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# Facile intramolecular silicon-carbon bond activation at Pt<sup>0</sup> and Pt<sup>II</sup> centers

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# ARTICLE INFO

## ABSTRACT

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Dedicated to Alfred Werner on the 100th Anniversary of his 1913 Nobel prize in Chemistry.

Keywords: Platinum Pincer Bond activation Silyl The compound  $(2-Cy_2PC_6H_4)_2SiMe_2$  (1) reacted readily with Pt(PPh\_3)\_4 to undergo Si-C(sp<sup>3</sup>) bond cleavage and form the Pt<sup>II</sup> species (Cy-PSiP)PtMe (2, Cy-PSiP =  $\kappa^3$ -(2-Cy\_2PC\_6H\_4)\_2SiMe<sup>-</sup>). The silane 1 also undergoes Si-C(sp<sup>3</sup>) bond activation with the Pt<sup>II</sup> precursor [(Me<sub>2</sub>S)PtMe<sub>2</sub>]<sub>2</sub> to generate 2. Two intermediate species were observed in situ during the reaction of 1 with [(Me<sub>2</sub>S)PtMe<sub>2</sub>]<sub>2</sub>. One intermediate was tentatively assigned as the bis(phosphino) Pt<sup>II</sup> species ( $\kappa^2$ -Cy-PSiP)PtMe<sub>2</sub> (4), which was crystallographically characterized. A second intermediate (5) was tentatively assigned as the Pt<sup>IV</sup> species (Cy-PSiP)PtMe<sub>3</sub> resulting from Si-C(sp<sup>3</sup>) bond cleavage in 4. In an effort to prepare a (Cy-PSiP)Pt<sup>IV</sup> species that may serve as a model for 5, complex 2 was reacted with MeI and I<sub>2</sub>, respectively; both reactions resulted in the quantitative formation of (Cy-PSiP)PtI (6), which could also be independently prepared by the reaction of (COD)PtI<sub>2</sub> with (Cy-PSiP)H. The reaction of (Cy-PSiP)H with PtMe<sub>3</sub>I resulted in the formation of a Pt<sup>IV</sup> species (7) as the major product. Complex 7 was tentatively assigned as (Cy-PSiP)PtMe<sub>2</sub>I, and undergoes relatively facile elimination of ethane to form 6.

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# 1. Introduction

The activation of chemical bonds (e.g. Si–H, B–H, C–H) at transition metal centers is a fundamental area of inquiry in organometallic chemistry, and has been shown to be a key step in numerous catalytic processes [1]. In this context, examples of  $Si-C(sp^3)$  bond activation by transition metals are exceedingly rare [2,3], due in part to the high bond dissociation energy and low polarity associated with Si–C linkages. The study of metal complexes that readily undergo Si–C(sp<sup>3</sup>) bond cleavage processes is anticipated to play an important role in furthering our understanding of Si–C bond activation and may have utility in the development of new metal catalyzed reactions for the functionalization of organosilanes [4].

We have recently reported on the facile and reversible cleavage of Si–C(sp<sup>2</sup>) and Si–C(sp<sup>3</sup>) bonds in Ni and Pd silyl pincer complexes of the type (Cy-PSiP)MMe (Cy-PSiP =  $\kappa^3$ -(2-Cy<sub>2</sub>-PC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>SiMe<sup>-</sup>; M=Ni, Pd; Fig. 1) [2a]. We proposed that complexes of the type (Cy-PSiP)MMe serve as a source of the M<sup>0</sup> species [ $\kappa^2$ -(2-Cy<sub>2</sub>PC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>SiMe<sub>2</sub>]M, which undergoes subsequent Si–C(sp<sup>2</sup>) or Si–C(sp<sup>3</sup>) bond cleavage. In accordance with this hypothesis, we observed that the silane (2-Cy<sub>2</sub>PC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>SiMe<sub>2</sub> (1) reacted quantitatively with Pd<sub>2</sub>(dba)<sub>3</sub> (dba = dibenzylidene acetone) to form [( $\kappa^2$ -Cy<sub>2</sub>PC<sub>6</sub>H<sub>4</sub>SiMe<sub>2</sub>)Pd( $\kappa^2$ -Cy<sub>2</sub>PC<sub>6</sub>H<sub>4</sub>)] via Si–C(sp<sup>2</sup>) bond cleavage in 1 (Scheme 1) [2a]. In an effort to expand this Si–C bond activation chemistry to Pt, we report herein that 1 undergoes facile

Si-C(sp<sup>3</sup>) bond cleavage involving both Pt<sup>0</sup> and Pt<sup>II</sup> precursors to ultimately form the known Pt<sup>II</sup> complex (Cy-PSiP)PtMe (**2**) [5]. We also report our attempts to observe (Cy-PSiP)Pt<sup>IV</sup> species that are proposed as intermediates in the formation of **2** via Si-C(sp<sup>3</sup>) oxidative addition to Pt<sup>II</sup>.

#### 2. Results and discussion

# 2.1. $Si-C(sp^3)$ bond activation at $Pt^0$

In an effort to observe Si–C bond cleavage mediated by Pt<sup>0</sup>, the silane  $(2-Cy_2PC_6H_4)_2SiMe_2$  (1) was reacted with Pt(PPh<sub>3</sub>)<sub>4</sub> (Scheme 1) in room temperature benzene- $d_6$  solution and the reaction was monitored by use of <sup>1</sup>H and <sup>31</sup>P NMR spectroscopy. Over the course of 48 h, complete conversion to the previously reported [5] Pt<sup>II</sup> complex (Cy-PSiP)PtMe (2; <sup>31</sup>P NMR: 57.9 ppm, <sup>1</sup>J<sub>PPt</sub> = 2938 Hz) was observed, and complex **2** was isolated in 86% yield from this reaction. No intermediates were observed by use of <sup>1</sup>H or <sup>31</sup>P NMR spectroscopy during the course of the reaction.

The mechanism of Si–C(sp<sup>3</sup>) bond activation by Pt<sup>0</sup> complexes has been previously investigated. Hofmann and co-workers have demonstrated that Si–C bond activation of tetramethylsilane by (dtbpm)Pt<sup>0</sup> (dtbpm =  ${}^{t}Bu_2PCH_2P^{t}Bu_2$ ) proceeds via an initial C–H bond activation of the silane, followed by a rearrangement to give the Si–C bond activation product [2c]. As such, it is possible that the formation of **2** proceeds via an initial C–H bond activation of a Si*Me* group in **1**, which is followed by a rearrangement to provide **2** as the final product. However, we do not currently have mecha-





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**Fig. 1.** Cleavage of Si–C(sp<sup>2</sup>) and Si–C(sp<sup>3</sup>) bonds in silyl pincer complexes of the type (Cy-PSiP)MMe (M=Ni, Pd).

nistic data to favor this mechanism over direct insertion of the Pt center into a Si–C bond.

Surprisingly, Si–C bond activation in **1** involving Pt<sup>0</sup> differs from the previously reported reaction of 1 with  $Pd_2(dba)_3$ , which also proceeds quantitatively in room temperature benzene- $d_6$  solution to provide complex **3**, the product of  $Si-C(sp^2)$  bond cleavage (Scheme 1); as in the case of the  $Pt(PPh_3)_4$  reaction, no intermediates were observed by use of <sup>1</sup>H or <sup>31</sup>P NMR spectroscopy during the course of this reaction [2a]. In contrast, our previous report of reversible Si-C(sp<sup>2</sup>) and Si-C(sp<sup>3</sup>) bond cleavage involving (Cy-PSiP)NiMe suggests that Ni<sup>0</sup> species of the type [ $\kappa^2$ -(2-Cy<sub>2</sub>- $PC_6H_4)_2SiMe_2$ Ni are able to access both Si-C(sp<sup>2</sup>) bond cleavage (to form the Ni analog of **3**,  $[(\kappa^2 - Cy_2PC_6H_4SiMe_2)Ni(\kappa^2 - Cy_2PC_6H_4)])$ and  $Si-C(sp^3)$  bond cleavage to reform (Cv-PSiP)NiMe [2a]. Thus it appears that the choice of metal influences the outcome of Si-C bond cleavage in this system, such that Pt favors the formation of products resulting from Si-C(sp<sup>3</sup>) bond cleavage, while Pd favors the formation of products resulting from Si–C(sp<sup>2</sup>) bond cleavage, and Ni is able to access both types of products in a reversible fashion.

# 2.2. Si-C(sp<sup>3</sup>) bond activation involving Pt<sup>II</sup>

We further investigated the reactivity of **1** with  $[(Me_2S)PtMe_2]_2$ in order to determine if Si–C bond activation could also be achieved by use of Pt<sup>II</sup> precursors. Thus, treatment of a benzene $d_6$  solution of **1** with half an equiv. of  $[(Me_2S)PtMe_2]_2$  led to the formation of three products (1:1:1 ratio by <sup>31</sup>P NMR) upon standing at room temperature for 5 days (Scheme 1). One of the three reaction products was identified as complex **2** on the basis of its <sup>31</sup>P NMR chemical shift (57.9 ppm, <sup>1</sup> $J_{PPt}$  = 2938 Hz). A second product (**4**) features a <sup>31</sup>P NMR resonance at 27.7 ppm (<sup>1</sup> $J_{PPt}$  = 2050 Hz), while the third species in solution (**5**) features a broad <sup>31</sup>P NMR resonance at 23.1 ppm ( ${}^{1}J_{PPt}$  = 934 Hz). The magnitude of the coupling constant observed for complex **5** suggests that this complex likely corresponds to a Pt<sup>IV</sup> species.

Despite exhaustive efforts, we have thus far not been able to isolate either of 4 or 5 in pure form; rather, mixtures of 2, 4, and 5 were invariably obtained. However, crystallization attempts enabled the isolation of a minute quantity of crystalline material (from a Et<sub>2</sub>O solution at -35 °C) that proved suitable for single crystal X-ray diffraction analysis. The crystallographically characterized material (Fig. 2 and Table 1) corresponds to  $[\kappa^2-(2-Cy_2 PC_6H_4)_2SiMe_2$  PtMe<sub>2</sub>, the product of phosphine coordination in **1** to the PtMe<sub>2</sub> fragment. We tentatively assign this compound as complex **4**, a putative intermediate in the formation of **2** via Si- $C(sp^3)$  bond activation in **1** at a Pt<sup>II</sup> center. The solid state structure of 4 features approximate square planar geometry at Pt, with cisdisposed phosphino groups  $(P1-Pt-P2 = 102.491(14)^{\circ})$ . The eightmembered metallacycle resulting from coordination of the phosphino groups in **1** to Pt adopts a "boat-boat"-type configuration, such that a Si-Me group is oriented directly above the square plane defined by the Pt center  $(Pt \cdots C(1) = 3.35 \text{ Å}; Pt \cdots Si = 3.53 \text{ Å})$ . The structure of **4** is related to that of  $(bps)PtMe_2$  (bps = bis(2-pyridyl)dimethylsilane), which adopts a similar orientation of a Si-Me substituent (Pt  $\cdot \cdot \cdot$  Si = 3.25 Å) [2g]. Interestingly, the structurally related complex (bps)PtMe<sub>2</sub> has been reported to undergo Si-C(sp<sup>3</sup>) bond cleavage only under oxidizing conditions to afford Pt<sup>IV</sup> species of the type  $[\kappa^3 N, N, O-(2-C_5H_4N)_2 \text{SiMeO}]$ PtMe<sub>3</sub> [2g]. No Si–C bond activation was reported for (bps)PtMe<sub>2</sub> in the absence of oxidants such as oxygen, hydrogen peroxide, or dibenzoyl peroxide, in contrast to the system presented herein. Mechanistic studies in the (bps)PtMe<sub>2</sub> system suggested that oxidation to Pt<sup>IV</sup> preceded methyl transfer from Si to Pt.

In the case of Si–C activation in **1** involving an  $L_nPtMe_2$  precursor, we propose that  $\kappa^2$ -coordination of **1** to Pt occurs initially to form the bis(phosphino) complex **4**. In previously reported examples of Si–C(sp<sup>3</sup>) activation at Pt<sup>II</sup> centers, it has been proposed that such transformations proceed via an initial C–H bond activation step [2e,f], followed by a subsequent concerted migration process that leads to the formation of the net Si–C bond cleavage product [2f]. Although such a mechanism is plausible in the case of **4**, we also cannot discount a process involving direct insertion of Pt into a Si–C bond. The product of such Si–C bond cleavage is the Pt<sup>IV</sup> species (Cy-PSiP)PtMe<sub>3</sub>, which we tentatively assign as complex **5**, and which was observed in situ during the course of the formation of **2** (*vide supra*) [6]. Reductive elimination of ethane from the putative



Scheme 1. Reaction of 1 with Pt<sup>0</sup>, Pd<sup>0</sup>, and Pt<sup>II</sup> complexes.



**Fig. 2.** ORTEP diagram for **4** shown with 50% displacement ellipsoids; all H-atoms have been omitted for clarity. Selected interatomic distances (Å) and angles (°) for **4**: Pt-P1 2.3078(4); Pt-P2 2.3106(4); Pt-C3 2.1032(16); Pt-C4 2.1051(16); Pt-··C(1) 3.35; Pt···Si 3.53; P1-Pt-P2 102.491(14); C3-Pt-C4 81.82(7); P1-Pt-C4 170.50(5); P2-Pt-C3 163.33(5).

Table 1Crystal data and refinement parameters for 4.

	4
Empirical formula	C <sub>40</sub> H <sub>64</sub> P <sub>2</sub> PtSi
Formula weight	830.03
Crystal dimensions	$0.63 \times 0.44 \times 0.31$
Crystal system	C2/c (No. 15)
Space group	monoclinic
a (Å)	38.7504(13)
b (Å)	9.3925(3)
c (Å)	20.8598(7)
α (°)	90
β (°)	96.2086(4)
γ (°)	90
$V(Å^3)$	7547.7(4)
Ζ	8
$\rho_{\rm calc} ({\rm g}{\rm cm}^{-3})$	1.461
$\mu ({\rm mm}^{-1})$	3.861
Range of transmission	0.3759-0.1940
$2\theta$ limit (°)	55.12
	$-49 \leqslant h \leqslant 50$
	$-12 \leqslant k \leqslant 12$
	$-26 \leqslant l \leqslant 27$
Total data collected	32378
Independent reflections	8699
R <sub>int</sub>	0.0123
Observed reflections	7991
Data/restraints/parameters	8699/0/401
Goodness-of-fit	1.053
$R_1 [F_o^2 \ge 2\sigma (F_o^2)]$	0.0154
$wR_2 [F_o^2 \ge -3\sigma(F_o^2)]$	0.0400
Largest peak, hole (eÅ <sup>-3</sup> )	0.684, -0.723
, ,	

intermediate **5** provides the final observed product of this reaction, complex **2** [7]. The <sup>1</sup>H NMR spectrum of the reaction mixture containing **4**, **5**, and **2** indeed indicates the evolution of ethane (0.80 ppm, benzene- $d_6$ ).



**Scheme 2.** Attempted synthesis of a (Cy-PSiP)Pt<sup>IV</sup> species.

# 2.3. Attempted synthesis of a (Cy-PSiP)Pt<sup>IV</sup> species

In an effort to synthesize a (Cy-PSiP)Pt<sup>IV</sup> species that may serve as a model for the proposed Pt<sup>IV</sup> intermediate (**5**) in the Si–C(sp<sup>3</sup>) bond activation process observed for **1** at Pt<sup>II</sup>, complex **2** was reacted with one equiv each of either MeI or I<sub>2</sub> (Scheme 2). No reaction was observed (by <sup>31</sup>P NMR) upon treatment of **2** with one equiv of MeI at room temperature in benzene-*d*<sub>6</sub> solution. Subsequent heating of the reaction mixture at 75 °C for 1 h resulted in quantitative (by <sup>31</sup>P NMR) formation of (Cy-PSiP)PtI (**6**; 58.9 ppm, <sup>1</sup>*J*<sub>PPt</sub> = 2948 Hz), which was independently synthesized by the reaction of (Cy-PSiP)H with (COD)PtI<sub>2</sub> (COD = 1,5-cyclooctadiene) in the presence of Et<sub>3</sub>N. Treatment of **2** with one equiv of I<sub>2</sub> resulted in the immediate and quantitative (by <sup>31</sup>P NMR) formation of **6**. No intermediates were observed in the reaction of **1** with either MeI or I<sub>2</sub>.

Alternatively, treatment of (Cy-PSiP)H with one equiv of PtMe<sub>3</sub>I in benzene- $d_6$  solution resulted in the formation of a mixture of two products (2:1 ratio by <sup>31</sup>P NMR) upon heating for 3.5 h at 75 °C. The major product (**7**) gives rise to a broad <sup>31</sup>P NMR resonance at 19.3 ppm ( ${}^{1}J_{PPt}$  = 1187 Hz), while the minor product corresponds to the Pt<sup>II</sup> iodo complex **6** (Scheme 2). The magnitude of the Pt–P one bond coupling in **7** is consistent with a Pt<sup>IV</sup> species of the type (Cy-PSiP)PtMe<sub>2</sub>I (**7**; *cf.*  ${}^{1}J_{PPt}$  = 1112 Hz for (dppe)PtMe<sub>3</sub>I; dppe = Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub> [7b]). The <sup>1</sup>H NMR spectrum of the reaction mixture features resonances for both methane (0.15 ppm) and ethane (0.80 ppm), which is consistent with initial Si-H activation in (Cy-PSiP)H to liberate methane and form complex 7, followed by C-C reductive elimination in 7 to give 6. Further heating of the reaction mixture for 12 h at 95 °C resulted in the quantitative formation of 6. Unfortunately, attempts to isolate the Pt<sup>IV</sup> species **7** were not successful, as **6** was always observed as a contaminant. However, the in situ observation of putative 7 would appear to suggest that (Cy-PSiP)Pt<sup>IV</sup> species of this type are synthetically accessible and readily undergo reductive elimination of ethane.

#### 3. Summary and conclusions

Examples of Si–C(sp<sup>3</sup>) bond activation in the silane  $(2-Cy_2-PC_6H_4)_2SiMe_2$  (1) involving both Pt<sup>0</sup> and Pt<sup>II</sup> precursors have been described. In the case of Si–C cleavage involving Pt<sup>0</sup>, **1** reacted readily with Pt(PPh<sub>3</sub>)<sub>4</sub> to form the Pt<sup>II</sup> complex (Cy–PSiP)PtMe (**2**) with no evidence of intermediate species. Interestingly, this example of Si–C(sp<sup>3</sup>) bond activation differs from the previously reported, analogous reaction of **1** with the Pd<sup>0</sup> source Pd<sub>2</sub>(dba)<sub>3</sub>, which led to formation of the Si–C(sp<sup>2</sup>) bond activation product

 $[(\kappa^2-Cy_2PC_6H_4SiMe_2)Pd(\kappa^2-Cy_2PC_6H_4)]$  (**3**). Previous results involving Ni are consistent with the formation of an equilibrium mixture containing both Si-C(sp<sup>3</sup>) and Si-C(sp<sup>2</sup>) bond activation products derived from **1**. Thus it is evident that the choice of metal (Ni versus Pd versus Pt) directs the outcome of Si-C bond cleavage involving **1**.

The silane **1** also reacted with  $[(Me_2S)PtMe_2]_2$  to generate **2**. Two intermediate species were observed in situ during the course of this reaction. One intermediate was tentatively assigned as the bis(phosphino) Pt<sup>II</sup> species ( $\kappa^2$ -Cy-PSiP)PtMe<sub>2</sub> (**4**), which was crystallographically characterized, and is structurally related to the bis(2-pyridyl) dimethylsilane complex (bps)PtMe<sub>2</sub>. The latter complex was also reported to undergo Si-C(sp<sup>3</sup>) bond cleavage, however only upon treatment with oxidants. As such, the mechanism of Si-C(sp<sup>3</sup>) cleavage in **4** is different, as no oxidants are required for the transformation. This disparity likely results from a ligand effect, as the electronic character of the bis(phosphino) Pt<sup>II</sup> center is likely quite different from that of a bis(pyridyl) Pt<sup>II</sup> center. We propose that  $Si-C(sp^3)$  cleavage in **4** leads to the formation of the Pt<sup>IV</sup> species (Cy-PSiP)PtMe<sub>3</sub> (5), which undergoes subsequent elimination of ethane to generate 2. The second intermediate observed in situ during the course of the reaction of 1 with  $[(Me_2S)PtMe_2]_2$ indeed appears to be a Pt<sup>IV</sup> species, and was thus tentatively assigned as 5. As we were unable to isolate complex 5, we attempted to prepare a model species that featured Cv-PSiP coordination to Pt<sup>IV</sup>. Indeed, the reaction of (Cy-PSiP)H with PtMe<sub>3</sub>I led to the formation of a  $Pt^{IV}$  complex (7), which we tentatively assign as (Cy-PSiP)PtMe<sub>2</sub>I. Complex **7** features a <sup>31</sup>P NMR chemical shift and <sup>1</sup>J<sub>PPt</sub> that are very similar to those observed for the proposed intermediate 5, and it also undergoes relatively facile reductive elimination of ethane to generate (Cy-PSiP)PtI (6). This data would appear to provide indirect evidence for the viability of the intermediate 5 and for C–C reductive elimination from **5** to generate a Pt<sup>II</sup> species.

#### 4. Experimental

#### 4.1. General

All experiments were conducted under nitrogen in an MBraun glovebox or using standard Schlenk techniques. Dry, oxygen-free solvents were used throughout. All non-deuterated solvents were deoxygenated and dried by sparging with nitrogen and subsequent passage through a double-column solvent purification system purchased from MBraun Inc. Tetrahydrofuran and diethyl ether were purified over two activated alumina columns, while benzene, toluene, and pentane were purified over one activated alumina column and one column packed with activated Q-5. All purified solvents were stored over 4 Å molecular sieves. Benzene- $d_6$  was degassed via three freeze-pump-thaw cycles and stored over 4 Å molecular sieves. The compounds Pt(PPh<sub>3</sub>)<sub>4</sub> and PtMe<sub>3</sub>I were purchased from Strem and used as received. The compounds (2-Cy<sub>2</sub>PC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>SiMe<sub>2</sub> [2a], (2-Cy<sub>2</sub>PC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>SiHMe [8], (COD)PtI<sub>2</sub> [9], [(Me<sub>2</sub>S)PtMe<sub>2</sub>]<sub>2</sub> [10], and (Cy-PSiP)PtMe [5] were prepared according to literature procedures. All other reagents were purchased from Aldrich and used without further purification. Unless otherwise stated, <sup>1</sup>H, <sup>13</sup>C, <sup>31</sup>P, and <sup>29</sup>Si characterization data were collected at 300 K on a Bruker AV-500 spectrometer operating at 500.1, 125.8, 202.5, and 99.4 MHz (respectively) with chemical shifts reported in parts per million downfield of SiMe<sub>4</sub> (for <sup>1</sup>H, <sup>13</sup>C, and <sup>29</sup>Si), or 85% H<sub>3</sub>PO<sub>4</sub> in D<sub>2</sub>O (for <sup>31</sup>P). <sup>29</sup>Si NMR assignments are based on <sup>1</sup>H-<sup>29</sup>Si HMQC and <sup>1</sup>H-<sup>29</sup>Si HMBC experiments.

# 4.2. (Cy-PSiP)PtMe (2)

The synthesis of this compound by an alternate route and its full characterization have been previously reported [5].

# 4.2.1. Synthesis of **2** via Si– $C(sp^3)$ bond cleavage involving $Pt^0$

A solution of **1** (0.10 g, 0.17 mmol) in ca. 5 mL of benzene was added to  $Pt(PPh_3)_4$  (0.21 g, 0.17 mmol). The resulting pale yellow solution was allowed to stand at room temperature over the course of 48 h. The volatile components of the reaction mixture were subsequently removed in vacuo and the remaining residue was washed with cold (-30 °C) pentane ( $5 \times 3$  mL) and dried under vacuum to afford **2** as a pale yellow solid (0.12 g, 86% yield). The spectroscopic characterization of the product obtained was in full agreement with previously published data [5].

# 4.2.2. Generation of **2** via Si– $C(sp^3)$ bond cleavage involving $Pt^{II}$

A solution of **1** (0.030 g, 0.050 mmol) in ca. 1 mL of benzene- $d_6$ was added to [Pt(SMe<sub>2</sub>)Me<sub>2</sub>]<sub>2</sub> (0.014 g, 0.025 mmol). The resulting yellow solution was allowed to stand at room temperature over the course of 5 days and was monitored by <sup>31</sup>P and <sup>1</sup>H NMR spectroscopy. After standing at room temperature for 18 h. <sup>31</sup>P NMR analysis of the reaction mixture indicated 80% consumption of 1 and the formation of a product mixture consisting of 4  $(27.7 \text{ ppm}, {}^{1}J_{PPt} = 2050 \text{ Hz})$  and **5**  $(23.1 \text{ ppm}, \text{ br s}, {}^{1}J_{PPt} = 934 \text{ Hz})$ in a 1:3 ratio. After standing at room temperature for 5 days, <sup>31</sup>P NMR analysis of the reaction mixture indicated complete consumption of **1** and the formation of a product mixture consisting of **2** (57.9 ppm,  ${}^{1}J_{PPt}$  = 2938 Hz), **4** (27.7 ppm,  ${}^{1}J_{PPt}$  = 2050 Hz) and **5** (23.1 ppm, br s,  ${}^{1}J_{PPt}$  = 934 Hz) in a 1:1:1 ratio. Although  ${}^{1}H$ NMR analysis of the resulting product mixtures was complicated by the overlap of aryl and cyclohexyl proton resonances, a resonance at 0.80 ppm corresponding to ethane was observed.

#### 4.3. (Cy-PSiP)PtI (**6**)

#### 4.3.1. Synthesis of 6 via (COD)PtI<sub>2</sub>

A solution of (Cy-PSiP)H (0.10 g, 0.17 mmol) in. ca 2 mL of benzene was added to (COD)PtI<sub>2</sub> (0.095 g, 0.17 mmol). The resulting reaction mixture was treated with NEt<sub>3</sub> (0.026 mL, 0.19 mmol). The reaction mixture was subsequently allowed to stand at room temperature for 1 h, and was then filtered through Celite. The volatile components of the filtrate solution were removed under vacuum. The remaining yellow residue was washed with ca. 3 mL of cold  $(-30 \circ C)$  pentane and dried under vacuum to afford **6** as a pale yellow solid (0.15 g, 96% yield). The spectroscopic data obtained for **6** is in good agreement with the previously reported analogous complexes (Cy-PSiP)PtCl and (Cy-PSiP)PtOTf [5]. <sup>1</sup>H NMR (500 MHz, benzene- $d_6$ ):  $\delta$  8.07 (d, 2H,  $H_{arom}$ , J = 7 Hz), 7.51 (m, 2H, *H*<sub>arom</sub>), 7.31 (t, 2H, *H*<sub>arom</sub>, *J* = 7 Hz), 7.19 (t, 2H, *H*<sub>arom</sub>, *J* = 7 Hz), 3.43 (m, 2H, PCH), 2.77 (m, 2H, PCH), 2.40 (m, 2H, PCy), 2.24-2.09 (overlapping resonances, 6H, PCy), 1.75–0.82 (overlapping resonances, 32H, PCy), 0.68 (s with Pt satellites, 3H, SiMe,  ${}^{3}J_{HPt} = 26 \text{ Hz}$ ).  ${}^{13}C{}^{1}H$  NMR (125.8 MHz, benzene- $d_{6}$ ):  $\delta$  156.4 (apparent t,  $C_{\text{arom}}$ , J = 22 Hz), 141.1 (apparent t,  $C_{\text{arom}}$ , J = 25 Hz), 133.3 (CH<sub>arom</sub>), 131.8 (CH<sub>arom</sub>), 130.9 (CH<sub>arom</sub>), 129.4 (CH<sub>arom</sub>), 39.5 (apparent t,  $CH_{Cy}$ , J = 15 Hz), 37.9 (apparent t,  $CH_{Cy}$ , *J* = 13 Hz), 31.6–26.3 (overlapping resonances, *C*H<sub>2Cv</sub>), 8.4 (Si*Me*). <sup>31</sup>P {<sup>1</sup>H} NMR (202.5 MHz, benzene- $d_6$ ):  $\delta$  59.0 (s with Pt satellites,  ${}^{1}J_{PPt}$  = 2948 Hz). <sup>29</sup>Si NMR (99.4 MHz, benzene-*d*<sub>6</sub>):  $\delta$  39.8 (s with Pt satellites,  ${}^{1}J_{SiPt} = 1155$  Hz).

#### 4.3.2. Generation of 6 via the reaction of 2 with MeI

A solution of **2** (0.015 g, 0.019 mmol) in ca. 1 mL of benzene- $d_6$  was treated with MeI (1.2 µl, 0.019 mmol). The resulting pale yellow reaction mixture was heated at 75 °C for 1 h, at which point <sup>31</sup>P NMR analysis indicated quantitative conversion to **6**.

# 4.3.3. Generation of **6** via the reaction of **2** with $I_2$

A solution of **2** (0.010 g, 0.013 mmol) in ca. 1 mL of benzene- $d_6$  was treated with I<sub>2</sub> (0.003 g, 0.013 mmol). The resulting purple

reaction mixture was allowed to stand at room temperature over the course of 10 min, at which point <sup>31</sup>P NMR analysis indicated quantitative conversion to **6**.

#### 4.3.4. Generation of $\mathbf{6}$ via PtMe<sub>3</sub>I

A solution of (Cy-PSiP)H (0.015 g, 0.025 mol) in ca. 1 mL of benzene- $d_6$  was added to PtMe<sub>3</sub>I (0.009 g, 0.025 mmol). The reaction mixture was subsequently heated at 75 °C over the course of 3.5 h, at which point <sup>31</sup>P NMR analysis indicated complete consumption of (Cy-PSiP)H and the formation of a product mixture consisting of **6** and **7** (19.3 ppm, br s, <sup>1</sup> $J_{PPt}$  = 1187 Hz) in a 1:2 ratio. Subsequent heating of the reaction mixture at 95 °C for 12 h resulted in the quantitative formation of **6**. <sup>1</sup>H NMR (500 MHz) analysis of the reaction mixture after heating at 75 °C for 3.5 h revealed several resonances that could be unambiguously assigned to **7** (as well as the formation of ethane and methane):  $\delta$  7.65 (d, 2H,  $H_{arom}$ , J = 7 Hz). 7.46 (m, 2H,  $H_{arom}$ ), 7.12 (t, 2H,  $H_{arom}$ , J = 7 Hz), 7.03 (t, 2H,  $H_{arom}$ , J = 7 Hz), 0.35–0.86 (overlapping resonances corresponding to PCy and PtMe protons in **6** and **7**), 0.61 (s with Pt satellites, 3H, SiMe, <sup>3</sup> $J_{HPt}$  = 17 Hz).

#### 4.4. X-ray crystallography

Crystallographic data for 4 were obtained at 173(±2) K on a Bruker D8/APEX II CCD diffractometer using graphite-monochromated MoK $\alpha$  ( $\lambda$  = 0.71073 Å) radiation, employing a sample that was mounted in inert oil and transferred to a cold gas stream on the diffractometer. Programs for diffractometer operation, data collection, and data reduction (including SAINT) were supplied by Bruker. Gaussian integration (face-indexed) was employed as the absorption correction method. The structure was solved by use of the Patterson search/structure expansion and were refined by use of full-matrix least-squares procedures (on  $F^2$ ) with  $R_1$  based on  $F_o^2 \ge 2\sigma(F_o^2)$  and  $wR_2$  based on  $F_o^2 \ge -3\sigma(F_o^2)$ . Anisotropic displacement parameters were employed for all the non-hydrogen atoms of 4. Hydrogen-atoms were added at calculated positions and refined by use of a riding model employing isotropic displacement parameters based on the isotropic displacement parameter of the attached atom. Additional crystallographic information is provided in Table 1.

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### Appendix A. Supplementary data

CCDC 879358 contains the supplementary crystallographic data for **4**. These data may be obtained free of charge via http:// www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223–336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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