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Reactivity of $\{(Ph_3P)Pt[\mu-\eta^2-H-SiH(Ar)]\}_2$ (Ar = 2-isopropyl-6-methylphenyl) with phosphines. X-ray crystal structure of *trans*- $\{(dppe)Pt[\mu-SiH(Ar)]\}_2$

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Dedicated to the memory of Professor Luigi Venanzi

Abstract

The dinuclear Pt–Si complex { $(Ph_3P)Pt{\mu-\eta^2-H-SiH(IMP)]}_2$ (*trans*-1a-*cis*-1b = 3:1; IMP = 2-isopropyl-6-methylphenyl) reacted with basic phosphines such as 1,2-bis(diphenylphosphino)ethane (dppe) and dimethylphenylphosphine (PMe₂Ph) to afford different dinuclear Pt–Si complexes with loss of H₂, { $(P)_2Pt[\mu-SiH(IMP)]$ } [P = dppe, *trans*-2a (major), *cis*-2b (trace); PMe₂Ph, 3 (*trans* only)]. Complexes 2 and 3 were characterized by multinuclear NMR spectroscopy and X-ray crystallography (2a). In contrast, the reaction of 1a,b with the sterically demanding tricyclohexylphosphine (PCy₃) afforded {(Cy₃P)Pt{ $\mu-\eta^2-H-SiH(IMP)}$ } (*trans*-4a-*cis*-4b 2:1) analogous to 1a,b where the central Pt₂Si₂($\mu-H$)₂ core remains intact but the PPh₃ ligands have been replaced by PCy₃. Complexes 4a and 4b was characterized by multinuclear NMR and IR spectroscopies. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

The study of transition metal complexes containing nonclassical M···H···Si interactions has been an active area of research over the last few decades [1,2]. A number of mononuclear, and to a lesser extent, dinuclear complexes containing these interactions are known. The 'arrested' addition of the Si–H bond to the metal center in these complexes has been established by NMR spectroscopy and/or X-ray crystallography. Surprisingly, the reactivity of complexes containing nonclassical M···H···Si interactions has been essentially unexplored. Dinuclear complexes containing bridgingsilylene moieties with (or without) nonclassical M···H···Si interactions may serve as exceptional dinuclear catalysts as well as model systems for developing an understanding of bimetallic reactivity. Dinuclear complexes containing bridging-silylene moieties are believed to play a role in catalytic dehydrocoupling reactions of silanes to oligomers and polymers [3]. For example, diplatinum bis(μ -silylene) complexes have been shown to catalyze the oligomerization (stepwise) of primary silanes to small chain oligosilanes [4]. Recently, a series of dinuclear rhodium (μ -silylene) and (μ - η^2 -silyl) complexes have been prepared and involvement of the latter in the catalytic dehydrocoupling of diphenylsilane to 1,1,2,2-tetraphenyldisilane was proposed [5].

We were interested in examining the effect of added phosphine to solutions of dinuclear complexes containing bridging-silylene moieties especially those with nonclassical hydrides, $[(R_3P)Pt(\mu-\eta^2-H-SiR'_2)]_2$. The possible products that one would expect from such reactions could be monoplatinum species, dinuclear complexes with changes in the central core, or simply an exchange of phosphines. We were also interested in determining how the nature of the phosphine affects the course of the reaction and whether basicity or steric

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constraints play a role. Herein, we report the reaction of 1,2-bis(diphenyphosphino)ethane (dppe) with the dinuclear Pt complex, { $(Ph_3P)Pt[\mu-\eta^2-H-SiH(Ar)]$ }₂ (1a,b) [*trans*-1a, *cis*-1b, ratio 3:1; Ar = 2-isopropyl-6methylphenyl (IMP)] [6,7] which contains two nonclassical Pt···H···Si interactions, to form a new four-membered ring { $(PhMe_2P)_2Pt[\mu-SiH(Ar)]$ }₂ with loss of H₂ [8].

In contrast, the reaction of tricyclohexylphosphine (PCy_3) with **1a**,**b** resulted in the overall replacement of PPh₃ by PCy₃ while the central $Pt_2Si_2(\mu-H)_2$ core remained intact.

2. Experimental

All reactions and manipulations were performed in dry glassware under an Ar atmosphere in an inert atmosphere drybox or with standard Schlenk techniques. All solvents were distilled under an atmosphere of N₂ and dried before use: C₆H₆ (CaH₂); Et₂O (sodium/benzophenone ketyl). Solvents were degassed by freeze-pump-thaw degassing cycles (liquid N₂) before transfer to the drybox. Toluene- d_8 and C_6D_6 were dried over activated alumina and Linde molecular sieves (4 Å) before use. $(Ph_3P)_2Pt(\eta^2-C_2H_4)$ was commercially available (Aldrich Chemical Co.) and used as received. The phosphine ligands: 1,2-bis(diphenylphosphino)ethane, tricyclohexylphosphine, dimethylphenylphosphine, and tris(2,4,6-trimethoxyphenyl)phosphine were purchased from Strem Chemicals and were used as received.

All ¹H, ¹H{³¹P}, ³¹P{¹H} and ²⁹Si{¹H} NMR data were recorded in either a Bruker ARX-500 MHz spectrometer or Varian Unity *Plus* 300 MHz WB spectrometer at ambient temperature (unless noted otherwise) using a 5 mm tunable broadband probe. Chemical shifts (δ) are reported in parts per million and coupling constants (*J*) in hertz. The solution ²⁹Si spectra were acquired using a DEPT pulse sequence [9] or a ¹H–²⁹Si HMQC sequence [10]. Infrared spectra were recorded on a Perkin–Elmer 1600 Series FT-IR. Elemental analyses were obtained from Atlantic Microlab Inc., Norcross, GA.

2.1. Reaction of $\{(Ph_3P)Pt[\mu-\eta^2-H-SiH(IMP)]\}_2$ (1a,b) with dppe

A slurry of $\{(Ph_3P)Pt[\mu-\eta^2-H-SiH(IMP)]\}_2$ (1a,b) (20 mg, 0.016 mmol) in 1.0 ml C₆H₆ was treated with a solution of dppe (14 mg, 0.04 mmol) in 1.0 ml C₆H₆ accompanied by vigorous evolution of gas. The reaction mixture turned bright yellow, was shaken until the solid dissolved, and then set aside overnight. Complex 2 was isolated as a mixture of *trans-*(2a) and *cis-*(2b,

trace) isomers. After 24 h, large X-ray quality round yellow crystals of $\{[(dppe)_2Pt][\mu-SiH(IMP)]\}_2$ (2a) had formed. The crystals were washed with C₆H₆ (3 × 1 ml) and dried in vacuo to give 17 mg of 2a. A second crop of 2a,b was obtained from the mother liquor providing an overall yield of 23 mg (94%).

¹H{³¹P} NMR (C₆D₆, 300 MHz) for **2a** and **2b**:¹ δ 1.31 (d, 12H, ${}^{3}J_{HH} = 7$ Hz, ArCH(CH₃)₂), 1.74 (bm, 4H, ${}^{3}J_{\text{PtH}} = 21$ Hz, ${}^{3}J_{\text{HH}} = 9$ Hz, P(CH₂)₂P), 1.95 (bm, 4H, ${}^{3}J_{PtH} = 21$ Hz, ${}^{3}J_{HH} = 9$ Hz, P(CH₂)₂P), 2.13 (s, 6H, ArCH₃), 4.57 (bm, 2H, ArCH(CH₃)₂), ArH region 6.42-8.10 (46H), 7.28 (s, 2H, ${}^{2}J_{PtH} = 29$ Hz, SiH). ³¹P{¹H} NMR (C₆D₆, 121 MHz) for **2a**: δ 56.5 (¹J_{PtP} = 1565 Hz, ${}^{3}J_{PtP} = 272$ Hz, ${}^{4}J_{PP} = 11$ Hz (cis), ${}^{4}J_{PP} = 24$ Hz (trans)); for **2b**: δ 57.8 (Js not resolved). ¹H-²⁹Si HMQC NMR (C₆D₆, 99 MHz) for **2a**: δ -132. IR (KBr, cm⁻¹): v 2011 (s, Si-H, trans), 2040 (b, Si-H, cis).² A sample of **2a**,**b** was placed under vacuum for 24 h before submitting for analysis. Anal. Calc. for C₇₂H₇₆P₄Pt₂Si₂·C₆H₆: C, 58.93; H, 5.20. Found: C, 58.92; H, 5.22% (consistent with one molecule of C_6H_6 per molecule of 2a,b). Crystals of 2a used for X-ray structural analysis were not dried in vacuo and were found to contain five molecules of benzene per unit cell (drying in vacuo resulted in solvent loss). It was not possible to determine the exact ratio of benzene to 2a,b (before drying) by NMR due to overlapping aromatic resonances in the ¹H NMR spectrum.

2.2. Reaction of $\{(Ph_3P)Pt[\mu-\eta^2-H-SiH(IMP)]\}_2$ (1a,b) with PMe_2Ph

A slurry of { $(Ph_3P)Pt[\mu-\eta^2-H-SiH(IMP)]$ }₂ (1a,b) (16 mg, 0.013 mmol) in 0.5 ml C₆D₆ was reacted with a solution of PMe₂Ph (8 mg, 0.05 mmol) in 0.5 ml C₆D₆ resulting in vigorous gas evolution. The cloudy colorless reaction mixture changed to a clear intense yellow within 30 min. The ¹H and ³¹P{¹H} NMR data indicated the quantitative formation of {[(PhMe₂P)₂Pt][μ -SiH(IMP)]}₂ (3) exclusively as the *trans* isomer. Diethyl ether (1.5 ml) was added to the reaction mixture causing slow precipitation of 3 as a yellow solid. The solid was washed with cold Et₂O (1 × 1 ml) then dried in vacuo to give 14 mg of 3 (86%). Spectroscopic data are identical with the data for 3 obtained from the Me₂Pt(PMe₂Ph)₂/(IMP)SiH₃ route [8].

¹ cis and trans isomers show overlapping resonances.

² Assignment of *cis* versus *trans* was made on the assumption that the Si–H stretching for **2b** will occur at higher energy due to a more sterically hindered environment.

2.3. Reaction of $\{(Ph_3P)Pt[\mu-\eta^2-H-SiH(IMP)]\}_2$ (1*a*,*b*) with PCy_3

To a slurry of { $(Ph_3P)Pt[\mu-\eta^2-H-SiH(IMP)]$ }₂ (**1a**,**b**) (18 mg, 0.015 mmol) was added a solution of PCy₃ (9 mg, 0.03 mmol) in 1.5 ml C₆H₆. After 1 h the solution became clear and was set aside for 24 h. The solution was layered with Et₂O (2 ml) and after several days, an off-white solid precipitated. The solid was washed with Et₂O (3 × 1 ml) and dried in vacuo to give 16 mg of { $(Cy_3P)Pt[\mu-\eta^2-H-SiH(IMP)]$ }₂ (**4a**,**b**) (86% yield as a mixture of *trans*-(**4a**) and *cis*-(**4b**) isomers (ratio of ~ 2:1 by NMR)).³

¹H NMR (C₆D₆, 500 MHz) for **4a**: δ 0.9–2.1 (m, 66H, PCy₃),¹ 1.26 (s, 2H, ¹J_{PtH} = 635 Hz, Pt···H···Si),⁴ 1.57 (d, 12H, ³J_{HH} = 6.6 Hz, ArCH(CH₃)₂),⁵ 2.72 (s, 3H, ArCH₃), 2.84 (s, 3H, ArCH₃), 4.29 (bm, 1H, ArCH(CH₃)₂), 4.42 (bm, 1H, ArCH(CH₃)₂), 7.01–7.13, 7.18–7.33 (m, 6H, ArH), 9.12 (m, 2H, ²J_{PtH} = 88 Hz, SiH). ³¹P{¹H} NMR (C₆D₆, 121 MHz): δ 58.8 (¹J_{PtP} = 3985 Hz, ²J_{PtP} = 272 Hz, ³J_{PP} = 51 Hz). ²⁹Si{¹H} NMR (C₆D₆, DEPT, 99 MHz): δ 139.7 (d, ¹J_{PtSi} = 1467 Hz,

Table 1

Crystal data and structure refinement parameters for 2a

C51H53P2PtSi
1951.05
223 (2)
$0.38 \times 0.30 \times 0.16$
triclinic
$P\overline{1}$
13.7171 (8)
13.8672 (8)
14.1798 (8)
84.520 (4)
69.640 (3)
60.632 (3)
2194.4 (2)
2
1.439
3.331
0.0689
0.0959
1.115
1.190 and -0.904

 ${}^{1}J_{PtSi} = 199 \text{ Hz}, {}^{2}J_{PSi} = 78 \text{ Hz}$). IR (KBr, cm⁻¹): v 2101 (s, Si–H), 1642 (mb, Pt–H). *Anal.* Calc. for C₅₆H₉₆P₂Pt₂Si₂: C, 52.64; H, 7.57. Found: C, 51.99; H, 7.47%.

¹H NMR (C₆D₆, 500 MHz) for **4b**: δ 0.9–2.1 (m, 66H, PCy₃),¹ 1.18 (bs, 2H, ¹J_{PtH} = 615 Hz, Pt···H···Si),⁴ 1.39 (d, 12H, ³J_{HH} = 6.9 Hz, ArCH(CH₃)₃), 3.06 (br s, 6H, ArCH₃), 4.08 (bm, 1H, ArCH(CH₃)₂), 4.14 (bm, 1H, ArCH(CH₃)₂), 7.01–7.13, 7.18–7.33 (m, 6H, ArH), 8.43 (s, 1H, ²J_{PtH} = 105 Hz, SiH). ³¹P{¹H} NMR (C₆D₆, 121 MHz): δ 58.4 (Js not resolved). ²⁹Si{¹H} NMR (C₆D₆, DEPT, 99 MHz): δ 139.4 (d, ¹J_{PtSi} = 1576 Hz, ¹J_{PtSi} = 241 Hz, ²J_{PSi} = 64 Hz).

2.4. Reaction of $\{(Ph_3P)Pt[\mu-\eta^2-H-SiH(IMP)]\}_2$ (1a,b) with $P(TMP)_3$

A sample of $\{(Ph_3P)Pt[\mu-\eta^2-H-SiH(IMP)]\}_2$ (1a,b) (8 mg, 0.006 mmol) was added to a solution of $P(TMP)_3$ (23 mg, 0.04 mmol) in 1 ml C₆D₆. No visible reaction was observed (e.g. no color change or evolution of gas). The reaction was monitored by ¹H and ³¹P{¹H} NMR and the spectra remained unchanged for 2 days at room temperature and after heating to 60 °C for 24 h. Eventual decomposition of **1a,b** occurred.

2.5. X-ray crystallography

X-ray crystal structure determinations were performed in a Bruker SMART diffractometer equipped with a CCD area detector at 233 K. Crystals of 2a were grown from a dilute C_6D_6 solution by slow evaporation over several days. Preliminary examination and data collection were performed using a Bruker SMART CCD Detector system. Preliminary unit cell constants were determined with a set of 45 narrow frames (0.3° in ϖ scans). The data sets collected consisted of 4028 frames with a frame width of 0.3° in π and counting time of 15 s per frame at a crystal to detector distance of 4.930 cm. The double pass method of scanning was used to exclude any noise. SMART and SAINT software packages [11] were used for data collection and data integration. Analysis of the integrated data did not show any decay. Final cell constants were determined by a global refinement of xyz centroids. Collected data were corrected for systematic errors using SADABS [12] based on the Laue symmetry using equivalent reflections.

Crystal data and intensity data collection parameters are listed in Table 1. Structure solution and refinement were carried out using the SHELXTL-PLUS software

 $^{^3}$ The reaction was quantitative by 1H and $^{31}P\{^1H\}$ NMR spectroscopies.

⁴ The chemical shifts for Pt···*H*···Si were determined from a 2D EXSY experiment; resonances for the *cis* and *trans* bridging hydrides were found to overlap with the PCy₃ resonances.

 $^{^{5}}$ Chemical shift and coupling constant was determined from 2D 1 H-¹H COSY experiment.

⁶ No coupling to the *cis* ³¹P signal was observed in the ${}^{1}H{-}^{31}P$ COSY experiment, possibly due to the weak intensity of the ${}^{31}P$ peaks for *cis*-(**2b**).

 $^{^{7}}$ Estimated from a horizontal slice from the 2D-EXSY data through the terminal hydride (**4a**) and the cross peak correlation to the bridging hydrides.



Fig. 1. Molecular structure of 2a (without benzene solvates).

package [11]. The structures were solved by direct method and refined successfully in the space group $P\overline{1}$. Full matrix least-squares refinement was carried out by minimizing $\Sigma w (F_o^2 - F_c^2)^2$. The non-hydrogen atoms were refined anisotropically to convergence. The Si–H hydrogen was located and refined freely. All the remaining hydrogen atoms were treated using the appropriate riding model. Two and one-half molecules of benzene were found in the crystal lattice for **2a**. Projection view of the molecules with non-hydrogen atoms represented by 50% probability ellipsoids, and showing the atom labeling is presented in Fig. 1.

3. Results and discussion

There are only a few complexes of the Group 10 metals that contain a nonclassical M···H···Si interaction and these include several diplatinum derivatives with the basic structure $\{(R'_{3}P)Pt(\mu-\eta^{2}-H-SiR_{2})\}_{2}$ (R' = alkyl or aryl; R = Me, Ph) prepared by Stone and coworkers [13]. Tessier and coworkers synthesized the novel dinuclear platinum complex { $(Pr_3P)Pt[\mu-\eta^2-H-Si(Hex) PtH(PPr_3)$], (Pr = n-propyl) [14]. More recently, Kim and coworkers reported several dinuclear Pd complexes containing bridging-silylene groups bridging the Pd centers, $[(R_3P)Pd(\mu-\eta^2-H-SiR'R''_2)]_2$ [15]. Little is known of the reactivity of complexes of this structural type. A recent density functional study by Lin and coworkers has shown that dinuclear transition metal bis(µ-η-silane) complexes display noticeably shorter Si-H distances compared to mononuclear metal (μ - η -silane) complexes [16]. The shorter Si-H bonds imply a weaker metal(d) \rightarrow SiH(σ^*) interaction [16].

The dinuclear complex, { $(Ph_3P)Pt[\mu-\eta^2-H-Si(IMP)]$ }₂ (**1a,b**) was prepared by reaction of $(Ph_3P)_2Pt(\eta^2-C_2H_4)$ with (IMP)SiH₃ [6,7]. The nonclassical Pt···H···Si interaction in **1a,b** was supported by multinuclear NMR spectroscopy and X-ray crystallography (*trans*-**1** only).

Recently, we examined the reactivity of 1a,b with

basic phosphines. Reaction of **1a,b** with dppe (cone angle 125°) afforded the dinuclear complex **2** in 94% yield (Eq. (1)) with concomitant loss of H₂. Complex **2** was formed as a mixture of *trans*-(**2a**) and *cis*-(**2b**, trace) isomers and was characterized by multinuclear NMR, IR, elemental analysis, and X-ray crystallography. Several Pt₂Si₂ ring systems analogous to **2a,b** have been prepared by Tessier [4,17], Fink [18], Tilley [19], and Tanaka [20].



Compounds **1a,b** and **2a** both display ¹H NMR chemical shifts for the terminal Si–H proton resonances at very low field. The ¹H{³¹P} NMR spectrum for complex **2a** exhibited the Si–*H* resonance at 7.28 ppm as a singlet flanked by platinum satellites. The NMR resonances associated with **2b** were too weak to be observed except in the ³¹P{¹H} spectrum. The terminal Si–H resonances for **1a,b** appeared at 8.42 and 8.92 ppm flanked by two sets of Pt satellites [6,7]. The terminal Si–H resonances for **1a,b** and **2a** appear significantly further downfield than the typical region for Si–H chemical shifts in free silanes or other reported M–SiH moieties [1].

The dppe ligand in **2a** exhibited two separate methylene peaks in the ¹H{³¹P} spectrum as broad multiplets with platinum satellites. The possibility that these two peaks is due to two different isomers have been excluded by a ¹H-³¹P COSY experiment, that indicated coupling of both resonances to the signal for the *trans* isomer. In addition, the ¹H-³¹P COSY experiment indicated a strong correlation of the *trans* isomer to two different resonances of the *ortho*-P(C₆H₅)₂ unit on the dppe ligand. Thus, it appears that in solution the molecule is unsymmetrical.⁶

The ³¹P{¹H} NMR spectra for **1a,b** and **2a,b** display a characteristic pattern for a dinuclear platinum complex but differ in the splitting of the satellite peaks due to the number of phosphines bound to Pt. The ³¹P{¹H} NMR spectrum for **2a,b** shows part of an AA'A"A"XX' spin system pattern centered at 56 ppm (¹J_{PtP} = 1565 Hz). The value of ¹J_{PtP} for **2a** decreased by approximately 200 Hz relative to the related dinuclear complexes, $[(R_3P)_2Pt(\mu-SiR'R'')]_2$ [8]. The angle constraints associated with a chelating phosphine ligand have been shown to cause a reduction in the value of ¹J_{PtP} [21]. Unlike the ³¹P spectra for related derivatives, $[(Ph_nMe_{3-n}P)_2Pt[\mu-SiH(IMP)]_2$ (n = 0-2) [8] which exhibited platinum satellites as pseudo-triplets, a second-order doublet of doublets pattern was seen for the platinum satellites for complex **2a**. The low solubility of **2a** precluded resolution of the remaining peaks for the case where both Pt nuclei are NMR active.

A dramatic difference is seen in the ²⁹Si NMR chemical shifts for **1a**,**b** and **2a**. Compounds **1a**,**b** exhibits a low field chemical shift of 131 (**1a**) and 126 (**1b**) ppm [6,7] which falls in the typical range for silylene moieties bridging the two metal centers (M–SiR₂–M; with and without bridging hydrides) [3]. In sharp contrast, a high field resonance is seen for **2a** at -132 ppm. The reason for the nearly 250 ppm difference in chemical shifts is currently unknown.

Dinuclear complexes of the structural type, $[(R_3P)_2Pt(\mu-SiR'R'')]_2$ are generally prepared by reaction of a primary or secondary hydrosilane with an appropriate platinum phosphine complex. Results from our studies [8] as well as those of Fink and coworkers [18] and Tilley and coworkers [19] have found that the precursors to these dimers are bis(phosphine)platinum bis(silyl) $(R_3P)_2Pt(SiHR'R'')_2$. complexes Although (Ph.,- $Me_{3-n}P_2Pt(SiH_2IMP)_2$ (n = 0-2) reacts rapidly with the starting platinum precursor $(Ph_nMe_{3-n}P)_2$ -PtMe₂ to form the dinuclear complexes, $\{(R_3P)_2Pt[\mu-Si-$ H(IMP)]₂ [8], the bis(silyl) precursor (dppe)Pt(SiH₂-IMP)₂ did not react.

The reaction shown in (Eq. (1)) is uncommon and we have now shown that the two types of phosphines can initiate this type of transformation of a dinuclear bis(μ - η^2 -H–SiR₂) complex to a bis(μ -silylene) species. Earlier, we found that compound **1a**,**b** undergoes reaction with the more basic, less sterically demanding phosphine, dimethylphenylphosphine (PPhMe₂; cone angle 122°) to form {(PhMe₂P)₂Pt[μ -SiH(IMP)]}₂ *trans*-(**3**) in 87% yield along with the elimination of H₂ [8]. Complex **3** was independently prepared by reaction of (PhMe₂P)₂PtMe₂ with (IMP)SiH₃ and was characterized by multinuclear NMR, X-ray crystallography, and elemental analysis [8].

Table 2

Selected bond lengths (A)	and bond	angles (°)) for	2a
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Bond lengths	
Pt1–Si1	2.412(2)
Pt1-Si # 1	2.395(2)
Pt1–P1	2.315(2)
Pt1–P2	2.328(2)
Pt1…Pt # 1	4.019
Si1…Si # 1	2.637(5)
Bond angles	
P1-Pt1-P2	86.26(8)
P1–Pt1–Si # 1	168.12(7)
P2-Pt1-Si1	169.62(7)
P1-Pt1-Si1	101.74(8)
P2-Pt1-Si # 1	105.60(7)
Pt1–Si1–Pt # 1	113.44(9)
Pt1-Si1-Si # 1	56.41(8)
Pt # 1-Si1-Si # 1	57.04(8)
Sil-Pt1-Si # 1	66.56(9)

In fact, the reverse reaction of a bridging silylene complex containing no metal-metal bond to a system with a metal-metal bond is fairly common [3]. In contrast, mononuclear complexes containing M···H···Si interactions have been reported to undergo reductive elimination of HSiR₃ upon reaction with phosphines. For example $(\eta^6-C_6Me_6)(OC)_2Cr(\eta^2-H-SiHPh_2)$ reacted with P(ⁿBu)₃ to give Ph₂SiH₂ and $(\eta^6-C_6Me_6)(OC)_2-$ Cr[P(ⁿBu)₃] [22].

X-ray quality crystals of 2a were grown from a dilute C_6D_6 solution by slow evaporation and five benzene solvate molecules were found per dimer (Fig. 1). Crystal data and structure refinement parameters are listed in Table 1 and selected bond distances and angles are listed in Table 2. The hydrogens bound to Si were located and refined freely. The isopropyl substituents on the IMP group were found to be positioned over the Pt₂Si₂ core, while hydrogens at silicon were pointing away from the central plane. Complex 2a exhibited similar structural features to those found in the solid state structures of $[(Ph_nMe_{3-n}P)_2Pt(\mu-SiH(IMP)]_2 (n = 0-2) [8], i.e. short$ Si...Si cross ring distances, acute Si-Pt-Si angles, and obtuse Pt-Si-Pt angles (see Table 2). Tessier and coworkers have structurally characterized several related complexes with the formula, $[(R_3P)_2Pt(\mu-SiR'R'')]_2$ and have observed similar trends [4,14,17]. The main difference between these structures is the P-Pt-P angles and the spatial arrangement of substituents on the phosphorus center. For example, due to the configuration associated with the five-membered chelate ring, the P-Pt-P angles in 2a were significantly smaller than the corresponding angles in $[(PhMe_2P)_2Pt(\mu-SiH(IMP)]_2 (86.26(8)^\circ \text{ vs.})$ 99.28(3)°) [8].

A different reactivity pattern was exhibited when **1a.b** was treated with the more basic and bulky phosphine (PCy₃) (4 equiv., cone angle 170°). No gas evolution was observed, in contrast to the dppe and PMe₂Ph reactions described above. The reaction mixture was analyzed by NMR spectroscopy which indicated that the central $Pt_2Si_2(\mu-H)_2$ core remained intact (Eq. (2)) and that exchange of the phosphine ligands had taken place. Complex 4 { $(Cy_3P)Pt[\mu-\eta^2-H-SiH(IMP)]$ } was formed as a mixture of trans-(4a) and cis-(4b) isomers (4a major isomer; exact ratio could not be determined but an upper limit of 2:1 could be established from NMR spectroscopy from the terminal Si-H region) and 4a,b was isolated as an off-white solid in 86% yield. Complexes 4a,b is quite soluble in aromatic solvents and was characterized by multinuclear NMR and IR spectroscopies.



The ¹H NMR spectrum of **4a**,**b** showed two terminal Si-H resonances at low field. The signal for 4a appeared as an unresolved multiplet centered at 9.12 ppm and seems to indicate that two unique terminal hydride resonances are overlapping, suggesting that 4a is unsymmetrical in solution. The terminal hydride resonance for 4b was found at 8.43 ppm as a singlet flanked by one set of platinum satellites. The bridging Pt···H···Si resonances were located by a $^{1}H^{-1}H$ EXSY experiment and were found at 1.26 ppm for 4a and 1.18 ppm for 4b. Data from the EXSY experiment showed that both bridging hydride signals were flanked by one set of Pt satellites.⁷ The ¹H-¹H EXSY experiment also revealed that the terminal and bridging hydrides of 4a were exchanging with each other in addition to the exchange with 4b: the mechanism for exchange is believed to be analogous to that proposed for 1a,b [7] where exchange between terminal and bridging hydrides as well as concomitant cis-trans isomerization was observed.

Variable temperature ¹H and ³¹P{¹H} NMR experiments for **4a,b** gave inconclusive results and the coalescence temperature could not be determined (appears to be >90 °C). Attempts are in progress to obtain a X-ray quality crystals of **4a** and/or **4b** to examine closely the environment around the central $Pt_2Si_2(\mu-H)_2$ core.

The ${}^{31}P{}^{1}H$ NMR spectrum of **4a,b** exhibited a characteristic pattern for a dinuclear platinum complex (part of an AA'XX' spin system) and two central single lines were observed for both *trans-*(**4a**) and *cis-*(**4b**) isomers centered around 58 ppm. These data are similar to those of **1a,b** and related dinuclear complexes [6,7].

The ²⁹Si{¹H} spectrum of **4a**,**b** showed a central doublet for both *cis* and *trans* isomers of **4** at 139 ppm with each exhibiting two sets of Pt satellites (${}^{1}J_{\text{SiPt}} \sim 1500$ and ~ 200 Hz). The larger coupling constant corresponds to Pt that is bound directly to Si, whereas the smaller value of ${}^{1}J_{\text{PtSi}}$ is attributed to the Pt that participates in the 3c-2e Pt···H···Si interaction with Si. The chemical shift of **4a**,**b** was in good agreement with that for complexes **1a**,**b** [6,7].

In addition, the reactivity of **1a**,**b** was explored with the more sterically demanding and basic phosphine, tris(2,4,6-trimethoxyphenyl)phosphine (P(TMP)₃) (cone angle 184°). When a benzene-d₆ solution of **1a**,**b** was treated with P(TMP)₃, no reaction was detected by NMR spectroscopy. The spectrum remained unchanged for 2 days at room temperature and after heating to 60 °C for 24 h. Thus, it appears that P(TMP)₃ is too sterically hindered to undergo an exchange reaction with PPh₃ to give the complex, {[(TMP)₃P]Pt[μ - η^2 -H–SiH(IMP)]}₂.

This study has shown that at least two different types of reactivity are observed with phosphines and the dinuclear complexes 1a,b: (1) formation of a dinuclear complex with change in the central core (with loss of H_2 ; and (2) simple exchange of phosphines (leaving the central $Pt_2Si_2(\mu-H)_2$ core intact). There are two features of phosphines that can influence their reactivity, basicity and the size of the phosphine (cone angle). The results described in this paper indicate that the basicity of the phosphine at the Pt center did not seem to have a significant influence on the formation of a particular type of a dimer. For example, the dinuclear Pt₂Si₂ complexes 4a,b and [(Me₃P)₂Pt(µ-Si-H(IMP)] [8] contain PCy₃ and PMe₃, ligands, respectively, that exhibit similar pK_a values (9.7 vs. 8.65). On the other hand, complexes 1a,b and 4a,b contain PPh₃ and PCy₃ ligands with very different pK_a values (2.73) vs. 9.7). One significantly different feature found in these phosphine ligands is the cone angle [21]. The phosphines with smaller cone angles, dppe (127°) and PMe₂Ph (122°) form the dinuclear complexes with the general formula $[(P)_2Pt(\mu-SiH(IMP))]_2$. In contrast, when the cone angle is $145 \ge x \le 170^\circ$ as with PPh₃ and PCy₃, respectively, then steric constraints favor the formation of the nonclassical dimer $\{(R_3P)Pt[\mu-\eta^2-$ H-SiH(IMP)]}2. Phosphines with cone angles larger than $\sim 170^{\circ}$ appear to be too large to fit into the dinuclear core.

4. Supplementary material

Atomic coordinates, anisotropic displacement parameters, and a complete list of geometrical parameters are deposited with the Cambridge Crystallographic Data Center. Complete listings of the atomic coordinates for the non-hydrogen atoms, the geometrical parameters positional and isotropic displacement coefficients for hydrogen atoms, anisotropic displacement coefficients for the non-hydrogen atoms for **2a** and NMR spectroscopic data for **2a,b** and **4a,b** are available from the corresponding author on request.

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