	0.21830(16)	0.6473(3)	0.28832(15)	0.031(1)
C(16)	0.21587(16)	0.5871(3)	0.24206(16)	0.038(1)
C(21)	0.19990(16)	0.4802(3)	0.13058(15)	0.034(1)
C(22)	0.20819(15)	0.3898(3)	0.10030(14)	0.028(1)
C(23)	0.2504(2)	0.3944(4)	0.07139(19)	0.057(1)
C(24)	0.2838(2)	0.4882(4)	0.07075(19)	0.065(2)
C(25)	0.27287(17)	0.5813(3)	0.09714(15)	0.038(1)
C(26)	0.23173(16)	0.5771(3)	0.12628(16)	0.036(1)
C(32)	−0.01196(15)	0.4914(3)	0.20001(14)	0.032(1)
C(31)	0.06260(16)	0.3244(3)	0.27146(14)	0.029(1)
C(33)	0.12021(17)	0.2555(3)	0.28330(15)	0.040(1)
C(34)	0.05533(19)	0.3772(3)	0.32287(15)	0.040(1)
C(35)	−0.06542(15)	0.4122(3)	0.18853(15)	0.033(1)
C(36)	−0.01628(19)	0.5696(3)	0.15230(16)	0.047(1)
C	0.1463(2)	0.4875(4)	0.15454(19)	0.019(2)
C(3)	0.1787(5)	0.4285(8)	0.1832(4)	0.021(3)
C(41)	0.19345(18)	0.1491(3)	0.11822(19)	0.048(1)
C(42)	0.1220(2)	0.2699(4)	0.02101(16)	0.052(1)
C(43)	0.2194(2)	0.1570(4)	0.1794(2)	0.067(2)
C(44)	0.24107(19)	0.1155(4)	0.0902(2)	0.068(2)
C(45)	0.0849(2)	0.1692(4)	0.00401(19)	0.065(1)
C(46)	0.0867(2)	0.3755(4)	0.00124(18)	0.077(2)
C(51)	0.05544(14)	0.0316(3)	0.13095(14)	0.025(1)
C(52)	0.04290(15)	−0.0311(3)	0.08399(15)	0.031(1)
C(53)	0.06546(18)	−0.1374(3)	0.08373(19)	0.047(1)
C(54)	0.10079(19)	−0.1829(3)	0.1302(2)	0.049(1)
C(55)	0.11379(16)	−0.1239(3)	0.17756(18)	0.041(1)
C(56)	0.09148(15)	−0.0179(3)	0.17774(15)	0.031(1)
C(61)	−0.05226(14)	0.1947(3)	0.07705(13)	0.022(1)
C(62)	−0.06819(16)	0.2912(3)	0.04672(14)	0.029(1)
C(63)	−0.12386(17)	0.3023(3)	0.00912(15)	0.037(1)

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Table S32. – continued from previous page

atom	x	y	x	U(eq)
C(64)	−0.16496(16)	0.2176(3)	0.00077(16)	0.037(1)
C(65)	−0.15038(16)	0.1213(3)	0.02994(15)	0.036(1)
C(66)	−0.09477(15)	0.1100(3)	0.06745(14)	0.030(1)
H(2)	0.0007(14)	0.169(3)	0.1797(13)	0.032(9)
H(13)	0.0850	0.5923	0.2995	0.035
H(14)	0.1698	0.6998	0.3385	0.040
H(15)	0.2544	0.6851	0.3063	0.037
H(16)	0.2501	0.5856	0.2281	0.045
H(23)	0.2565	0.3312	0.0514	0.069
H(24)	0.3144	0.4885	0.0522	0.078
H(25)	0.2939	0.6482	0.0950	0.045
H(26)	0.2243	0.6421	0.1444	0.044
H(32)	−0.0125	0.5370	0.2325	0.038
H(31)	0.0281	0.2716	0.2588	0.034
H(33A)	0.1215	0.2141	0.2507	0.059
H(33B)	0.1208	0.2035	0.3128	0.059
H(33C)	0.1554	0.3047	0.2940	0.059
H(34A)	0.0224	0.4315	0.3137	0.061
H(34B)	0.0930	0.4146	0.3418	0.061
H(34C)	0.0459	0.3198	0.3464	0.061
H(35A)	−0.1030	0.4547	0.1819	0.050
H(35B)	−0.0617	0.3633	0.2198	0.050
H(35C)	−0.0659	0.3675	0.1565	0.050
H(36A)	−0.0113	0.5272	0.1212	0.070
H(36B)	0.0156	0.6258	0.1624	0.070
H(36C)	−0.0559	0.6060	0.1426	0.070
H(1)	0.1186	0.5449	0.1331	0.023
H(3)	0.2106	0.3796	0.2063	0.026
H(41)	0.1625	0.0886	0.1113	0.058
H(42)	0.1568	0.2667	0.0045	0.062
H(43A)	0.2425	0.0897	0.1929	0.101
H(43B)	0.1863	0.1645	0.1966	0.101
H(43C)	0.2460	0.2217	0.1883	0.101
H(44A)	0.2241	0.1207	0.0508	0.102
H(44B)	0.2539	0.0391	0.1000	0.102
H(44C)	0.2760	0.1652	0.1015	0.102
H(45A)	0.0700	0.1675	−0.0356	0.097
H(45B)	0.0506	0.1702	0.0198	0.097
H(45C)	0.1096	0.1032	0.0166	0.097
H(46A)	0.0719	0.3740	−0.0384	0.115
H(46B)	0.1131	0.4399	0.0125	0.115
H(46C)	0.0523	0.3806	0.0169	0.115

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Table S32. – continued from previous page

atom	x	y	x	U(eq)
H(52)	0.0183	−0.0005	0.0513	0.037
H(53)	0.0563	−0.1788	0.0510	0.056
H(54)	0.1164	−0.2557	0.1298	0.058
H(55)	0.1380	−0.1558	0.2101	0.049
H(56)	0.1010	0.0227	0.2107	0.037
H(62)	−0.0402	0.3508	0.0519	0.035
H(63)	−0.1336	0.3691	−0.0110	0.044
H(64)	−0.2032	0.2254	−0.0250	0.045
H(65)	−0.1787	0.0621	0.0243	0.044
H(66)	−0.0854	0.0426	0.0871	0.035

Table S33. Anisotropic displacement parameters (Å^2) for [PC(H)P]Pd(GeHPh$_2$) (**11**). The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11} + ...+ 2hka^*b^*U_{12}]$.

atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Pd	0.0266(2)	0.0208(1)	0.0266(2)	−0.0088(1)	0.0112(1)	−0.0088(1)
Ge	0.0241(2)	0.0181(2)	0.0217(2)	−0.0030(1)	0.0059(2)	−0.0048(1)
P(1)	0.0304(5)	0.0237(5)	0.0299(5)	−0.0090(4)	0.0136(4)	−0.0086(4)
P(2)	0.0280(5)	0.0215(4)	0.0267(5)	−0.0050(4)	0.0101(4)	−0.0028(4)
C(11)	0.048(2)	0.0267(19)	0.061(3)	−0.0243(19)	0.033(2)	−0.0194(18)
C(12)	0.031(2)	0.0202(17)	0.034(2)	−0.0075(15)	0.0134(17)	−0.0083(15)
C(13)	0.030(2)	0.0233(17)	0.035(2)	−0.0067(15)	0.0114(17)	−0.0014(15)
C(14)	0.039(2)	0.0279(19)	0.032(2)	−0.0102(16)	0.0067(18)	−0.0049(17)
C(15)	0.030(2)	0.0215(18)	0.038(2)	−0.0003(15)	0.0057(17)	−0.0081(15)
C(16)	0.035(2)	0.0222(19)	0.062(3)	−0.0091(18)	0.025(2)	−0.0095(16)
C(21)	0.027(2)	0.041(2)	0.039(2)	−0.0162(18)	0.0155(17)	−0.0127(17)
C(22)	0.030(2)	0.0234(17)	0.033(2)	−0.0008(15)	0.0135(17)	−0.0030(15)
C(23)	0.070(3)	0.047(3)	0.074(3)	−0.034(2)	0.050(3)	−0.026(2)
C(24)	0.085(4)	0.065(3)	0.067(3)	−0.033(3)	0.060(3)	−0.041(3)
C(25)	0.042(2)	0.037(2)	0.032(2)	0.0002(17)	0.0082(19)	−0.0158(18)
C(26)	0.031(2)	0.0285(19)	0.050(2)	−0.0150(17)	0.0117(19)	−0.0069(16)
C(32)	0.035(2)	0.0293(19)	0.033(2)	−0.0067(16)	0.0136(17)	−0.0020(16)
C(31)	0.029(2)	0.0282(19)	0.030(2)	−0.0066(15)	0.0091(16)	−0.0080(15)
C(33)	0.042(2)	0.046(2)	0.030(2)	−0.0013(18)	0.0090(18)	−0.0005(19)
C(34)	0.055(3)	0.035(2)	0.035(2)	−0.0076(18)	0.021(2)	−0.0053(19)
C(35)	0.030(2)	0.034(2)	0.036(2)	−0.0074(17)	0.0098(17)	−0.0020(16)
C(36)	0.059(3)	0.038(2)	0.046(3)	0.0057(19)	0.018(2)	0.005(2)
C	0.026(3)	0.012(2)	0.021(3)	−0.001(2)	0.008(2)	−0.001(2)
C(3)	0.025(6)	0.016(5)	0.020(6)	−0.001(4)	0.001(5)	−0.010(5)
C(41)	0.036(2)	0.028(2)	0.085(4)	−0.001(2)	0.025(2)	−0.0024(17)
C(42)	0.077(3)	0.053(3)	0.027(2)	−0.008(2)	0.017(2)	−0.021(2)
C(43)	0.043(3)	0.074(3)	0.079(4)	0.040(3)	0.006(3)	0.010(2)
C(44)	0.043(3)	0.044(3)	0.122(5)	−0.023(3)	0.032(3)	0.004(2)
C(45)	0.074(3)	0.077(3)	0.045(3)	−0.023(2)	0.019(3)	−0.033(3)
C(46)	0.100(4)	0.071(3)	0.036(3)	0.025(2)	−0.021(3)	−0.035(3)
C(51)	0.0230(18)	0.0211(17)	0.032(2)	−0.0001(15)	0.0111(16)	−0.0061(14)
C(52)	0.030(2)	0.0311(19)	0.033(2)	−0.0067(16)	0.0101(17)	−0.0024(16)
C(53)	0.045(3)	0.037(2)	0.061(3)	−0.021(2)	0.018(2)	−0.0009(19)
C(54)	0.041(2)	0.025(2)	0.083(4)	−0.002(2)	0.022(2)	0.0063(18)
C(55)	0.027(2)	0.040(2)	0.055(3)	0.014(2)	0.0129(19)	0.0074(17)
C(56)	0.028(2)	0.0312(19)	0.035(2)	0.0039(16)	0.0106(17)	−0.0008(16)
C(61)	0.0249(18)	0.0200(16)	0.0229(18)	−0.0041(13)	0.0075(15)	−0.0015(14)
C(62)	0.034(2)	0.0198(17)	0.032(2)	−0.0060(15)	0.0062(17)	−0.0031(15)
C(63)	0.043(2)	0.0275(19)	0.035(2)	−0.0008(16)	0.0027(19)	0.0116(18)
C(64)	0.021(2)	0.047(2)	0.039(2)	−0.0058(19)	0.0015(17)	0.0087(18)

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Table S33. – continued from previous page

atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C(65)	0.027(2)	0.042(2)	0.038(2)	−0.0066(18)	0.0057(18)	−0.0108(17)
C(66)	0.031(2)	0.0287(19)	0.028(2)	0.0014(15)	0.0062(16)	−0.0068(16)

Table S34. Distances [Å] for [PC(H)P]Pd(GeHPh$_2$) (**11**).

atom – atom	distance	atom – atom	distance
Pd – C	2.139(4)	Pd – C(3)	2.186(9)
Pd – P(2)	2.2655(9)	Pd – P(1)	2.2793(9)
Pd – Ge	2.4369(4)	Ge – C(61)	1.977(3)
Ge – C(51)	1.980(3)	Ge – H(2)	1.40(3)
P(1) – C(12)	1.820(3)	P(1) – C(32)	1.828(4)
P(1) – C(31)	1.851(3)	P(2) – C(22)	1.822(3)
P(2) – C(42)	1.830(4)	P(2) – C(41)	1.839(4)
C(11) – C(16)	1.387(5)	C(11) – C(12)	1.391(5)
C(11) – C(3)	1.548(10)	C(11) – C	1.584(6)
C(12) – C(13)	1.388(5)	C(13) – C(14)	1.377(5)
C(13) – H(13)	0.9500	C(14) – C(15)	1.364(5)
C(14) – H(14)	0.9500	C(15) – C(16)	1.378(5)
C(15) – H(15)	0.9500	C(16) – H(16)	0.9500
C(21) – C(22)	1.380(5)	C(21) – C(26)	1.399(5)
C(21) – C	1.520(6)	C(21) – C(3)	1.673(10)
C(22) – C(23)	1.372(5)	C(23) – C(24)	1.371(5)
C(23) – H(23)	0.9500	C(24) – C(25)	1.369(5)
C(24) – H(24)	0.9500	C(25) – C(26)	1.356(5)
C(25) – H(25)	0.9500	C(26) – H(26)	0.9500
C(32) – C(35)	1.521(5)	C(32) – C(36)	1.526(5)
C(32) – H(32)	1.0000	C(31) – C(34)	1.513(5)
C(31) – C(33)	1.523(5)	C(31) – H(31)	1.0000
C(33) – H(33A)	0.9800	C(33) – H(33B)	0.9800
C(33) – H(33C)	0.9800	C(34) – H(34A)	0.9800
C(34) – H(34B)	0.9800	C(34) – H(34C)	0.9800
C(35) – H(35A)	0.9800	C(35) – H(35B)	0.9800
C(35) – H(35C)	0.9800	C(36) – H(36A)	0.9800
C(36) – H(36B)	0.9800	C(36) – H(36C)	0.9800
C – H(1)	1.0000	C(3) – H(3)	1.0000
C(41) – C(44)	1.519(6)	C(41) – C(43)	1.523(6)
C(41) – H(41)	1.0000	C(42) – C(45)	1.480(6)
C(42) – C(46)	1.522(7)	C(42) – H(42)	1.0000
C(43) – H(43A)	0.9800	C(43) – H(43B)	0.9800
C(43) – H(43C)	0.9800	C(44) – H(44A)	0.9800
C(44) – H(44B)	0.9800	C(44) – H(44C)	0.9800
C(45) – H(45A)	0.9800	C(45) – H(45B)	0.9800
C(45) – H(45C)	0.9800	C(46) – H(46A)	0.9800
C(46) – H(46B)	0.9800	C(46) – H(46C)	0.9800
C(51) – C(52)	1.383(5)	C(51) – C(56)	1.393(5)
C(52) – C(53)	1.383(5)	C(52) – H(52)	0.9500
C(53) – C(54)	1.363(6)	C(53) – H(53)	0.9500

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Table S34. – continued from previous page

atom – atom	distance	atom – atom	distance
C(54) – C(55)	1.367(6)	C(54) – H(54)	0.9500
C(55) – C(56)	1.378(5)	C(55) – H(55)	0.9500
C(56) – H(56)	0.9500	C(61) – C(66)	1.389(4)
C(61) – C(62)	1.392(5)	C(62) – C(63)	1.384(5)
C(62) – H(62)	0.9500	C(63) – C(64)	1.368(5)
C(63) – H(63)	0.9500	C(64) – C(65)	1.373(5)
C(64) – H(64)	0.9500	C(65) – C(66)	1.382(5)
C(65) – H(65)	0.9500	C(66) – H(66)	0.9500

Table S35. Angles [°] for [PC(H)P]Pd(GeHPh$_2$) (**11**).

atom – atom – atom	angle	atom – atom – atom	angle
C – Pd – C(3)	30.6(3)	C – Pd – P(2)	84.81(12)
C(3) – Pd – P(2)	79.0(3)	C – Pd – P(1)	82.74(12)
C(3) – Pd – P(1)	85.5(3)	P(2) – Pd – P(1)	164.45(3)
C – Pd – Ge	172.05(14)	C(3) – Pd – Ge	156.8(3)
P(2) – Pd – Ge	99.24(2)	P(1) – Pd – Ge	94.27(2)
C(61) – Ge – C(51)	106.54(13)	C(61) – Ge – Pd	118.22(9)
C(51) – Ge – Pd	118.37(9)	C(61) – Ge – H(2)	99.3(13)
C(51) – Ge – H(2)	98.9(13)	Pd – Ge – H(2)	112.2(13)
C(12) – P(1) – C(32)	105.43(16)	C(12) – P(1) – C(31)	106.14(16)
C(32) – P(1) – C(31)	106.12(16)	C(12) – P(1) – Pd	102.35(11)
C(32) – P(1) – Pd	122.70(12)	C(31) – P(1) – Pd	112.71(11)
C(22) – P(2) – C(42)	101.20(17)	C(22) – P(2) – C(41)	108.58(17)
C(42) – P(2) – C(41)	108.0(2)	C(22) – P(2) – Pd	103.50(11)
C(42) – P(2) – Pd	120.85(16)	C(41) – P(2) – Pd	113.36(14)
C(16) – C(11) – C(12)	117.2(3)	C(16) – C(11) – C(3)	112.4(5)
C(12) – C(11) – C(3)	121.4(4)	C(16) – C(11) – C	127.1(3)
C(12) – C(11) – C	114.3(3)	C(13) – C(12) – C(11)	120.7(3)
C(13) – C(12) – P(1)	123.8(3)	C(11) – C(12) – P(1)	115.2(2)
C(14) – C(13) – C(12)	120.1(3)	C(14) – C(13) – H(13)	119.9
C(12) – C(13) – H(13)	119.9	C(15) – C(14) – C(13)	119.4(3)
C(15) – C(14) – H(14)	120.3	C(13) – C(14) – H(14)	120.3
C(14) – C(15) – C(16)	120.5(3)	C(14) – C(15) – H(15)	119.7
C(16) – C(15) – H(15)	119.7	C(15) – C(16) – C(11)	121.3(3)
C(15) – C(16) – H(16)	119.3	C(11) – C(16) – H(16)	119.3
C(22) – C(21) – C(26)	117.4(3)	C(22) – C(21) – C	121.6(3)
C(26) – C(21) – C	118.8(3)	C(22) – C(21) – C(3)	105.9(4)
C(26) – C(21) – C(3)	130.3(4)	C(23) – C(22) – C(21)	119.8(3)
C(23) – C(22) – P(2)	124.4(3)	C(21) – C(22) – P(2)	115.1(3)
C(24) – C(23) – C(22)	121.4(4)	C(24) – C(23) – H(23)	119.3
C(22) – C(23) – H(23)	119.3	C(25) – C(24) – C(23)	119.5(4)
C(25) – C(24) – H(24)	120.3	C(23) – C(24) – H(24)	120.3
C(26) – C(25) – C(24)	119.4(3)	C(26) – C(25) – H(25)	120.3
C(24) – C(25) – H(25)	120.3	C(25) – C(26) – C(21)	122.2(3)
C(25) – C(26) – H(26)	118.9	C(21) – C(26) – H(26)	118.9
C(35) – C(32) – C(36)	111.1(3)	C(35) – C(32) – P(1)	112.6(2)
C(36) – C(32) – P(1)	108.1(3)	C(35) – C(32) – H(32)	108.3
C(36) – C(32) – H(32)	108.3	P(1) – C(32) – H(32)	108.3
C(34) – C(31) – C(33)	110.6(3)	C(34) – C(31) – P(1)	116.5(2)
C(33) – C(31) – P(1)	109.2(2)	C(34) – C(31) – H(31)	106.7
C(33) – C(31) – H(31)	106.7	P(1) – C(31) – H(31)	106.7
C(31) – C(33) – H(33A)	109.5	C(31) – C(33) – H(33B)	109.5

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Table S35. – continued from previous page

atom – atom – atom	angle	atom – atom – atom	angle
H(33A) – C(33) – H(33B)	109.5	C(31) – C(33) – H(33C)	109.5
H(33A) – C(33) – H(33C)	109.5	H(33B) – C(33) – H(33C)	109.5
C(31) – C(34) – H(34A)	109.5	C(31) – C(34) – H(34B)	109.5
H(34A) – C(34) – H(34B)	109.5	C(31) – C(34) – H(34C)	109.5
H(34A) – C(34) – H(34C)	109.5	H(34B) – C(34) – H(34C)	109.5
C(32) – C(35) – H(35A)	109.5	C(32) – C(35) – H(35B)	109.5
H(35A) – C(35) – H(35B)	109.5	C(32) – C(35) – H(35C)	109.5
H(35A) – C(35) – H(35C)	109.5	H(35B) – C(35) – H(35C)	109.5
C(32) – C(36) – H(36A)	109.5	C(32) – C(36) – H(36B)	109.5
H(36A) – C(36) – H(36B)	109.5	C(32) – C(36) – H(36C)	109.5
H(36A) – C(36) – H(36C)	109.5	H(36B) – C(36) – H(36C)	109.5
C(21) – C – C(11)	113.1(4)	C(21) – C – Pd	114.1(3)
C(11) – C – Pd	109.5(3)	C(21) – C – H(1)	106.5
C(11) – C – H(1)	106.5	Pd – C – H(1)	106.5
C(11) – C(3) – C(21)	107.0(6)	C(11) – C(3) – Pd	108.7(6)
C(21) – C(3) – Pd	105.6(5)	C(11) – C(3) – H(3)	111.8
C(21) – C(3) – H(3)	111.8	Pd – C(3) – H(3)	111.8
C(44) – C(41) – C(43)	111.9(4)	C(44) – C(41) – P(2)	115.9(3)
C(43) – C(41) – P(2)	107.9(3)	C(44) – C(41) – H(41)	106.9
C(43) – C(41) – H(41)	106.9	P(2) – C(41) – H(41)	106.9
C(45) – C(42) – C(46)	112.0(4)	C(45) – C(42) – P(2)	112.6(3)
C(46) – C(42) – P(2)	108.4(3)	C(45) – C(42) – H(42)	107.9
C(46) – C(42) – H(42)	107.9	P(2) – C(42) – H(42)	107.9
C(41) – C(43) – H(43A)	109.5	C(41) – C(43) – H(43B)	109.5
H(43A) – C(43) – H(43B)	109.5	C(41) – C(43) – H(43C)	109.5
H(43A) – C(43) – H(43C)	109.5	H(43B) – C(43) – H(43C)	109.5
C(41) – C(44) – H(44A)	109.5	C(41) – C(44) – H(44B)	109.5
H(44A) – C(44) – H(44B)	109.5	C(41) – C(44) – H(44C)	109.5
H(44A) – C(44) – H(44C)	109.5	H(44B) – C(44) – H(44C)	109.5
C(42) – C(45) – H(45A)	109.5	C(42) – C(45) – H(45B)	109.5
H(45A) – C(45) – H(45B)	109.5	C(42) – C(45) – H(45C)	109.5
H(45A) – C(45) – H(45C)	109.5	H(45B) – C(45) – H(45C)	109.5
C(42) – C(46) – H(46A)	109.5	C(42) – C(46) – H(46B)	109.5
H(46A) – C(46) – H(46B)	109.5	C(42) – C(46) – H(46C)	109.5
H(46A) – C(46) – H(46C)	109.5	H(46B) – C(46) – H(46C)	109.5
C(52) – C(51) – C(56)	116.7(3)	C(52) – C(51) – Ge	124.0(3)
C(56) – C(51) – Ge	119.2(2)	C(53) – C(52) – C(51)	121.4(4)
C(53) – C(52) – H(52)	119.3	C(51) – C(52) – H(52)	119.3
C(54) – C(53) – C(52)	120.3(4)	C(54) – C(53) – H(53)	119.9
C(52) – C(53) – H(53)	119.9	C(53) – C(54) – C(55)	120.1(4)
C(53) – C(54) – H(54)	120.0	C(55) – C(54) – H(54)	120.0
C(54) – C(55) – C(56)	119.6(4)	C(54) – C(55) – H(55)	120.2

Continued on next page

Table S35. – continued from previous page

atom – atom – atom	angle	atom – atom – atom	angle
C(56) – C(55) – H(55)	120.2	C(55) – C(56) – C(51)	121.9(4)
C(55) – C(56) – H(56)	119.0	C(51) – C(56) – H(56)	119.0
C(66) – C(61) – C(62)	116.7(3)	C(66) – C(61) – Ge	121.5(2)
C(62) – C(61) – Ge	121.6(2)	C(63) – C(62) – C(61)	121.6(3)
C(63) – C(62) – H(62)	119.2	C(61) – C(62) – H(62)	119.2
C(64) – C(63) – C(62)	120.4(3)	C(64) – C(63) – H(63)	119.8
C(62) – C(63) – H(63)	119.8	C(63) – C(64) – C(65)	119.3(3)
C(63) – C(64) – H(64)	120.3	C(65) – C(64) – H(64)	120.3
C(64) – C(65) – C(66)	120.3(3)	C(64) – C(65) – H(65)	119.8
C(66) – C(65) – H(65)	119.8	C(65) – C(66) – C(61)	121.7(3)
C(65) – C(66) – H(66)	119.2	C(61) – C(66) – H(66)	119.2

4.8 Crystal data for [PC(H)P]Pd($GePh_3$) (12)

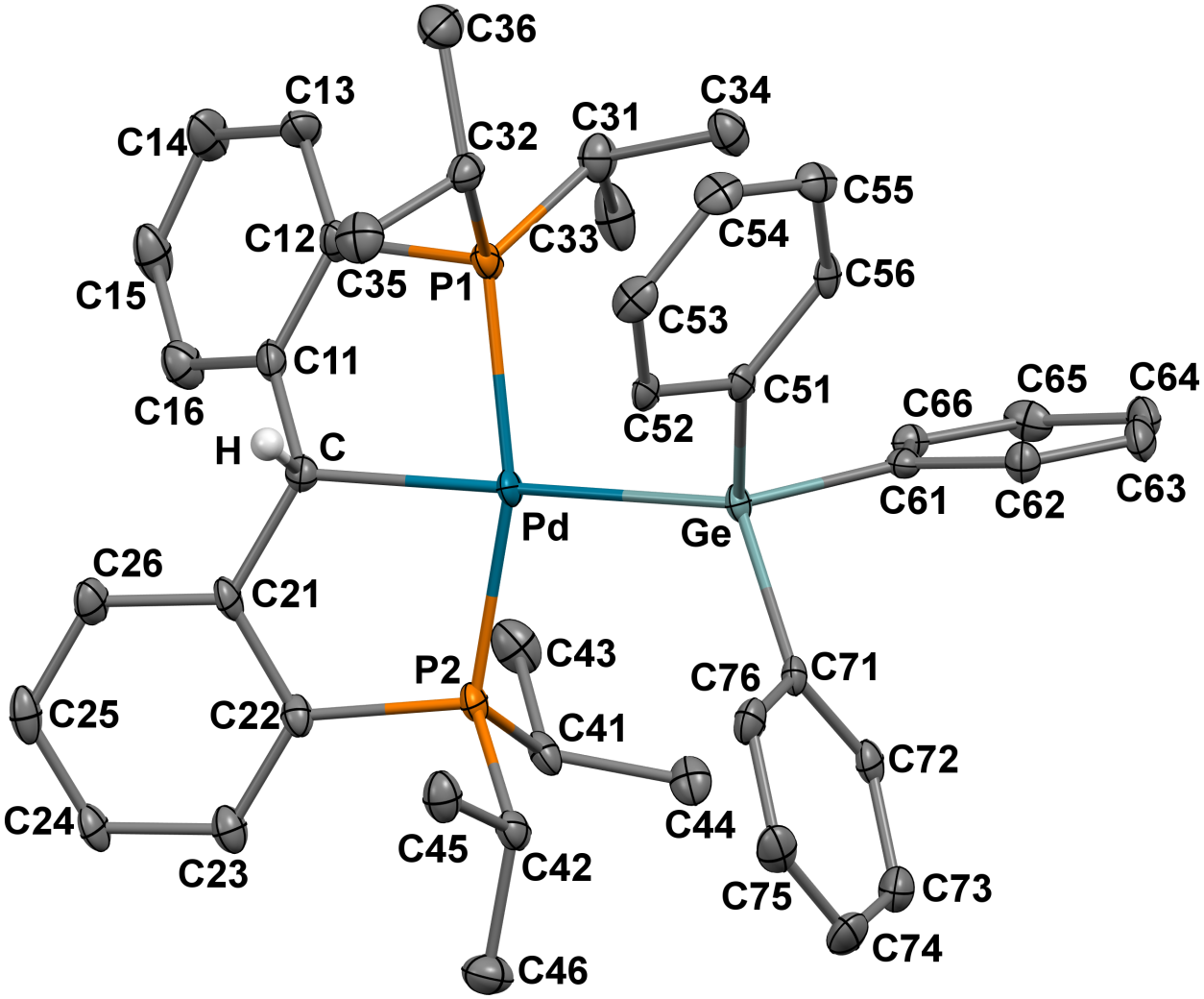

Figure S62. Thermal-ellipsoid representation of [PC(H)P]Pd($GePh_3$) (**12**) at 50% probability. Most hydrogen atoms were omitted for clarity.

Table S36. Crystal data and structure refinement for [PC(H)P]Pd($GePh_3$) (**12**).

Identification code:	cc294	
Empirical formula:	$C_{43}H_{52}GeP_2Pd$	
Formula weight:	809.78	
Temperature:	120(2) K	
Wavelength:	0.71073 Å	
Crystal system:	Monoclinic	
Space group:	$P2_1/c$	
Unit cell dimensions:	a = 11.6399(15) Å	$\alpha = 90°$
	b = 19.396(3) Å	$\beta = 105.713(2)°$
	c = 17.6306(18) Å	$\gamma = 90°$
Volume:	3831.6(8) Å^3	
Z:	4	
Density (calculated):	1.404 g·cm^{-3}	
Absorption coefficient (μ):	1.366 mm^{-1}	
F(000):	1672	
Crystal size:	0.09 × 0.08 × 0.06 mm^3	
θ range for data collection:	1.59 to 25.00°	
Index ranges:	$-13 \le h \le 13$, $-23 \le k \le 23$, $-13 \le l \le 20$	
Reflections collected:	28856	
Independent reflections:	6706 [R_{int} = 0.1035]	
Completeness to θ = 25.00°:	99.6 %	
Absorption correction:	Semi−empirical from equivalents	
Max. and min. transmission:	0.7454 and 0.5708	
Refinement method:	Full-matrix least-squares on F^2	
Data / restraints / parameters:	6706 / 0 / 426	
Goodness-of-fit on F^2:	0.986	
Final R indices [I>2σ(I)]:	R_1 = 0.0499, wR_2 = 0.0946	
R indices (all data):	R_1 = 0.0976, wR_2 = 0.1041	
Largest diff. peak and hole:	1.045 and −1.175 e$^-$·Å^{-3}	

Table S37. Atomic coordinates and equivalent isotropic displacement parameters (Å^2) for [PC(H)P]Pd($GePh_3$) (**12**). U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor

atom	x	y	z	U(eq)
Pd	0.34093(3)	0.53317(2)	0.27519(2)	0.019(1)
P(1)	0.29412(11)	0.43823(8)	0.19210(8)	0.021(1)
Ge	0.13522(4)	0.56408(3)	0.28232(3)	0.018(1)
P(2)	0.44506(11)	0.62511(7)	0.33964(8)	0.021(1)
C	0.5161(4)	0.4907(3)	0.2914(3)	0.020(1)
C(21)	0.6198(4)	0.5327(3)	0.3385(3)	0.022(1)
C(22)	0.6020(4)	0.5999(3)	0.3620(3)	0.021(1)
C(23)	0.6993(4)	0.6402(3)	0.4009(3)	0.026(1)
C(24)	0.8137(4)	0.6133(3)	0.4182(3)	0.025(1)
C(25)	0.8309(4)	0.5459(3)	0.3994(3)	0.029(2)
C(26)	0.7358(4)	0.5058(3)	0.3599(3)	0.026(1)
C(31)	0.1942(4)	0.4471(3)	0.0924(3)	0.029(1)
C(32)	0.2507(4)	0.3565(3)	0.2302(3)	0.026(1)
C(33)	0.2283(5)	0.5111(3)	0.0520(3)	0.043(2)
C(34)	0.0630(4)	0.4467(3)	0.0907(3)	0.031(2)
C(35)	0.3394(5)	0.3383(3)	0.3074(3)	0.035(2)
C(36)	0.2318(5)	0.2964(3)	0.1734(4)	0.039(2)
C(41)	0.4371(4)	0.7028(3)	0.2787(3)	0.024(1)
C(42)	0.4221(4)	0.6517(3)	0.4349(3)	0.024(1)
C(43)	0.4530(5)	0.6817(3)	0.1985(3)	0.037(2)
C(44)	0.3226(4)	0.7433(3)	0.2679(3)	0.029(1)
C(45)	0.4421(4)	0.5887(3)	0.4894(3)	0.030(1)
C(46)	0.4942(5)	0.7138(3)	0.4770(3)	0.036(2)
C(51)	0.0629(4)	0.4756(3)	0.3029(3)	0.020(1)
C(52)	0.1229(4)	0.4326(3)	0.3646(3)	0.020(1)
C(53)	0.0821(5)	0.3666(3)	0.3745(3)	0.027(1)
C(54)	−0.0189(5)	0.3412(3)	0.3224(3)	0.027(1)
C(55)	−0.0817(4)	0.3825(3)	0.2617(3)	0.026(1)
C(56)	−0.0423(4)	0.4483(3)	0.2526(3)	0.020(1)
C(61)	0.0084(4)	0.6095(3)	0.1977(3)	0.019(1)
C(62)	−0.1066(4)	0.6158(3)	0.2079(3)	0.023(1)
C(63)	−0.1972(4)	0.6481(3)	0.1527(3)	0.029(1)
C(64)	−0.1754(5)	0.6765(3)	0.0860(3)	0.029(1)
C(65)	−0.0628(5)	0.6723(3)	0.0752(3)	0.027(1)
C(66)	0.0273(4)	0.6388(3)	0.1300(3)	0.020(1)
C(71)	0.1222(4)	0.6246(3)	0.3713(3)	0.018(1)
C(72)	0.1009(4)	0.6945(3)	0.3603(3)	0.024(1)
C(73)	0.1068(4)	0.7400(3)	0.4215(3)	0.031(1)
C(74)	0.1336(5)	0.7153(3)	0.4980(4)	0.036(2)

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Table S37. – continued from previous page

atom	x	y	x	U(eq)
C(75)	0.1497(4)	0.6453(3)	0.5116(3)	0.031(2)
C(76)	0.1444(4)	0.6004(3)	0.4489(3)	0.026(1)
C(11)	0.5295(4)	0.4640(3)	0.2136(3)	0.024(1)
C(12)	0.4360(4)	0.4241(3)	0.1674(3)	0.023(1)
C(13)	0.4483(5)	0.3909(3)	0.1001(3)	0.033(2)
C(14)	0.5496(5)	0.3999(3)	0.0746(3)	0.039(2)
C(15)	0.6366(5)	0.4434(3)	0.1159(3)	0.036(2)
C(16)	0.6277(4)	0.4744(3)	0.1850(3)	0.031(1)
H	0.5166	0.4483	0.3238	0.024
H(23)	0.6871	0.6862	0.4156	0.032
H(24)	0.8802	0.6414	0.4429	0.030
H(25)	0.9090	0.5269	0.4139	0.035
H(26)	0.7490	0.4595	0.3469	0.032
H(31)	0.2079	0.4060	0.0617	0.035
H(32)	0.1726	0.3650	0.2420	0.031
H(33A)	0.3130	0.5086	0.0535	0.065
H(33B)	0.2140	0.5526	0.0797	0.065
H(33C)	0.1798	0.5128	−0.0029	0.065
H(34A)	0.0141	0.4439	0.0359	0.046
H(34B)	0.0438	0.4892	0.1147	0.046
H(34C)	0.0464	0.4069	0.1202	0.046
H(35A)	0.3138	0.2960	0.3285	0.053
H(35B)	0.3437	0.3761	0.3451	0.053
H(35C)	0.4182	0.3311	0.2988	0.053
H(36A)	0.1665	0.3071	0.1267	0.058
H(36B)	0.2117	0.2551	0.1991	0.058
H(36C)	0.3051	0.2881	0.1576	0.058
H(41)	0.5052	0.7335	0.3051	0.029
H(42)	0.3360	0.6643	0.4244	0.029
H(43A)	0.3876	0.6511	0.1717	0.056
H(43B)	0.5293	0.6576	0.2060	0.056
H(43C)	0.4523	0.7230	0.1663	0.056
H(44A)	0.3255	0.7847	0.2366	0.044
H(44B)	0.3136	0.7569	0.3195	0.044
H(44C)	0.2546	0.7147	0.2406	0.044
H(45A)	0.3924	0.5504	0.4627	0.045
H(45B)	0.4204	0.6002	0.5378	0.045
H(45C)	0.5263	0.5751	0.5025	0.045
H(46A)	0.4902	0.7513	0.4391	0.054
H(46B)	0.5776	0.7002	0.4994	0.054
H(46C)	0.4606	0.7296	0.5193	0.054
H(52)	0.1937	0.4489	0.4009	0.024

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Table S37. – continued from previous page

atom	x	y	x	U(eq)
H(53)	0.1244	0.3390	0.4175	0.033
H(54)	−0.0452	0.2957	0.3281	0.032
H(55)	−0.1525	0.3656	0.2260	0.032
H(56)	−0.0879	0.4762	0.2110	0.024
H(62)	−0.1223	0.5973	0.2540	0.028
H(63)	−0.2747	0.6509	0.1604	0.035
H(64)	−0.2378	0.6988	0.0478	0.035
H(65)	−0.0470	0.6925	0.0300	0.033
H(66)	0.1041	0.6356	0.1212	0.024
H(72)	0.0813	0.7120	0.3081	0.029
H(73)	0.0925	0.7878	0.4112	0.037
H(74)	0.1410	0.7462	0.5408	0.043
H(75)	0.1644	0.6277	0.5637	0.038
H(76)	0.1560	0.5524	0.4590	0.031
H(13)	0.3863	0.3617	0.0713	0.040
H(14)	0.5586	0.3763	0.0293	0.047
H(15)	0.7041	0.4526	0.0969	0.044
H(16)	0.6906	0.5034	0.2134	0.037

Table S38. Anisotropic displacement parameters (Å^2) for [PC(H)P]Pd(GePh$_3$) (**12**). The anisotropic displacement factor exponent takes the form: $-2\pi^2$[h^{2}a*^{2}U$_{11}$ + ...+ 2hka*b*U$_{12}$].

atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Pd	0.0082(2)	0.0240(2)	0.0256(2)	−0.0029(2)	0.0058(2)	−0.0005(2)
P(1)	0.0118(6)	0.0291(9)	0.0235(8)	−0.0042(7)	0.0055(6)	−0.0022(6)
Ge	0.0094(3)	0.0228(3)	0.0214(3)	0.0012(3)	0.0055(2)	0.0001(2)
P(2)	0.0103(6)	0.0256(9)	0.0264(9)	−0.0005(7)	0.0051(6)	−0.0002(6)
C	0.017(3)	0.020(3)	0.024(3)	0.000(3)	0.005(2)	0.002(2)
C(21)	0.009(2)	0.034(3)	0.023(3)	0.001(3)	0.005(2)	−0.001(2)
C(22)	0.015(3)	0.022(3)	0.027(3)	0.005(3)	0.006(2)	−0.001(2)
C(23)	0.017(3)	0.035(4)	0.029(3)	0.004(3)	0.008(2)	−0.001(2)
C(24)	0.011(3)	0.038(4)	0.027(3)	0.003(3)	0.007(2)	−0.003(2)
C(25)	0.016(3)	0.048(4)	0.027(3)	0.013(3)	0.010(2)	0.006(3)
C(26)	0.018(3)	0.039(4)	0.026(3)	−0.001(3)	0.011(2)	0.002(2)
C(31)	0.023(3)	0.035(4)	0.033(4)	0.002(3)	0.013(3)	0.001(3)
C(32)	0.020(3)	0.023(4)	0.036(4)	−0.005(3)	0.012(3)	−0.001(2)
C(33)	0.024(3)	0.068(5)	0.038(4)	0.017(4)	0.010(3)	0.006(3)
C(34)	0.020(3)	0.045(4)	0.028(3)	−0.002(3)	0.007(2)	−0.002(3)
C(35)	0.037(3)	0.033(4)	0.037(4)	0.006(3)	0.011(3)	0.000(3)
C(36)	0.029(3)	0.034(4)	0.055(4)	−0.009(3)	0.014(3)	−0.006(3)
C(41)	0.014(3)	0.030(3)	0.027(3)	0.004(3)	0.000(2)	−0.004(2)
C(42)	0.015(3)	0.031(4)	0.027(3)	−0.004(3)	0.006(2)	−0.002(2)
C(43)	0.031(3)	0.053(5)	0.029(4)	0.005(3)	0.009(3)	−0.007(3)
C(44)	0.026(3)	0.026(3)	0.035(4)	0.010(3)	0.008(3)	−0.001(3)
C(45)	0.024(3)	0.041(4)	0.028(4)	0.005(3)	0.010(3)	0.004(3)
C(46)	0.034(3)	0.038(4)	0.037(4)	−0.012(3)	0.011(3)	−0.010(3)
C(51)	0.0130(17)	0.026(2)	0.022(2)	−0.0037(18)	0.0087(15)	0.0031(16)
C(52)	0.0130(17)	0.026(2)	0.022(2)	−0.0037(18)	0.0087(15)	0.0031(16)
C(53)	0.037(3)	0.024(3)	0.024(3)	0.007(3)	0.013(3)	0.004(3)
C(54)	0.031(3)	0.020(3)	0.036(4)	0.002(3)	0.020(3)	−0.009(3)
C(55)	0.020(3)	0.030(4)	0.034(4)	−0.007(3)	0.015(3)	−0.009(3)
C(56)	0.012(2)	0.029(4)	0.023(3)	0.004(2)	0.010(2)	0.005(2)
C(61)	0.018(3)	0.018(3)	0.022(3)	−0.006(2)	0.005(2)	−0.003(2)
C(62)	0.020(3)	0.028(3)	0.022(3)	0.002(3)	0.006(2)	0.004(2)
C(63)	0.013(3)	0.031(4)	0.041(4)	0.000(3)	0.004(3)	0.002(2)
C(64)	0.022(3)	0.026(4)	0.031(4)	0.001(3)	−0.004(3)	0.005(2)
C(65)	0.035(3)	0.027(4)	0.018(3)	0.004(3)	0.005(3)	−0.005(3)
C(66)	0.018(3)	0.022(3)	0.022(3)	−0.003(3)	0.011(2)	−0.004(2)
C(71)	0.010(2)	0.021(3)	0.023(3)	0.003(3)	0.004(2)	0.003(2)
C(72)	0.011(3)	0.033(4)	0.027(3)	0.002(3)	0.006(2)	0.002(2)
C(73)	0.022(3)	0.031(4)	0.039(4)	−0.003(3)	0.006(3)	0.006(3)
C(74)	0.032(3)	0.041(4)	0.035(4)	−0.013(3)	0.011(3)	0.011(3)
C(75)	0.026(3)	0.049(4)	0.021(3)	−0.003(3)	0.010(2)	0.006(3)

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Table S38. – continued from previous page

atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C(76)	0.019(3)	0.029(4)	0.034(4)	0.001(3)	0.012(2)	0.006(2)
C(11)	0.013(2)	0.026(3)	0.031(3)	0.001(3)	0.004(2)	0.003(2)
C(12)	0.016(3)	0.035(4)	0.019(3)	−0.003(3)	0.006(2)	0.003(2)
C(13)	0.024(3)	0.045(4)	0.030(4)	−0.017(3)	0.007(3)	0.001(3)
C(14)	0.023(3)	0.067(5)	0.032(4)	−0.013(3)	0.016(3)	0.002(3)
C(15)	0.020(3)	0.063(5)	0.028(4)	0.007(3)	0.010(3)	0.002(3)
C(16)	0.023(3)	0.043(4)	0.030(4)	0.000(3)	0.010(2)	−0.005(3)

Table S39. Distances [Å] for [PC(H)P]Pd($GePh_3$) (**12**).

atom – atom	distance	atom – atom	distance
Pd – C	2.145(5)	Pd – P(2)	2.2791(15)
Pd – P(1)	2.3242(15)	Pd – Ge	2.5043(7)
P(1) – C(31)	1.834(6)	P(1) – C(12)	1.839(5)
P(1) – C(32)	1.845(6)	Ge – C(51)	1.989(5)
Ge – C(71)	1.997(5)	Ge – C(61)	1.997(5)
P(2) – C(22)	1.828(5)	P(2) – C(41)	1.838(5)
P(2) – C(42)	1.843(5)	C – C(21)	1.507(7)
C – C(11)	1.513(7)	C – H	1.0000
C(21) – C(22)	1.399(7)	C(21) – C(26)	1.400(6)
C(22) – C(23)	1.393(7)	C(23) – C(24)	1.386(7)
C(23) – H(23)	0.9500	C(24) – C(25)	1.376(7)
C(24) – H(24)	0.9500	C(25) – C(26)	1.378(7)
C(25) – H(25)	0.9500	C(26) – H(26)	0.9500
C(31) – C(34)	1.519(7)	C(31) – C(33)	1.536(8)
C(31) – H(31)	1.0000	C(32) – C(35)	1.511(7)
C(32) – C(36)	1.513(7)	C(32) – H(32)	1.0000
C(33) – H(33A)	0.9800	C(33) – H(33B)	0.9800
C(33) – H(33C)	0.9800	C(34) – H(34A)	0.9800
C(34) – H(34B)	0.9800	C(34) – H(34C)	0.9800
C(35) – H(35A)	0.9800	C(35) – H(35B)	0.9800
C(35) – H(35C)	0.9800	C(36) – H(36A)	0.9800
C(36) – H(36B)	0.9800	C(36) – H(36C)	0.9800
C(41) – C(44)	1.514(7)	C(41) – C(43)	1.532(7)
C(41) – H(41)	1.0000	C(42) – C(45)	1.534(7)
C(42) – C(46)	1.539(7)	C(42) – H(42)	1.0000
C(43) – H(43A)	0.9800	C(43) – H(43B)	0.9800
C(43) – H(43C)	0.9800	C(44) – H(44A)	0.9800
C(44) – H(44B)	0.9800	C(44) – H(44C)	0.9800
C(45) – H(45A)	0.9800	C(45) – H(45B)	0.9800
C(45) – H(45C)	0.9800	C(46) – H(46A)	0.9800
C(46) – H(46B)	0.9800	C(46) – H(46C)	0.9800
C(51) – C(52)	1.398(7)	C(51) – C(56)	1.405(7)
C(52) – C(53)	1.393(7)	C(52) – H(52)	0.9500
C(53) – C(54)	1.372(7)	C(53) – H(53)	0.9500
C(54) – C(55)	1.377(7)	C(54) – H(54)	0.9500
C(55) – C(56)	1.381(7)	C(55) – H(55)	0.9500
C(56) – H(56)	0.9500	C(61) – C(66)	1.393(7)
C(61) – C(62)	1.403(6)	C(62) – C(63)	1.378(7)
C(62) – H(62)	0.9500	C(63) – C(64)	1.383(7)
C(63) – H(63)	0.9500	C(64) – C(65)	1.377(7)
C(64) – H(64)	0.9500	C(65) – C(66)	1.380(7)

Continued on next page

Table S39. – continued from previous page

atom – atom	distance	atom – atom	distance
C(65) – H(65)	0.9500	C(66) – H(66)	0.9500
C(71) – C(72)	1.382(7)	C(71) – C(76)	1.403(7)
C(72) – C(73)	1.381(7)	C(72) – H(72)	0.9500
C(73) – C(74)	1.386(8)	C(73) – H(73)	0.9500
C(74) – C(75)	1.383(8)	C(74) – H(74)	0.9500
C(75) – C(76)	1.395(7)	C(75) – H(75)	0.9500
C(76) – H(76)	0.9500	C(11) – C(16)	1.384(7)
C(11) – C(12)	1.403(7)	C(12) – C(13)	1.390(7)
C(13) – C(14)	1.382(7)	C(13) – H(13)	0.9500
C(14) – C(15)	1.367(8)	C(14) – H(14)	0.9500
C(15) – C(16)	1.388(8)	C(15) – H(15)	0.9500
C(16) – H(16)	0.9500		

Table S40. Angles [°] for [PC(H)P]Pd($GePh_3$) (**12**).

atom – atom – atom	angle	atom – atom – atom	angle
C – Pd – P(2)	82.89(14)	C – Pd – P(1)	80.31(14)
P(2) – Pd – P(1)	159.47(5)	C – Pd – Ge	166.50(14)
P(2) – Pd – Ge	100.04(4)	P(1) – Pd – Ge	99.04(4)
C(31) – P(1) – C(12)	99.5(2)	C(31) – P(1) – C(32)	105.3(2)
C(12) – P(1) – C(32)	108.0(2)	C(31) – P(1) – Pd	120.6(2)
C(12) – P(1) – Pd	101.26(18)	C(32) – P(1) – Pd	119.48(18)
C(51) – Ge – C(71)	103.8(2)	C(51) – Ge – C(61)	104.7(2)
C(71) – Ge – C(61)	97.4(2)	C(51) – Ge – Pd	105.09(13)
C(71) – Ge – Pd	117.19(13)	C(61) – Ge – Pd	126.27(14)
C(22) – P(2) – C(41)	103.6(2)	C(22) – P(2) – C(42)	105.2(2)
C(41) – P(2) – C(42)	107.8(3)	C(22) – P(2) – Pd	105.29(18)
C(41) – P(2) – Pd	114.47(18)	C(42) – P(2) – Pd	118.97(17)
C(21) – C – C(11)	114.9(4)	C(21) – C – Pd	117.2(3)
C(11) – C – Pd	109.8(3)	C(21) – C – H	104.5
C(11) – C – H	104.5	Pd – C – H	104.5
C(22) – C(21) – C(26)	118.5(5)	C(22) – C(21) – C	120.4(4)
C(26) – C(21) – C	121.1(5)	C(23) – C(22) – C(21)	120.2(5)
C(23) – C(22) – P(2)	126.0(4)	C(21) – C(22) – P(2)	113.8(4)
C(24) – C(23) – C(22)	120.1(5)	C(24) – C(23) – H(23)	119.9
C(22) – C(23) – H(23)	119.9	C(25) – C(24) – C(23)	119.9(5)
C(25) – C(24) – H(24)	120.1	C(23) – C(24) – H(24)	120.1
C(24) – C(25) – C(26)	120.6(5)	C(24) – C(25) – H(25)	119.7
C(26) – C(25) – H(25)	119.7	C(25) – C(26) – C(21)	120.6(5)
C(25) – C(26) – H(26)	119.7	C(21) – C(26) – H(26)	119.7
C(34) – C(31) – C(33)	112.2(5)	C(34) – C(31) – P(1)	113.1(4)
C(33) – C(31) – P(1)	110.1(4)	C(34) – C(31) – H(31)	107.0
C(33) – C(31) – H(31)	107.0	P(1) – C(31) – H(31)	107.0
C(35) – C(32) – C(36)	111.0(5)	C(35) – C(32) – P(1)	109.9(4)
C(36) – C(32) – P(1)	115.2(4)	C(35) – C(32) – H(32)	106.7
C(36) – C(32) – H(32)	106.7	P(1) – C(32) – H(32)	106.7
C(31) – C(33) – H(33A)	109.5	C(31) – C(33) – H(33B)	109.5
H(33A) – C(33) – H(33B)	109.5	C(31) – C(33) – H(33C)	109.5
H(33A) – C(33) – H(33C)	109.5	H(33B) – C(33) – H(33C)	109.5
C(31) – C(34) – H(34A)	109.5	C(31) – C(34) – H(34B)	109.5
H(34A) – C(34) – H(34B)	109.5	C(31) – C(34) – H(34C)	109.5
H(34A) – C(34) – H(34C)	109.5	H(34B) – C(34) – H(34C)	109.5
C(32) – C(35) – H(35A)	109.5	C(32) – C(35) – H(35B)	109.5
H(35A) – C(35) – H(35B)	109.5	C(32) – C(35) – H(35C)	109.5
H(35A) – C(35) – H(35C)	109.5	H(35B) – C(35) – H(35C)	109.5
C(32) – C(36) – H(36A)	109.5	C(32) – C(36) – H(36B)	109.5
H(36A) – C(36) – H(36B)	109.5	C(32) – C(36) – H(36C)	109.5

Continued on next page

Table S40. – continued from previous page

atom – atom – atom	angle	atom – atom – atom	angle
H(36A) – C(36) – H(36C)	109.5	H(36B) – C(36) – H(36C)	109.5
C(44) – C(41) – C(43)	110.2(4)	C(44) – C(41) – P(2)	113.8(4)
C(43) – C(41) – P(2)	108.8(4)	C(44) – C(41) – H(41)	108.0
C(43) – C(41) – H(41)	108.0	P(2) – C(41) – H(41)	108.0
C(45) – C(42) – C(46)	110.6(5)	C(45) – C(42) – P(2)	108.3(4)
C(46) – C(42) – P(2)	117.7(4)	C(45) – C(42) – H(42)	106.6
C(46) – C(42) – H(42)	106.6	P(2) – C(42) – H(42)	106.6
C(41) – C(43) – H(43A)	109.5	C(41) – C(43) – H(43B)	109.5
H(43A) – C(43) – H(43B)	109.5	C(41) – C(43) – H(43C)	109.5
H(43A) – C(43) – H(43C)	109.5	H(43B) – C(43) – H(43C)	109.5
C(41) – C(44) – H(44A)	109.5	C(41) – C(44) – H(44B)	109.5
H(44A) – C(44) – H(44B)	109.5	C(41) – C(44) – H(44C)	109.5
H(44A) – C(44) – H(44C)	109.5	H(44B) – C(44) – H(44C)	109.5
C(42) – C(45) – H(45A)	109.5	C(42) – C(45) – H(45B)	109.5
H(45A) – C(45) – H(45B)	109.5	C(42) – C(45) – H(45C)	109.5
H(45A) – C(45) – H(45C)	109.5	H(45B) – C(45) – H(45C)	109.5
C(42) – C(46) – H(46A)	109.5	C(42) – C(46) – H(46B)	109.5
H(46A) – C(46) – H(46B)	109.5	C(42) – C(46) – H(46C)	109.5
H(46A) – C(46) – H(46C)	109.5	H(46B) – C(46) – H(46C)	109.5
C(52) – C(51) – C(56)	115.6(5)	C(52) – C(51) – Ge	120.6(4)
C(56) – C(51) – Ge	123.3(4)	C(53) – C(52) – C(51)	122.0(5)
C(53) – C(52) – H(52)	119.0	C(51) – C(52) – H(52)	119.0
C(54) – C(53) – C(52)	120.3(5)	C(54) – C(53) – H(53)	119.8
C(52) – C(53) – H(53)	119.8	C(53) – C(54) – C(55)	119.4(5)
C(53) – C(54) – H(54)	120.3	C(55) – C(54) – H(54)	120.3
C(54) – C(55) – C(56)	120.3(5)	C(54) – C(55) – H(55)	119.9
C(56) – C(55) – H(55)	119.9	C(55) – C(56) – C(51)	122.3(5)
C(55) – C(56) – H(56)	118.8	C(51) – C(56) – H(56)	118.8
C(66) – C(61) – C(62)	116.9(5)	C(66) – C(61) – Ge	124.3(3)
C(62) – C(61) – Ge	118.7(4)	C(63) – C(62) – C(61)	121.6(5)
C(63) – C(62) – H(62)	119.2	C(61) – C(62) – H(62)	119.2
C(62) – C(63) – C(64)	120.0(5)	C(62) – C(63) – H(63)	120.0
C(64) – C(63) – H(63)	120.0	C(65) – C(64) – C(63)	119.6(5)
C(65) – C(64) – H(64)	120.2	C(63) – C(64) – H(64)	120.2
C(64) – C(65) – C(66)	120.2(5)	C(64) – C(65) – H(65)	119.9
C(66) – C(65) – H(65)	119.9	C(65) – C(66) – C(61)	121.7(5)
C(65) – C(66) – H(66)	119.2	C(61) – C(66) – H(66)	119.2
C(72) – C(71) – C(76)	116.3(5)	C(72) – C(71) – Ge	121.0(4)
C(76) – C(71) – Ge	122.5(4)	C(73) – C(72) – C(71)	123.4(5)
C(73) – C(72) – H(72)	118.3	C(71) – C(72) – H(72)	118.3
C(72) – C(73) – C(74)	119.3(6)	C(72) – C(73) – H(73)	120.4
C(74) – C(73) – H(73)	120.4	C(75) – C(74) – C(73)	119.5(5)

Continued on next page

Table S40. – continued from previous page

atom – atom – atom	angle	atom – atom – atom	angle
C(75) – C(74) – H(74)	120.2	C(73) – C(74) – H(74)	120.2
C(74) – C(75) – C(76)	120.0(5)	C(74) – C(75) – H(75)	120.0
C(76) – C(75) – H(75)	120.0	C(75) – C(76) – C(71)	121.4(5)
C(75) – C(76) – H(76)	119.3	C(71) – C(76) – H(76)	119.3
C(16) – C(11) – C(12)	117.2(5)	C(16) – C(11) – C	125.4(5)
C(12) – C(11) – C	117.4(4)	C(13) – C(12) – C(11)	120.5(5)
C(13) – C(12) – P(1)	125.3(4)	C(11) – C(12) – P(1)	112.6(4)
C(14) – C(13) – C(12)	120.9(5)	C(14) – C(13) – H(13)	119.5
C(12) – C(13) – H(13)	119.5	C(15) – C(14) – C(13)	118.6(5)
C(15) – C(14) – H(14)	120.7	C(13) – C(14) – H(14)	120.7
C(14) – C(15) – C(16)	120.9(5)	C(14) – C(15) – H(15)	119.5
C(16) – C(15) – H(15)	119.5	C(11) – C(16) – C(15)	121.5(5)
C(11) – C(16) – H(16)	119.2	C(15) – C(16) – H(16)	119.2

4.9 Crystal data for [PC(H)P]Pd(PMe$_3$)(GeHPh$_2$)·0.5C$_5$H$_{12}$ (**13**·0.5C$_5$H$_{12}$)

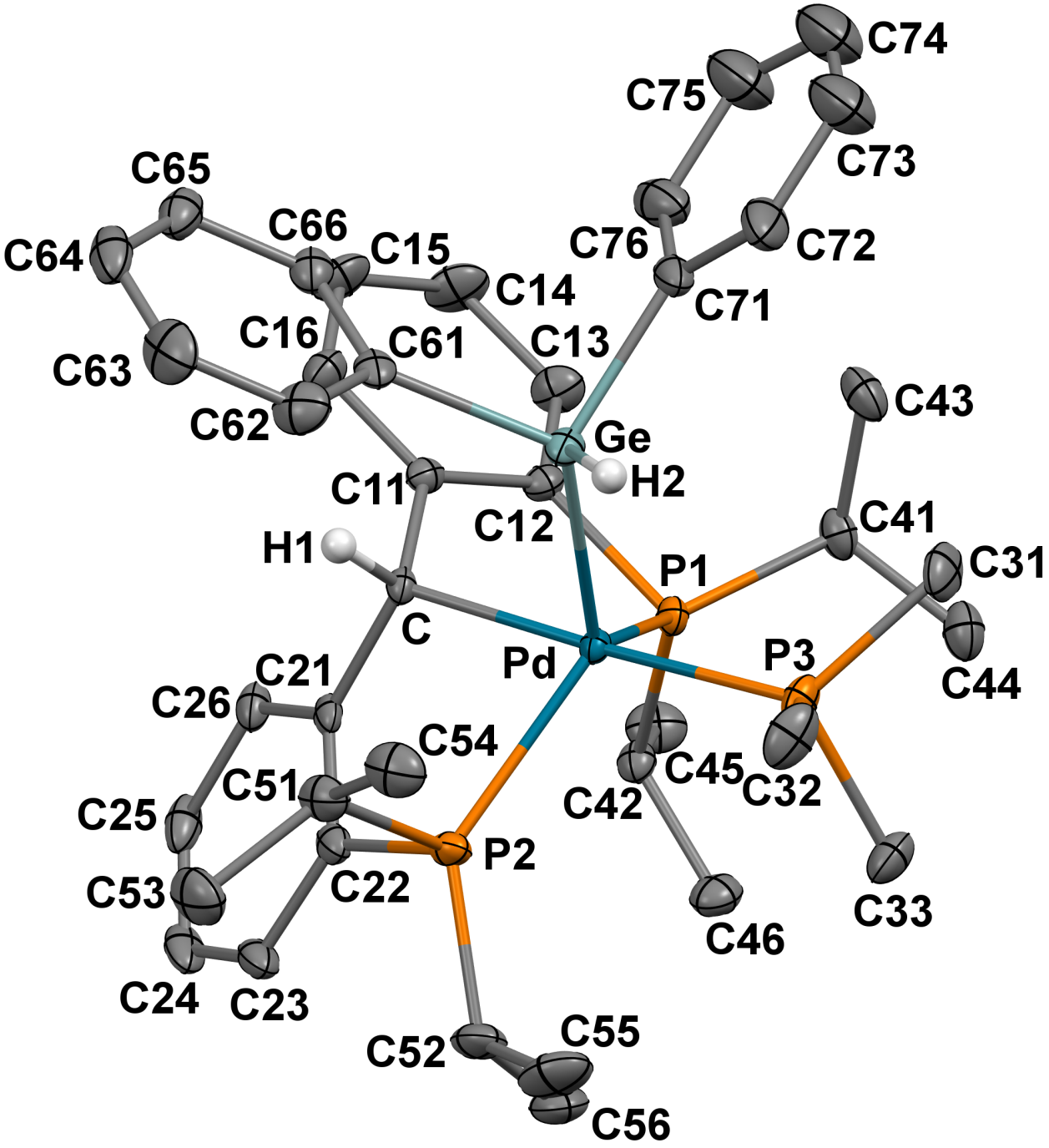

Figure S63. Thermal-ellipsoid representation of [PC(H)P]Pd(PMe$_3$)(GeHPh$_2$)·0.5C$_5$H$_{12}$ (**13**·**0.5C$_5$H$_{12}$**) at 50% probability. Most hydrogen atoms and the solvent were omitted for clarity.

Table S41. Crystal data and structure refinement for [PC(H)P]Pd(PMe_3)($GeHPh_2$)·0.5C_5H_{12} (**13·0.5C_5H_{12}**).

Identification code:	cc275	
Empirical formula:	$C_{85}H_{114}Ge_2P_6Pd_2$	
Formula weight:	1679.56	
Temperature:	120(2) K	
Wavelength:	0.71073 Å	
Crystal system:	Monoclinic	
Space group:	$P2_1/c$	
Unit cell dimensions:	a = 9.5430(4) Å	α = 90°
	b = 20.3870(10) Å	β = 99.3602(14)°
	c = 21.3674(11) Å	γ = 90°
Volume:	4101.7(3) Å^3	
Z:	2	
Density (calculated):	1.360 g·cm^{-3}	
Absorption coefficient (μ):	1.316 mm^{-1}	
F(000):	1740	
Crystal size:	0.12 × 0.09 × 0.08 mm^3	
θ range for data collection:	1.93 to 25.00°	
Index ranges:	$-11 \le h \le 11$, $-24 \le k \le 24$, $-25 \le l \le 25$	
Reflections collected:	98578	
Independent reflections:	7227 [R_{int} = 0.0462]	
Completeness to θ = 25.00°:	100.0 %	
Absorption correction:	Semi−empirical from equivalents	
Max. and min. transmission:	0.7458 and 0.6908	
Refinement method:	Full-matrix least-squares on F^2	
Data / restraints / parameters:	7227 / 0 / 442	
Goodness-of-fit on F^2:	1.062	
Final R indices [I>2σ(I)]:	R_1 = 0.0296, wR_2 = 0.0661	
R indices (all data):	R_1 = 0.0369, wR_2 = 0.0681	
Largest diff. peak and hole:	0.761 and −0.551 e$^-$·Å^{-3}	

Table S42. Atomic coordinates and equivalent isotropic displacement parameters (Å^2) for [PC(H)P]Pd(PMe_3)($GeHPh_2$)·0.5C_5H_{12} (**13·0.5C_5H_{12}**). U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor

atom	x	y	z	U(eq)
Pd	0.39060(2)	0.85971(1)	0.19690(1)	0.015(1)
Ge	0.39830(3)	0.79238(2)	0.29317(1)	0.022(1)
P(1)	0.42680(7)	0.97796(3)	0.20088(3)	0.018(1)
P(3)	0.61304(8)	0.81877(4)	0.18838(4)	0.025(1)
P(2)	0.24669(8)	0.81122(4)	0.10323(3)	0.023(1)
C(11)	0.1931(3)	0.95042(13)	0.25466(12)	0.019(1)
C(12)	0.2960(3)	0.99844(13)	0.25200(13)	0.021(1)
C(13)	0.2955(3)	1.05516(15)	0.28847(15)	0.032(1)
C(14)	0.1955(4)	1.06328(16)	0.32810(16)	0.040(1)
C(15)	0.0955(4)	1.01549(17)	0.33215(16)	0.039(1)
C(16)	0.0936(3)	0.95982(15)	0.29524(14)	0.028(1)
C(21)	0.0931(3)	0.90973(14)	0.14624(13)	0.020(1)
C(22)	0.1043(3)	0.87207(14)	0.09243(13)	0.024(1)
C(23)	0.0147(3)	0.88494(18)	0.03508(14)	0.034(1)
C(24)	−0.0796(3)	0.93640(19)	0.02990(16)	0.040(1)
C(25)	−0.0872(3)	0.97504(17)	0.08147(16)	0.037(1)
C(26)	−0.0026(3)	0.96193(15)	0.13977(15)	0.027(1)
C(31)	0.7607(3)	0.83655(18)	0.25135(16)	0.038(1)
C(81)	0.0000	1.0000	0.5000	0.081(3)
C(82)	0.1247(10)	0.9855(8)	0.5180(6)	0.102(4)
C(84)	−0.2110(12)	1.0573(4)	0.4993(5)	0.162(4)
C(83)	−0.049(3)	1.0496(13)	0.5191(7)	0.180(12)
C(32)	0.6339(4)	0.73049(16)	0.18152(19)	0.042(1)
C	0.1833(3)	0.89286(13)	0.21004(12)	0.017(1)
C(41)	0.5851(3)	1.02448(14)	0.24120(14)	0.027(1)
C(33)	0.6841(3)	0.84623(17)	0.11840(16)	0.035(1)
C(43)	0.6305(3)	0.99882(16)	0.30876(15)	0.036(1)
C(44)	0.7078(3)	1.02243(16)	0.20422(16)	0.036(1)
C(45)	0.3567(4)	1.10018(15)	0.13565(16)	0.036(1)
C(46)	0.4417(3)	1.00812(16)	0.07363(14)	0.033(1)
C(51)	0.1484(3)	0.73868(15)	0.12805(15)	0.032(1)
C(52)	0.2702(4)	0.79272(17)	0.02012(14)	0.037(1)
C(53)	0.0207(4)	0.71724(19)	0.07968(18)	0.049(1)
C(54)	0.2454(4)	0.68061(16)	0.15130(17)	0.042(1)
C(55)	0.3685(5)	0.73486(19)	0.01586(18)	0.053(1)
C(56)	0.3253(4)	0.85273(19)	−0.01128(15)	0.043(1)
C(61)	0.2199(3)	0.76284(14)	0.32178(13)	0.024(1)
C(62)	0.1658(4)	0.70062(17)	0.30742(17)	0.041(1)
C(63)	0.0435(4)	0.67861(19)	0.32856(19)	0.050(1)

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Table S42. – continued from previous page

atom	x	y	x	U(eq)
C(64)	−0.0261(3)	0.71854(19)	0.36455(17)	0.042(1)
C(65)	0.0244(3)	0.78078(18)	0.37959(16)	0.037(1)
C(66)	0.1466(3)	0.80241(15)	0.35833(14)	0.029(1)
C(71)	0.5084(3)	0.82604(18)	0.37222(14)	0.034(1)
C(72)	0.6200(4)	0.7876(2)	0.40476(17)	0.053(1)
C(73)	0.6991(5)	0.8081(3)	0.4606(2)	0.080(1)
C(74)	0.6687(5)	0.8665(3)	0.4848(2)	0.080(1)
C(75)	0.5595(5)	0.9061(3)	0.4551(2)	0.080(1)
C(76)	0.4790(4)	0.8852(2)	0.39767(17)	0.049(1)
C(42)	0.3623(3)	1.02607(14)	0.12759(13)	0.023(1)
H(2)	0.466(3)	0.7282(16)	0.2897(15)	0.038(9)
H(13)	0.3642	1.0884	0.2861	0.038
H(14)	0.1959	1.1021	0.3527	0.048
H(15)	0.0285	1.0208	0.3601	0.047
H(16)	0.0233	0.9273	0.2974	0.034
H(23)	0.0192	0.8578	−0.0007	0.040
H(24)	−0.1391	0.9450	−0.0093	0.048
H(25)	−0.1507	1.0112	0.0776	0.044
H(26)	−0.0104	0.9888	0.1754	0.032
H(31A)	0.8459	0.8138	0.2427	0.057
H(31B)	0.7374	0.8216	0.2920	0.057
H(31C)	0.7783	0.8839	0.2532	0.057
H(32A)	0.5662	0.7141	0.1454	0.063
H(32B)	0.6157	0.7092	0.2205	0.063
H(32C)	0.7309	0.7206	0.1749	0.063
H(1)	0.1356	0.8561	0.2293	0.020
H(41)	0.5563	1.0714	0.2442	0.032
H(33A)	0.6273	0.8276	0.0802	0.053
H(33B)	0.7828	0.8316	0.1215	0.053
H(33C)	0.6803	0.8942	0.1160	0.053
H(43A)	0.6462	0.9514	0.3075	0.054
H(43B)	0.5558	1.0081	0.3340	0.054
H(43C)	0.7187	1.0206	0.3280	0.054
H(44A)	0.7248	0.9770	0.1925	0.054
H(44B)	0.7933	1.0400	0.2305	0.054
H(44C)	0.6845	1.0490	0.1657	0.054
H(45A)	0.3097	1.1201	0.0960	0.054
H(45B)	0.4535	1.1174	0.1463	0.054
H(45C)	0.3032	1.1107	0.1698	0.054
H(46A)	0.3895	1.0248	0.0335	0.049
H(46B)	0.4500	0.9603	0.0712	0.049
H(46C)	0.5368	1.0277	0.0815	0.049

Continued on next page

Table S42. – continued from previous page

atom	x	y	x	U(eq)
H(51)	0.1080	0.7537	0.1660	0.039
H(52)	0.1750	0.7813	−0.0044	0.044
H(53A)	−0.0386	0.7555	0.0659	0.073
H(53B)	−0.0351	0.6850	0.0992	0.073
H(53C)	0.0539	0.6975	0.0429	0.073
H(54A)	0.2817	0.6609	0.1153	0.063
H(54B)	0.1912	0.6477	0.1708	0.063
H(54C)	0.3251	0.6961	0.1826	0.063
H(55A)	0.3848	0.7299	−0.0280	0.080
H(55B)	0.3247	0.6948	0.0292	0.080
H(55C)	0.4592	0.7425	0.0437	0.080
H(56A)	0.3225	0.8441	−0.0566	0.065
H(56B)	0.4233	0.8618	0.0086	0.065
H(56C)	0.2654	0.8907	−0.0060	0.065
H(62)	0.2134	0.6722	0.2825	0.049
H(63)	0.0085	0.6357	0.3179	0.060
H(64)	−0.1092	0.7034	0.3792	0.051
H(65)	−0.0240	0.8088	0.4044	0.045
H(66)	0.1808	0.8454	0.3691	0.034
H(72)	0.6408	0.7464	0.3875	0.064
H(73)	0.7740	0.7817	0.4820	0.096
H(74)	0.7237	0.8810	0.5234	0.096
H(75)	0.5395	0.9468	0.4733	0.096
H(76)	0.4044	0.9119	0.3766	0.059
H(42)	0.2619	1.0119	0.1134	0.027

Table S43. Anisotropic displacement parameters (Å^2) for [PC(H)P]Pd(PMe_3)($GeHPh_2$)·0.5C_5H_{12} (**13·0.5C_5H_{12}**). The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11} + ...+ 2hka^*b^*U_{12}]$.

atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Pd	0.0128(1)	0.0159(1)	0.0170(1)	0.0026(1)	0.0032(1)	0.0010(1)
Ge	0.0201(2)	0.0256(2)	0.0199(2)	0.0081(1)	0.0034(1)	0.0036(1)
P(1)	0.0149(3)	0.0173(4)	0.0206(4)	0.0021(3)	0.0034(3)	−0.0019(3)
P(3)	0.0200(4)	0.0238(4)	0.0335(4)	0.0066(3)	0.0106(3)	0.0065(3)
P(2)	0.0275(4)	0.0244(4)	0.0164(4)	−0.0028(3)	0.0031(3)	−0.0061(3)
C(11)	0.0193(14)	0.0218(14)	0.0169(14)	0.0022(11)	0.0025(11)	0.0055(11)
C(12)	0.0233(14)	0.0216(15)	0.0187(14)	0.0022(11)	0.0051(11)	0.0008(11)
C(13)	0.0403(18)	0.0219(16)	0.0335(17)	−0.0036(13)	0.0097(14)	−0.0016(13)
C(14)	0.056(2)	0.0292(18)	0.039(2)	−0.0116(15)	0.0191(17)	0.0054(16)
C(15)	0.043(2)	0.041(2)	0.0374(19)	−0.0034(16)	0.0224(16)	0.0091(16)
C(16)	0.0253(16)	0.0315(17)	0.0292(17)	0.0030(13)	0.0102(13)	0.0041(13)
C(21)	0.0124(13)	0.0249(15)	0.0224(14)	0.0075(12)	0.0026(11)	−0.0053(11)
C(22)	0.0199(14)	0.0306(17)	0.0214(15)	0.0060(12)	0.0014(11)	−0.0090(12)
C(23)	0.0264(16)	0.053(2)	0.0191(15)	0.0085(14)	−0.0030(12)	−0.0113(15)
C(24)	0.0230(16)	0.065(2)	0.0276(18)	0.0249(17)	−0.0062(13)	−0.0074(16)
C(25)	0.0179(15)	0.048(2)	0.044(2)	0.0265(17)	0.0055(14)	0.0047(14)
C(26)	0.0154(14)	0.0328(17)	0.0321(17)	0.0119(13)	0.0041(12)	0.0008(12)
C(31)	0.0183(15)	0.050(2)	0.045(2)	0.0121(17)	0.0039(14)	0.0110(14)
C(81)	0.087(7)	0.052(5)	0.096(8)	−0.007(4)	−0.007(5)	0.018(4)
C(82)	0.035(5)	0.164(13)	0.110(10)	−0.034(9)	0.020(6)	0.031(7)
C(84)	0.217(11)	0.093(6)	0.170(9)	0.040(6)	0.011(8)	0.020(7)
C(83)	0.20(2)	0.29(3)	0.054(8)	−0.025(13)	0.044(11)	−0.16(2)
C(32)	0.042(2)	0.0274(18)	0.062(2)	0.0074(16)	0.0240(18)	0.0126(15)
C	0.0124(12)	0.0189(14)	0.0195(14)	0.0043(11)	0.0031(10)	−0.0006(10)
C(41)	0.0220(15)	0.0219(16)	0.0351(17)	−0.0006(13)	0.0001(13)	−0.0051(12)
C(33)	0.0299(17)	0.040(2)	0.0397(19)	0.0088(15)	0.0187(14)	0.0061(14)
C(43)	0.0302(17)	0.0342(19)	0.0385(19)	0.0016(15)	−0.0077(14)	−0.0096(14)
C(44)	0.0252(16)	0.0346(19)	0.047(2)	0.0042(15)	0.0035(14)	−0.0064(14)
C(45)	0.048(2)	0.0256(17)	0.0349(18)	0.0083(14)	0.0051(15)	0.0095(15)
C(46)	0.0375(18)	0.0377(18)	0.0242(16)	0.0075(14)	0.0079(13)	0.0036(15)
C(51)	0.0410(18)	0.0277(17)	0.0285(17)	−0.0015(13)	0.0051(14)	−0.0135(14)
C(52)	0.047(2)	0.045(2)	0.0187(16)	−0.0100(14)	0.0070(14)	−0.0108(16)
C(53)	0.049(2)	0.048(2)	0.045(2)	−0.0060(18)	−0.0003(17)	−0.0243(18)
C(54)	0.056(2)	0.0277(18)	0.040(2)	0.0005(15)	0.0051(17)	−0.0104(16)
C(55)	0.080(3)	0.047(2)	0.038(2)	−0.0177(18)	0.026(2)	−0.006(2)
C(56)	0.051(2)	0.060(2)	0.0200(16)	0.0005(16)	0.0100(15)	−0.0068(18)
C(61)	0.0242(15)	0.0290(16)	0.0187(14)	0.0111(12)	0.0000(12)	−0.0020(12)
C(62)	0.052(2)	0.0322(19)	0.039(2)	0.0044(15)	0.0121(16)	−0.0102(16)
C(63)	0.052(2)	0.041(2)	0.055(2)	0.0081(19)	0.0078(19)	−0.0250(18)

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Table S43. – continued from previous page

atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C(64)	0.0268(17)	0.057(2)	0.042(2)	0.0242(18)	0.0018(15)	−0.0092(16)
C(65)	0.0265(17)	0.051(2)	0.0345(18)	0.0162(16)	0.0074(14)	0.0047(15)
C(66)	0.0255(15)	0.0319(17)	0.0278(16)	0.0106(13)	0.0026(13)	−0.0008(13)
C(71)	0.0247(16)	0.056(2)	0.0210(16)	0.0085(15)	0.0000(13)	−0.0121(15)
C(72)	0.0283(18)	0.094(3)	0.035(2)	0.017(2)	−0.0024(15)	0.0000(19)
C(73)	0.0682(18)	0.119(3)	0.0460(16)	−0.0077(16)	−0.0107(13)	−0.0269(19)
C(74)	0.0682(18)	0.119(3)	0.0460(16)	−0.0077(16)	−0.0107(13)	−0.0269(19)
C(75)	0.0682(18)	0.119(3)	0.0460(16)	−0.0077(16)	−0.0107(13)	−0.0269(19)
C(76)	0.054(2)	0.062(3)	0.0314(19)	−0.0007(18)	0.0040(17)	−0.027(2)
C(42)	0.0206(14)	0.0229(15)	0.0240(15)	0.0066(12)	0.0038(12)	−0.0010(11)

Table S44. Distances [Å] for [PC(H)P]Pd(PMe_3)($GeHPh_2$)·0.5C_5H_{12} (**13·0.5C_5H_{12}**).

atom – atom	distance	atom – atom	distance
Pd – C	2.151(2)	Pd – P(3)	2.3155(7)
Pd – P(1)	2.4349(7)	Pd – P(2)	2.4444(7)
Pd – Ge	2.4642(4)	Ge – C(71)	1.962(3)
Ge – C(61)	1.994(3)	Ge – H(2)	1.47(3)
P(1) – C(12)	1.835(3)	P(1) – C(42)	1.865(3)
P(1) – C(41)	1.871(3)	P(3) – C(32)	1.819(3)
P(3) – C(31)	1.819(3)	P(3) – C(33)	1.827(3)
P(2) – C(22)	1.827(3)	P(2) – C(52)	1.864(3)
P(2) – C(51)	1.873(3)	C(11) – C(12)	1.394(4)
C(11) – C(16)	1.400(4)	C(11) – C	1.505(4)
C(12) – C(13)	1.395(4)	C(13) – C(14)	1.385(4)
C(13) – H(13)	0.9500	C(14) – C(15)	1.376(5)
C(14) – H(14)	0.9500	C(15) – C(16)	1.381(4)
C(15) – H(15)	0.9500	C(16) – H(16)	0.9500
C(21) – C(26)	1.395(4)	C(21) – C(22)	1.401(4)
C(21) – C	1.529(4)	C(22) – C(23)	1.400(4)
C(23) – C(24)	1.375(5)	C(23) – H(23)	0.9500
C(24) – C(25)	1.366(5)	C(24) – H(24)	0.9500
C(25) – C(26)	1.395(4)	C(25) – H(25)	0.9500
C(26) – H(26)	0.9500	C(31) – H(31A)	0.9800
C(31) – H(31B)	0.9800	C(31) – H(31C)	0.9800
C(81) – C(83)#1	1.21(3)	C(81) – C(83)	1.21(3)
C(81) – C(82)	1.226(11)	C(81) – C(82)#1	1.226(10)
C(82) – C(83)1	1.216(18)	C(82) – C(84)#1	1.295(14)
C(84) – C(82)1	1.295(14)	C(84) – C(83)	1.55(3)
C(83) – C(82)1	1.216(18)	C(32) – H(32A)	0.9800
C(32) – H(32B)	0.9800	C(32) – H(32C)	0.9800
C – H(1)	1.0000	C(41) – C(44)	1.516(4)
C(41) – C(43)	1.530(4)	C(41) – H(41)	1.0000
C(33) – H(33A)	0.9800	C(33) – H(33B)	0.9800
C(33) – H(33C)	0.9800	C(43) – H(43A)	0.9800
C(43) – H(43B)	0.9800	C(43) – H(43C)	0.9800
C(44) – H(44A)	0.9800	C(44) – H(44B)	0.9800
C(44) – H(44C)	0.9800	C(45) – C(42)	1.523(4)
C(45) – H(45A)	0.9800	C(45) – H(45B)	0.9800
C(45) – H(45C)	0.9800	C(46) – C(42)	1.524(4)
C(46) – H(46A)	0.9800	C(46) – H(46B)	0.9800
C(46) – H(46C)	0.9800	C(51) – C(53)	1.528(4)
C(51) – C(54)	1.535(5)	C(51) – H(51)	1.0000
C(52) – C(55)	1.518(5)	C(52) – C(56)	1.529(5)

Symmetry transformations used to generate equivalent atoms: #1 −x,−y+2,−z+1

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Table S44. – continued from previous page

atom – atom	distance	atom – atom	distance
C(52) – H(52)	1.0000	C(53) – H(53A)	0.9800
C(53) – H(53B)	0.9800	C(53) – H(53C)	0.9800
C(54) – H(54A)	0.9800	C(54) – H(54B)	0.9800
C(54) – H(54C)	0.9800	C(55) – H(55A)	0.9800
C(55) – H(55B)	0.9800	C(55) – H(55C)	0.9800
C(56) – H(56A)	0.9800	C(56) – H(56B)	0.9800
C(56) – H(56C)	0.9800	C(61) – C(62)	1.385(4)
C(61) – C(66)	1.388(4)	C(62) – C(63)	1.392(5)
C(62) – H(62)	0.9500	C(63) – C(64)	1.364(5)
C(63) – H(63)	0.9500	C(64) – C(65)	1.377(5)
C(64) – H(64)	0.9500	C(65) – C(66)	1.390(4)
C(65) – H(65)	0.9500	C(66) – H(66)	0.9500
C(71) – C(76)	1.371(5)	C(71) – C(72)	1.411(5)
C(72) – C(73)	1.370(6)	C(72) – H(72)	0.9500
C(73) – C(74)	1.348(7)	C(73) – H(73)	0.9500
C(74) – C(75)	1.388(7)	C(74) – H(74)	0.9500
C(75) – C(76)	1.404(5)	C(75) – H(75)	0.9500
C(76) – H(76)	0.9500	C(42) – H(42)	1.0000
Symmetry transformations used to generate equivalent atoms: #1 −x,−y+2,−z+1			

Table S45. Angles [°] for [PC(H)P]Pd(PMe_3)($GeHPh_2$)·0.5C_5H_{12} (**13·0.5C_5H_{12}**).

atom – atom – atom	angle	atom – atom – atom	angle
C – Pd – P(3)	175.99(7)	C – Pd – P(1)	79.20(7)
P(3) – Pd – P(1)	103.47(3)	C – Pd – P(2)	80.09(7)
P(3) – Pd – P(2)	100.95(3)	P(1) – Pd – P(2)	119.12(3)
C – Pd – Ge	88.24(7)	P(3) – Pd – Ge	87.80(2)
P(1) – Pd – Ge	122.52(2)	P(2) – Pd – Ge	113.25(2)
C(71) – Ge – C(61)	101.91(12)	C(71) – Ge – Pd	117.57(10)
C(61) – Ge – Pd	120.88(8)	C(71) – Ge – H(2)	100.3(12)
C(61) – Ge – H(2)	98.5(12)	Pd – Ge – H(2)	114.2(12)
C(12) – P(1) – C(42)	102.51(12)	C(12) – P(1) – C(41)	100.77(13)
C(42) – P(1) – C(41)	104.56(13)	C(12) – P(1) – Pd	98.03(9)
C(42) – P(1) – Pd	117.76(9)	C(41) – P(1) – Pd	128.12(10)
C(32) – P(3) – C(31)	100.08(17)	C(32) – P(3) – C(33)	100.20(16)
C(31) – P(3) – C(33)	101.43(16)	C(32) – P(3) – Pd	118.46(12)
C(31) – P(3) – Pd	118.66(11)	C(33) – P(3) – Pd	114.89(11)
C(22) – P(2) – C(52)	102.68(15)	C(22) – P(2) – C(51)	100.10(14)
C(52) – P(2) – C(51)	104.68(15)	C(22) – P(2) – Pd	97.82(9)
C(52) – P(2) – Pd	136.30(11)	C(51) – P(2) – Pd	109.14(10)
C(12) – C(11) – C(16)	118.8(3)	C(12) – C(11) – C	119.6(2)
C(16) – C(11) – C	121.4(3)	C(11) – C(12) – C(13)	119.5(3)
C(11) – C(12) – P(1)	114.6(2)	C(13) – C(12) – P(1)	125.8(2)
C(14) – C(13) – C(12)	120.4(3)	C(14) – C(13) – H(13)	119.8
C(12) – C(13) – H(13)	119.8	C(15) – C(14) – C(13)	120.5(3)
C(15) – C(14) – H(14)	119.7	C(13) – C(14) – H(14)	119.7
C(14) – C(15) – C(16)	119.4(3)	C(14) – C(15) – H(15)	120.3
C(16) – C(15) – H(15)	120.3	C(15) – C(16) – C(11)	121.3(3)
C(15) – C(16) – H(16)	119.4	C(11) – C(16) – H(16)	119.4
C(26) – C(21) – C(22)	118.2(3)	C(26) – C(21) – C	121.7(3)
C(22) – C(21) – C	120.1(2)	C(23) – C(22) – C(21)	119.9(3)
C(23) – C(22) – P(2)	125.0(2)	C(21) – C(22) – P(2)	115.0(2)
C(24) – C(23) – C(22)	120.8(3)	C(24) – C(23) – H(23)	119.6
C(22) – C(23) – H(23)	119.6	C(25) – C(24) – C(23)	119.7(3)
C(25) – C(24) – H(24)	120.2	C(23) – C(24) – H(24)	120.2
C(24) – C(25) – C(26)	120.7(3)	C(24) – C(25) – H(25)	119.6
C(26) – C(25) – H(25)	119.6	C(21) – C(26) – C(25)	120.6(3)
C(21) – C(26) – H(26)	119.7	C(25) – C(26) – H(26)	119.7
P(3) – C(31) – H(31A)	109.5	P(3) – C(31) – H(31B)	109.5
H(31A) – C(31) – H(31B)	109.5	P(3) – C(31) – H(31C)	109.5
H(31A) – C(31) – H(31C)	109.5	H(31B) – C(31) – H(31C)	109.5
C(83)#1 – C(81) – C(83)	180.0(13)	C(83)#1 – C(81) – C(82)	59.9(10)
C(83) – C(81) – C(82)	120.1(10)	C(83)#1 – C(81) – C(82)#1	120.1(10)

Symmetry transformations used to generate equivalent atoms: #1 −x,−y+2,−z+1

Continued on next page

Table S45. – continued from previous page

atom – atom – atom	angle	atom – atom – atom	angle
C(83) – C(81) – C(82)#1	59.9(10)	C(82) – C(81) – C(82)#1	180.000(4)
C(83)#1 – C(82) – C(81)	59.4(16)	C(83)#1 – C(82) – C(84)#1	75.9(17)
C(81) – C(82) – C(84)#1	134.7(13)	C(82)#1 – C(84) – C(83)	49.7(10)
C(81) – C(83) – C(82)#1	60.7(12)	C(81) – C(83) – C(84)	114.6(13)
C(82)#1 – C(83) – C(84)	54.3(12)	P(3) – C(32) – H(32A)	109.5
P(3) – C(32) – H(32B)	109.5	H(32A) – C(32) – H(32B)	109.5
P(3) – C(32) – H(32C)	109.5	H(32A) – C(32) – H(32C)	109.5
H(32B) – C(32) – H(32C)	109.5	C(11) – C – C(21)	111.0(2)
C(11) – C – Pd	111.33(17)	C(21) – C – Pd	110.53(17)
C(11) – C – H(1)	108.0	C(21) – C – H(1)	108.0
Pd – C – H(1)	108.0	C(44) – C(41) – C(43)	111.0(3)
C(44) – C(41) – P(1)	112.4(2)	C(43) – C(41) – P(1)	110.2(2)
C(44) – C(41) – H(41)	107.7	C(43) – C(41) – H(41)	107.7
P(1) – C(41) – H(41)	107.7	P(3) – C(33) – H(33A)	109.5
P(3) – C(33) – H(33B)	109.5	H(33A) – C(33) – H(33B)	109.5
P(3) – C(33) – H(33C)	109.5	H(33A) – C(33) – H(33C)	109.5
H(33B) – C(33) – H(33C)	109.5	C(41) – C(43) – H(43A)	109.5
C(41) – C(43) – H(43B)	109.5	H(43A) – C(43) – H(43B)	109.5
C(41) – C(43) – H(43C)	109.5	H(43A) – C(43) – H(43C)	109.5
H(43B) – C(43) – H(43C)	109.5	C(41) – C(44) – H(44A)	109.5
C(41) – C(44) – H(44B)	109.5	H(44A) – C(44) – H(44B)	109.5
C(41) – C(44) – H(44C)	109.5	H(44A) – C(44) – H(44C)	109.5
H(44B) – C(44) – H(44C)	109.5	C(42) – C(45) – H(45A)	109.5
C(42) – C(45) – H(45B)	109.5	H(45A) – C(45) – H(45B)	109.5
C(42) – C(45) – H(45C)	109.5	H(45A) – C(45) – H(45C)	109.5
H(45B) – C(45) – H(45C)	109.5	C(42) – C(46) – H(46A)	109.5
C(42) – C(46) – H(46B)	109.5	H(46A) – C(46) – H(46B)	109.5
C(42) – C(46) – H(46C)	109.5	H(46A) – C(46) – H(46C)	109.5
H(46B) – C(46) – H(46C)	109.5	C(53) – C(51) – C(54)	111.8(3)
C(53) – C(51) – P(2)	114.5(2)	C(54) – C(51) – P(2)	113.4(2)
C(53) – C(51) – H(51)	105.4	C(54) – C(51) – H(51)	105.4
P(2) – C(51) – H(51)	105.4	C(55) – C(52) – C(56)	109.6(3)
C(55) – C(52) – P(2)	112.7(2)	C(56) – C(52) – P(2)	111.1(2)
C(55) – C(52) – H(52)	107.8	C(56) – C(52) – H(52)	107.8
P(2) – C(52) – H(52)	107.8	C(51) – C(53) – H(53A)	109.5
C(51) – C(53) – H(53B)	109.5	H(53A) – C(53) – H(53B)	109.5
C(51) – C(53) – H(53C)	109.5	H(53A) – C(53) – H(53C)	109.5
H(53B) – C(53) – H(53C)	109.5	C(51) – C(54) – H(54A)	109.5
C(51) – C(54) – H(54B)	109.5	H(54A) – C(54) – H(54B)	109.5
C(51) – C(54) – H(54C)	109.5	H(54A) – C(54) – H(54C)	109.5
H(54B) – C(54) – H(54C)	109.5	C(52) – C(55) – H(55A)	109.5

Symmetry transformations used to generate equivalent atoms: #1 −x,−y+2,−z+1

Continued on next page

Table S45. – continued from previous page

atom – atom – atom	angle	atom – atom – atom	angle
C(52) – C(55) – H(55B)	109.5	H(55A) – C(55) – H(55B)	109.5
C(52) – C(55) – H(55C)	109.5	H(55A) – C(55) – H(55C)	109.5
H(55B) – C(55) – H(55C)	109.5	C(52) – C(56) – H(56A)	109.5
C(52) – C(56) – H(56B)	109.5	H(56A) – C(56) – H(56B)	109.5
C(52) – C(56) – H(56C)	109.5	H(56A) – C(56) – H(56C)	109.5
H(56B) – C(56) – H(56C)	109.5	C(62) – C(61) – C(66)	117.0(3)
C(62) – C(61) – Ge	121.0(2)	C(66) – C(61) – Ge	122.0(2)
C(61) – C(62) – C(63)	121.7(3)	C(61) – C(62) – H(62)	119.2
C(63) – C(62) – H(62)	119.2	C(64) – C(63) – C(62)	120.1(3)
C(64) – C(63) – H(63)	120.0	C(62) – C(63) – H(63)	120.0
C(63) – C(64) – C(65)	119.8(3)	C(63) – C(64) – H(64)	120.1
C(65) – C(64) – H(64)	120.1	C(64) – C(65) – C(66)	119.8(3)
C(64) – C(65) – H(65)	120.1	C(66) – C(65) – H(65)	120.1
C(61) – C(66) – C(65)	121.7(3)	C(61) – C(66) – H(66)	119.1
C(65) – C(66) – H(66)	119.1	C(76) – C(71) – C(72)	118.7(3)
C(76) – C(71) – Ge	122.2(3)	C(72) – C(71) – Ge	119.0(3)
C(73) – C(72) – C(71)	121.6(5)	C(73) – C(72) – H(72)	119.2
C(71) – C(72) – H(72)	119.2	C(74) – C(73) – C(72)	118.7(5)
C(74) – C(73) – H(73)	120.6	C(72) – C(73) – H(73)	120.6
C(73) – C(74) – C(75)	122.1(5)	C(73) – C(74) – H(74)	119.0
C(75) – C(74) – H(74)	119.0	C(74) – C(75) – C(76)	119.1(5)
C(74) – C(75) – H(75)	120.4	C(76) – C(75) – H(75)	120.4
C(71) – C(76) – C(75)	119.7(4)	C(71) – C(76) – H(76)	120.1
C(75) – C(76) – H(76)	120.1	C(45) – C(42) – C(46)	110.8(2)
C(45) – C(42) – P(1)	116.1(2)	C(46) – C(42) – P(1)	111.8(2)
C(45) – C(42) – H(42)	105.8	C(46) – C(42) – H(42)	105.8
P(1) – C(42) – H(42)	105.8		

Symmetry transformations used to generate equivalent atoms: #1 −x,−y+2,−z+1