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INTRAMOLECULAR Si-C AND C-H BOND ACTIVATION IN A PLATINUM COMPLEX LEADING TO THE FORMATION OF THE PLATINACYCLES

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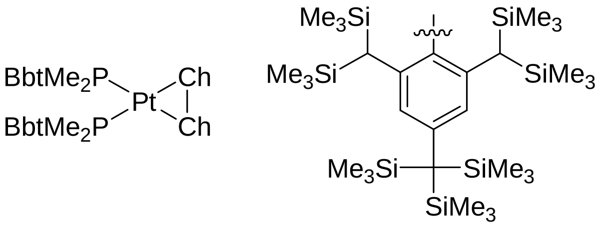
Abstract – Reduction of dichloroplatinum complex *dl*-**1** bearing two bulky aromatic substituents, Bbt groups (2,6-bis[bis(trimethylsilyl)methyl]-4-[tris(trimethylsilyl)methyl]phenyl), by sodium metal gave a unique platinacycle **2**, a hydridoplatinum complex of [PtH{$CH_2SiMe_2CH(SiMe_3)C_6H_2$-3-$CH(SiMe_3)_2$-5-$C(SiMe_3)_3$-2-$P(Me)CH_2CH_2$ (Me)PBbt}], which seems to be most likely formed *via* the initial formation of the corresponding Pt(0) complex and the subsequent intramolecular insertion of the Pt(0) center to the H-CH_2 bond of the *o*-bis(trimethylsilyl)methyl group of the Bbt group. On heating, the hydridoplatinum complex **2** underwent further intramolecular Si-C activation giving another type of platinacycle, [PtMe{$SiMe_2CH(SiMe_3)C_6H_2$-3$CH(SiMe_3)_2$-5-$C(SiMe_3)_3$-2-$P(Me)CH_2CH_2$(Me)PBbt}] (**4**), which has a (methyl)(silyl)-platinum complex structure.

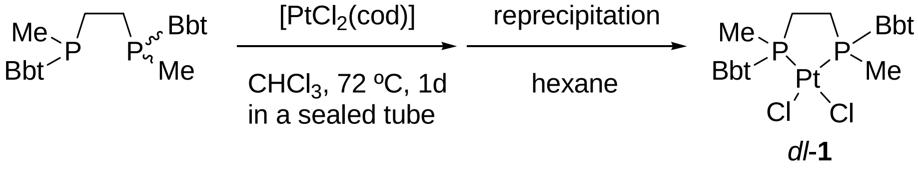
[#] In memory of late Prof. Dr. John Daly.

A wide variety of single bonds have been known to be activated by transition metal complexes. However, there have been few examples for the Si-C bond activation by transition metal complexes.[1] For example, Tilley's group has reported some examples of σ-bond metathesis of Si-C bonds with transition metal complexes, such as hafnium, samarium, and lutetium complexes.[2] Especially, there are very few examples for the Si-C(sp^3) bond activation by Pt complexes.[3] Tanaka and co-workers reported the intermolecular insertion of Pt(0) to the Si-C bond of distorted silacyclobutanes.[3a] Hofmann and co-workers reported the Si-C activation of tetramethylsilane by *cis*-[PtH(CH_2*t*-Bu)(dtbpm)] (dtbpm = bis(di-*tert*-butylphosphino)methane) giving the corresponding (methyl)(trimethylsilyl)platinum complex, *cis*-[Pt(Me)($SiMe_3$)(dtbpm)].[3b] They explained the formation of the Si-C activation product in terms of the insertion of the initially generated Pt(0) complex, [Pt(dtbpm)], into the C-H bond of tetramethylsilane, followed by the isomerization of the resulting [PtH(CH_2SiMe_3)(dtbpm)] to the product. Although the intermediary formation of the C-H activation product could not be observed spectroscopically in this reaction, they confirmed the isomerization of the C–H activation product, which was independently prepared by an alternative synthetic method, to the C–Si activation product. Puddephett and co-workers have also proposed the Si-C bond activation *via* the protonolysis of trimethylsilylmethylplatinum(II) complexes followed by the concerted rearrangement of the resulting cationic hydroplatinum(IV) complexes to the corresponding (methyl)(trimethylsilyl)platinum(IV) complexes.[4]

On the other hand, we have already reported the synthesis of the first platinum-dichalcogenido complexes bearing bulky monophosphine ligands, [$PtE_2(PMe_2Bbt)_2$] (E = S, Se), *via* the reaction of the corresponding Pt(0) complex with elemental chalcogens.[5] In the course of our studies on the synthesis of Pt(0) complexes bearing a bulky bisphosphine ligand, BbtP(Me)CH_2CH_2(Me)PBbt, we found an unexpected intramolecular Si-C activation leading to the formation of unique platinacycles.



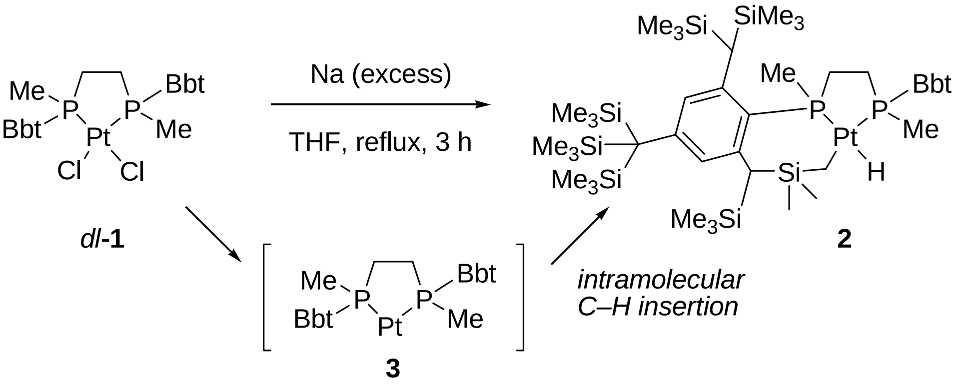
Scheme 1



Scheme 2

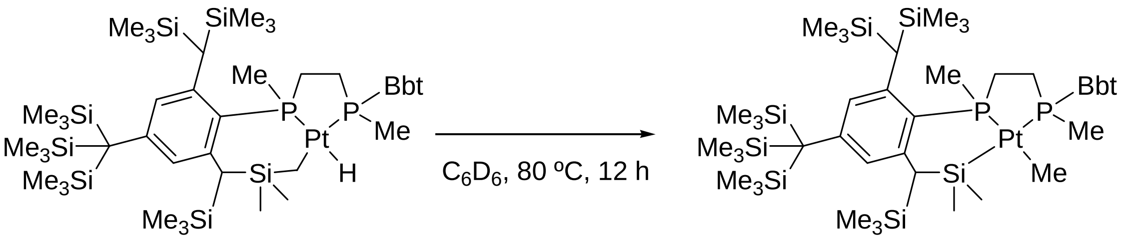
Dichloroplatinum complex *dl*-**1** bearing the bisphosphine ligand, BbtP(Me)CH_2CH_2(Me)PBbt, was prepared by the method shown in Scheme 2.[6]

Reduction of *dl*-**1** with excess Na metal in a refluxing THF solution gave a hydrido complex of platinum **2**.[7] The ^{1}H NMR signal assigned to the Pt-H was observed at −2.85 ppm (dd with platinum satellites, $^2J_{HP}$ = 234, 18 Hz, $^1J_{HPt}$ = 1227 Hz). The ^{31}P{^{1}H} NMR signal of the phosphorus atom situated in the trans position of the hydrido ligand was observed at 12.2 ppm (s with platinum satellites, $^1J_{PPt}$ = 1843 Hz) and that situated in the trans position of the methylene group was observed at 21.1 ppm (s with platinum satellites, $^1J_{PPt}$ = 1573 Hz). The ^{13}C NMR chemical shift assigned to the methylene carbon was observed at −11.00 ppm (dd, $^2J_{CP}$ = 71, 7.1 Hz). These NMR spectral data were similar to those of previously reported hydrido complexes of platinum.[8] Hydridoplatinum complex **2** was most likely generated by the initial formation of the corresponding Pt(0) complex **3**[8,9] followed by the intramolecular insertion of the Pt(0) center into the H-CH$_2$ bond of the *o*-bis(trimethylsilyl)methyl group of the Bbt group (Scheme 3). Intermediary Pt(0) complex **3** could not be observed spectroscopically even under the milder conditions, *i.e.* in the reaction at −78 °C using lithium naphthalenide (4 eq) as reductant, and only the formation of **2** (ca. 80%) was confirmed by ^{31}P{^{1}H} NMR spectroscopy. This result suggests the intramolecular C-H insertion of Pt(0) in **3** should be a very fast process.



Scheme 3

Thermal reaction of hydrido complex **2** in C_6D_6 at 80 °C for 12 h gave a silyl complex of platinum **4** in 29% yield (Scheme 4). The structure of **4** was determined by NMR spectra, elemental analysis, and X-ray structural analysis (Figure 1).[10] The thermal reaction of **2** gave only the silyl complex **4** in 79% yield even in the presence of trapping reagent such as PhI. The ^{31}P{^{1}H} NMR signal of phosphorus atom situated in the trans position of the methyl group was observed at 14.6 ppm (s with platinum satellites, $^1J_{PPt}$ = 1743 Hz) and those situated in the trans position of the silyl group was observed at −6.0 ppm (s with platinum and silicon satellites, $^1J_{PPt}$ = 631 Hz, $^2J_{PSi}$ = 165 Hz). The ^{29}Si NMR signal of the silicon atom bound to the platinum atom was observed at 2.9 ppm (dd, $^2J_{SiP}$ = 177, 15 Hz). These NMR spectral data were similar to those for the previously reported silyl-substituted platinum complexes.[3,11,12]



2 **4**

Scheme 4

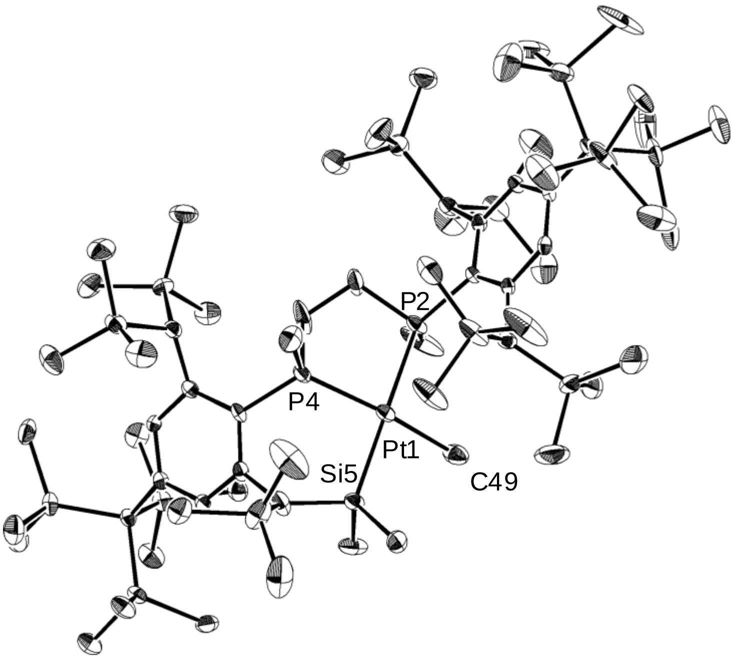
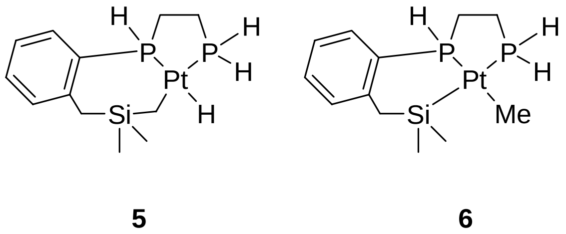


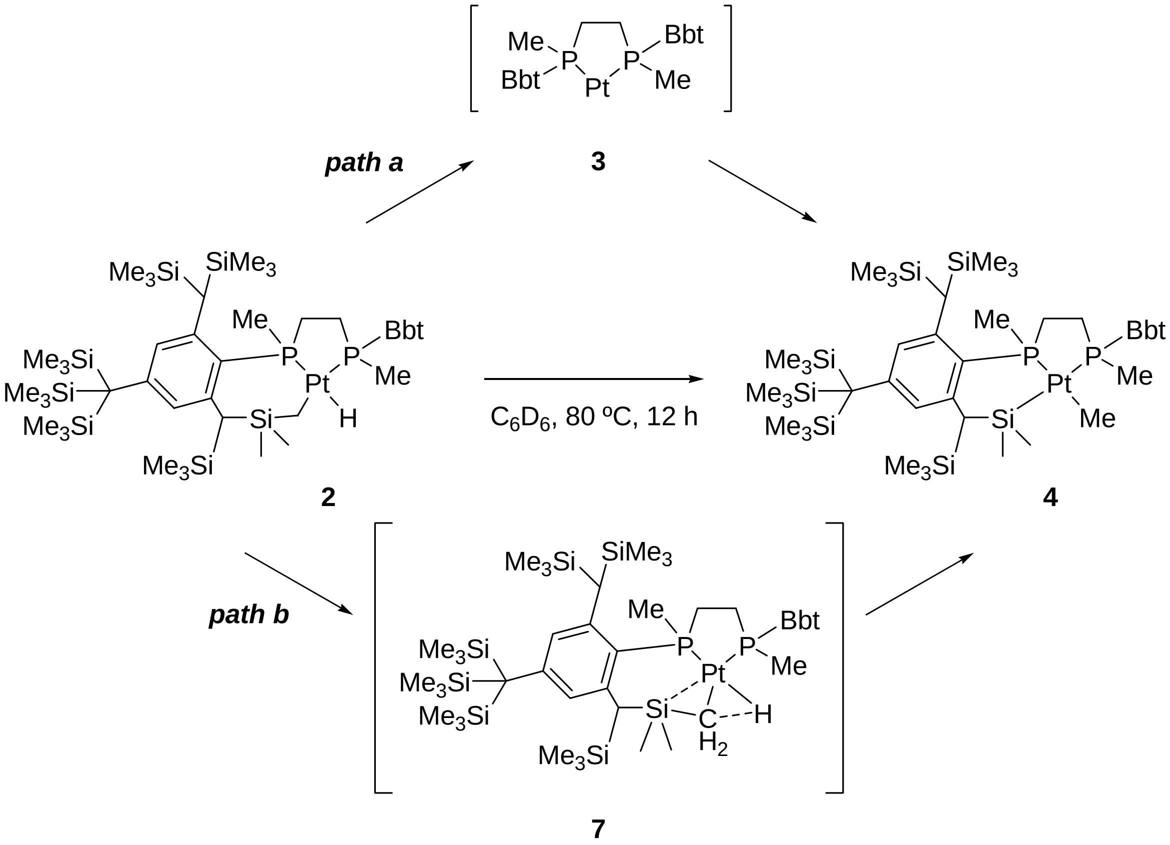
Figure 1. Molecular structure of **4**. Displacement ellipsoids were drawn at the 30% probability level. Selected bond lengths (Å) and angles (°): Pt1-C49 2.118(8), Pt1-Si5 2.3212(18), Pt1-P4 2.275(4), Pt1-P2 2.4190(17), P2-Pt1-P4 88.38(6), P4-Pt1-Si5 93.63(7), Si5-Pt1-C49 83.6(2), C49-Pt1-P2 92.6(2).

In theoretical calculations, geometry optimization of *cis*-$[PtH(CH_2SiMe_3)L_2]$ and *cis*-$[PtMe(SiMe_3)L_2]$ ($L_2 = (PH_3)_2$, $H_2PCH_2CH_2PH_2$) at the B3LYP/6-31G(2d,p) (LANL2DZ on Pt atom) level showed that *cis*-$PtMe(SiMe_3)L_2$ was more stable than *cis*-$[PtH(CH_2SiMe_3)L_2]$ by 2.02 kcal/mol ($L_2 = (PH_3)_2$) and 6.43 kcal/mol ($L_2 = H_2PCH_2CH_2PH_2$), respectively. In the system of using $H_2PCH_2CH_2$-$PH\{C_6H_4(CH_2SiMe_3)$-*o*$\}$ as a ligand, silyl complex **6** was found to be more stable than hydrido complex **5** by 5.27 kcal/mol (Scheme 5). These calculations can rationally explain the thermal isomerization of **2** to **4**.



Scheme 5

Two reaction pathways can be proposed for this thermal isomerization (Scheme 6). One is the initial formation of the corresponding Pt(0) complex **3** by the reductive elimination followed by the intramolecular Si-C insertion of the Pt center (*path a*), and the other is that based on concerted σ-bond metathesis (*path b*). If this thermal isomerization occurs through *path a*, the trapped products of Pt(0) complex **3** should be given by the thermal reaction in the presence of trapping reagents. Since the trapped products were not obtained at all under such conditions, this Si-C bond activation is most likely to proceed through *path b*. Although there has been a report in which the Si–C activation with platinum complexes *via* the initial C–H activation was postulated,[2b] this is the first example for the isolation of the intermediately formed hydridoplatinum complexes.



Scheme 6

In conclusion, the reduction of *dl*-**1** was found to give platinacycle **2** having a Pt–H bond, the formation of which is reasonably explained by the initial formation of the corresponding Pt(0) complex **3** followed by the intramolecular insertion of the Pt center into the H-CH_2 bond of the *o*-bis(trimethylsilyl)methyl group of the Bbt group. The thermal reaction of the resulting hydridoplatinum complex **2** resulted in the isomerization *via* σ-bond metathesis giving the corresponding (methyl)(silyl)platinum complex **4**.

ACKNOWLEDGEMENTS

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6. Detailed synthetic strategy and structural parameters of BbtP(Me)CH_2CH_2(Me)PBbt and *dl*-**1** will be reported as a full paper in the near future.
7. Chemical data for **2**: colorless crystals; m.p. 245-248 °C (decomp.); ^{1}H NMR (400 MHz, C_6D_6, 298 K) δ –2.85 (dd with ^{195}Pt satellites, $^2J_{HP}$ = 218, 18 Hz, $^1J_{HPt}$ = 1287 Hz, 1H), 0.12 (s, 9H), 0.25 (s, 9H), 0.26 (s, 9H), 0.29 (s, 18H), 0.33 (s, 27H), 0.36 (s, 27H), 0.37 (s, 18H), 0.51 (s, 3H), 0.73 (s, 3H),

1.10-1.68 (m, 2H), 2.1-2.2 (m, 3H), 1.85-2.11 (m, 1H), 2.2-2.5 (m, 3H + 4H), 3.79 (m, 1H), 4.20 (d, $^4J_{HP}$ = 4.5 Hz, 2H), 6.91 (d, $^4J_{HP}$ = 3 Hz, 2H), 6.99-7.00 (m, 2H); ^{13}C{^{1}H} NMR (75 MHz, C_6D_6, 298 K) δ −11.00 (dd, $^2J_{CP}$ = 71, 7.1 Hz, Pt-$\underline{C}H_2$), 1.64 (s, CH_3), 2.43 (s, CH_3), 2.62 (s, CH_3), 2.76 (s, CH_3), 4.07 (d, $^4J_{CP}$ = 6.8 Hz, CH_3), 5.23 (d, $^4J_{CP}$ = 15.4 Hz, CH_3), 5.80 (s, CH_3), 5.86 (s, CH_3), 18.13 (d, $^1J_{CP}$ = 25.8 Hz, P-$\underline{C}H_3$), 22.01 (d, $^1J_{CP}$ = 31.4 Hz, P-$\underline{C}H_3$), 22.34 (s, $\underline{C}$-$(SiMe_3)_3$), 22.55 (s, $\underline{C}$-$(SiMe_3)_3$), 28.15 (d, $^3J_{CP}$ = 8.0 Hz, *o*-CH), 28.78 (s, *o*-CH), 32.30 (dd, $^1J_{CP}$ = 24.6 Hz, $^2J_{CP}$ = 18.5 Hz, P-$\underline{C}H_2$), 34.64 (dd, $^1J_{CP}$ = 28.3 Hz, $^2J_{CP}$ = 17.9 Hz, P-$\underline{C}H_2$), 36.52 (d, $^3J_{CP}$ = 10.5 Hz, *o*-CH), 122.01 (d, $^1J_{CP}$ = 41.3 Hz, ipso Ar), 123.59 (d, $^1J_{CP}$ = 36.4 Hz, ipso Ar), 128.07 (d, $^3J_{CP}$ = 4.3 Hz, *m*-Ar), 128.84 (d, $^3J_{CP}$ = 8.0 Hz, *m*-Ar), 129.43 (d, $^3J_{CP}$ = 5.5 Hz, *m*-Ar), 147.78 (d, $^4J_{CP}$ = 1.9 Hz, *p*-Ar), 148.12 (d, $^4J_{CP}$ = 1.9 Hz, *p*-Ar), 149.72 (s, *o*-Ar), 151.90 (d, $^2J_{CP}$ = 10.5 Hz, *o*-Ar), 153.68 (d, $^2J_{CP}$ = 20.9 Hz, *o*-Ar); ^{31}P{^{1}H} NMR (120 MHz, C_6D_6, 298 K) δ 12.2 (s with ^{195}Pt satellites, $^1J_{PPt}$ = 1860 Hz), 21.1 (s with ^{195}Pt satellites, $^1J_{PPt}$ = 1588 Hz); ^{195}Pt{^{1}H} NMR (64 MHz, C_6D_6, 298 K) δ –4573 (dd, $^1J_{PtP}$ = 1860, 1588). High-resolution MS (FAB) m/z Calcd for $C_{64}H_{144}P_2{}^{195}PtSi_{14}$: 1561.7162. Found 1561.7161 ($[M]^+$). Anal. Calcd for $C_{64}H_{144}P_2PtSi_{14}$: C, 49.15; H, 9.28. Found: C, 49.42; H, 9.45.

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10. Chemical data for **4**: yellow crystals; m.p. 272-275 °C (decomp.); ^{1}H NMR (300 MHz, C_6D_6, 298 K) δ 0.09 (s, 9H), 0.32 (s, 27H), 0.33 (s, 18H), 0.34 (s, 36H), 0.37 (s, 9H), 0.39 (s, 18H), 0.51 ($^4J_{HP}$ = 2.2 Hz, 3H), 0.86 (d with platinum satellites, $^4J_{HP}$ = 2.4 Hz, $^3J_{HPt}$ = 19.3 Hz, 3H), 1.31 (dd with ^{195}Pt satellites, $^3J_{HP}$ = 6.7, 12.2 Hz, $^2J_{HPt}$ = 60.5 Hz, 3H), 1.67 (d, $^2J_{HP}$ = 5.6 Hz, 3H), 1.90 (d, $^2J_{HP}$ = 7.3 Hz, 3H), 1.60-2.24 (m, 4H), 2.38 (s, 1H), 2.61 (dd, $^4J_{HP}$ = 8.8, 5.6 Hz, 1H), 3.23-3.34 (br, 2H), 6.77-6.80 (m, 2H), 6.89 (d, $^4J_{HP}$ = 2.5 Hz, 2H); ^{13}C{^{1}H} NMR (75 MHz, C_6D_6, 298 K) δ –1.49 (dd, $^2J_{CP}$ = 86, 5.5 Hz, PtMe), 1.36 (s, CH_3), 1.92 (s, CH_3), 2.67 (s, CH_3), 2.90 (s, CH_3), 2.97 (s, CH_3), 3.00 (s, CH_3), 5.11 (s, CH_3), 5.84 (s, CH_3), 15.81 (d, $^1J_{CP}$ = 17.9 Hz, P-CH_3), 18.16 (d, $^1J_{CP}$ = 19.7 Hz, P-CH_3), 21.91 (s, $C(SiMe_3)_3$), 22.03 (s, $C(SiMe_3)_3$), 28.21 (d, $^3J_{CP}$ = 8.6 Hz, *o*-CH), 28.52 (s, *o*-CH), 30.10-31.10 (m, PCH_2CH_2P), 37.52 (dd, $^3J_{CP}$ = 8.6, 17.9 Hz, *o*-CH), 127.42 (d, $^3J_{CP}$ = 4.5 Hz, *m*-Ar), 128.52 (d, $^3J_{CP}$ = 0.6 Hz, *m*-Ar), 129.24 (d, $^2J_{CP}$ = 4.9 Hz, *o*-Ar), 130.42 (d, $^2J_{CP}$ = 6.8 Hz, *o*-Ar), 136.10 (d, $^3J_{CP}$ = 8.6 Hz, *m*-Ar), 146.03, 147.74, 149.70, 151.72 (d, $^1J_{CP}$ = 11.9 Hz, *ipso*-Ar), 155.05 (d, $^1J_{CP}$ = 20.9 Hz, *ipso*-Ar); ^{29}Si{^{1}H} NMR (60 MHz, C_6D_6, 25 ℃): δ 1.28, 1.51, 2.85 (dd,

$^2J_{SiP}$ = 165, 15 Hz); $^{31}P\{^1H\}$ NMR (120 MHz, C_6D_6, 298 K) δ –6.0 (s with ^{29}Si and ^{195}Pt satellites, $^2J_{PSi}$ = 165 Hz, $^1J_{PPt}$ = 631 Hz), 14.6 (s with ^{29}Si and ^{195}Pt satellites, $^1J_{PPt}$ = 1743 Hz); $^{195}Pt\{^1H\}$ NMR (64 MHz, C_6D_6, 298 K) δ –5179 (dd, $^1J_{PtP}$ = 631, 1743).; High-resolution MS (FAB) m/z Calcd for $C_{64}H_{144}P_2{}^{194}PtSi_{14}$: 1560.7140. Found 1560.7162 ($[M]^+$). X-Ray crystallographic data for **4** ($C_{64}H_{144}P_2PtSi_{14}$): M = 1564.08, T = 93(2) K, triclinic, P–1 (no.2), a = 12.5025(2) Å, b = 12.6805(2) Å, c = 31.2554(7) Å, α = 83.0773(13)°, β = 83.0773(13)°, γ = 62.0422(8)°, V = 4326.87(14) Å^3, Z = 2, D_{calc} = 1.201 g cm^{-3}, μ = 1.885 mm^{-1}, λ = 0.71070 Å, $2\theta_{max}$ = 50.0, 37023 measured reflections, 15169 independent reflections (R_{int} = 0.0368), 874 refined parameters, GOF = 1.052, R_1 = 0.0626 and wR_2 = 0.1529 [$I>2\sigma(I)$], R_1 = 0.0714 and wR_2 = 0.1596 [for all data]. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 693903. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; E-mail: deposit@ccdc.cam.ac.uk). The intensity data were collected on a Rigaku/MSC Mercury CCD diffractometer. The structure was solved by direct methods (SHELXS-97) and refined by full-matrix least-squares procedures on F^2 for all reflections (SHELXL-97).

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