

# The Reactions of *cis*-[PtMe<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>2</sub>] with R<sub>3</sub>SiH (R<sub>3</sub> = Ph<sub>3</sub>H and Ph<sub>2</sub>H) - A Reinvestigation

Latifah Abdol Latif

Centre for Foundation Studies in Science, University of Malaya, 59100 Kuala Lumpur, Malaysia

**Abstract** - The reaction between *cis*-[PtMe<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>2</sub>] and Ph<sub>3</sub>SiH at 70 °C gave *cis*-[PtH(SiPh<sub>3</sub>)(PMe<sub>2</sub>Ph)<sub>2</sub>] (II), Ph<sub>3</sub>SiMe, CH<sub>4</sub> and a small quantity of H<sub>2</sub>. However, with Ph<sub>2</sub>SiH<sub>2</sub>, the reaction occurs much more readily to give *cis*-[Pt(SiPh<sub>2</sub>H<sub>2</sub>)(PMe<sub>2</sub>Ph)<sub>2</sub>] (I), Ph<sub>2</sub>MeSiH, CH<sub>4</sub> and H<sub>2</sub>. The observed molar ratio of the products formed indicate that the reactions most probably occur *via* the two/three oxidative-additions of R<sub>3</sub>SiH (R<sub>3</sub> = Ph<sub>2</sub>H and Ph<sub>3</sub>) to form (I) and (II) respectively, with the liberation of R<sub>3</sub>SiMe.

**Abstrak** - Tindak balas antara *cis*-[PtMe<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>2</sub>] dengan Ph<sub>3</sub>SiH pada 70 °C menghasilkan *cis*-[PtH(SiPh<sub>3</sub>)(PMe<sub>2</sub>Ph)<sub>2</sub>] (II), Ph<sub>3</sub>SiMe, CH<sub>4</sub> dan sedikit gas H<sub>2</sub>. Walau bagaimanapun, tindak balas dengan Ph<sub>2</sub>SiH<sub>2</sub> berlaku dengan lebih cergas untuk menghasilkan *cis*-[Pt(SiPh<sub>2</sub>H<sub>2</sub>)(PMe<sub>2</sub>Ph)<sub>2</sub>] (I), Ph<sub>2</sub>MeSiH, CH<sub>4</sub> dan H<sub>2</sub>. Nisbah molar bagi bahan dan hasil tindak balas menunjukkan bahawa tindak balas tersebut mungkin berlaku melalui dua atau tiga penambahan-oksidan R<sub>3</sub>SiH (R<sub>3</sub> = Ph<sub>2</sub>H dan Ph<sub>3</sub>) untuk membentuk masing-masing (I) dan (II) dan disertai dengan penghasilan R<sub>3</sub>SiMe.

## Introduction

Eaborn and co-workers [1] have shown that the reactions of Ph<sub>3</sub>SiH (R<sub>3</sub> = (*p*-FC<sub>6</sub>H<sub>4</sub>)<sub>3</sub>, MePh<sub>2</sub> and Ph<sub>2</sub>H) with *cis*-[PtMe<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>2</sub>] gave either the hydrido(silyl) complexes, *cis*-[PtH(SiR<sub>3</sub>)(PMe<sub>2</sub>Ph)<sub>2</sub>] or the bis(silyl) species, *cis*-[Pt(SiR<sub>2</sub>)<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>2</sub>]. These reactions were thought to proceed *via* the oxidative-addition and reductive-elimination mechanisms involving Pt(IV)-Si intermediates. In the reaction, (*i.e.* *cis*-[PtMe<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>2</sub>]) with Ph<sub>2</sub>SiH<sub>2</sub>, a silicon containing product, Ph<sub>2</sub>MeSiH, was detected and this is of great interest since elimination of a tetraorganosilane is one of the steps postulated in the

mechanism of hydrosilylation of olefins catalysed by H<sub>2</sub>PtCl<sub>6</sub> [2]. These reactions were revisited to carefully examine the relative quantities and products in order to propose a likely route for the reactions.

## Experimental

### General

Ph<sub>2</sub>SiH<sub>2</sub> was supplied by Prof. C. Eaborn and Ph<sub>3</sub>SiH was obtained commercially. The Pt complex, *cis*-[PtMe<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>2</sub>] was prepared by treating *cis*-[PtCl<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>2</sub>] with ethereal MeLi [3]. The title compound was charac-

terised by m.p., <sup>1</sup>H and <sup>31</sup>P-{'<sup>1</sup>H} nmr spectroscopy. Both spectra are similar to those reported for similar complexes, *cis*-[PtMe<sub>2</sub>(PMe<sub>2</sub>)<sub>2</sub>] [4] and *cis*-[PtMe<sub>2</sub>(PEt<sub>2</sub>)<sub>2</sub>] [5].

#### Reaction of *cis*-[PtMe<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>2</sub>] with Ph<sub>2</sub>SiH<sub>2</sub> [reaction I]

The apparatus, which consisted of a D-tube with one end connected to a Schlenk flask and the other to the vacuum line, was rigorously evacuated and dried prior to use. An excess (*ca* 1 mL) of freshly degassed Ph<sub>2</sub>SiH<sub>2</sub> was put into a small tube, which was then placed in the flask containing *cis*-[PtMe<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>2</sub>] (0.2g, 0.4 mmol). Vigorous gas evolution occurred as the two reactants were mixed, and the mixed was kept at 70 °C for 45 min. The gas collected was characterised by mass spectrometry and gas-liquid chromatography (GLC). The former showed a molecular ion peak at *m/e* value of 16, and the GLC results indicate that the gas contains a mixture of CH<sub>4</sub> and H<sub>2</sub> (by comparing the retention times with those for authentic CH<sub>4</sub> and H<sub>2</sub> samples). The molar ratio of the gasses were determined by running volumes of H<sub>2</sub> and CH<sub>4</sub> at different sensitivities, from which the related volume to area units for H<sub>2</sub> and CH<sub>4</sub> were calculated. From the area units of the gas samples, the volume ratio was calculated under the same conditions of temperature and pressure, the volume ratio equals the molar ratio, and the latter was found to be 2.2 : 1 of CH<sub>4</sub> : H<sub>2</sub>. To the orange solution, C<sub>6</sub>H<sub>6</sub> (*ca* 1 mL) was added and its <sup>1</sup>H nmr spectrum recorded. Addition of *n*-hexane (5 mL) to this sample produced a pale yellow solid, which was washed with *n*-hexane and dried under *vacuo*, and its shown to be *cis*-[Pt(SiPh<sub>2</sub>H<sub>2</sub>)(PMe<sub>2</sub>Ph)<sub>2</sub>] (0.23g, 70%); m.p. 124-125 °C; IR (Nujol mull);  $\nu$  (SiH) 2000, 2065 cm<sup>-1</sup>. (Found C : 57.5; H : 4.7; Calc. for C<sub>14</sub>H<sub>24</sub>PtSi<sub>2</sub>O : C : 57.3; H : 5.3%). <sup>1</sup>H and <sup>31</sup>P-{'<sup>1</sup>H} nmr data are shown Table 1.

#### Reaction of *cis*-[PtMe<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>2</sub>] with

#### Ph<sub>3</sub>SiH [reaction II]

The reaction mixture, consisting of *cis*-[PtMe<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>2</sub>] (0.2g, 0.4 mmol) in C<sub>6</sub>H<sub>6</sub> (*ca* 5 mL) and an excess of Ph<sub>3</sub>SiH (0.42 g, 1.6 mmol) was kept at 75 °C for *ca* 3h using the same apparatus. When gas evolution has ceased, its <sup>1</sup>H and <sup>31</sup>P-{'<sup>1</sup>H} nmr spectra were recorded (Table 1). Most of the solvent was removed, *n*-hexane (*ca* 5 mL) was added and the mixture was agitated for 2h to yield *cis*-[PtH(SiPh<sub>3</sub>)(PMe<sub>2</sub>Ph)<sub>2</sub>] as cream crystals (0.2g, 73%) IR (Nujol Mull) :  $\nu$ (Pt-H) 2040 cm<sup>-1</sup>. <sup>1</sup>H and <sup>31</sup>P-{'<sup>1</sup>H} nmr data are shown in Table 1.

## Results

An addition of an excess (*ca* 1 mL) of freshly degassed Ph<sub>2</sub>SiH<sub>2</sub> to *cis*-[PtMe<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>2</sub>] [reaction I] under N<sub>2</sub> gave *cis*-[Pt(SiPh<sub>2</sub>H<sub>2</sub>)(PMe<sub>2</sub>Ph)<sub>2</sub>] (I), Ph<sub>3</sub>MeSiH, CH<sub>4</sub> and H<sub>2</sub>. The ratio of the gasses CH<sub>4</sub> : H<sub>2</sub> was 2.2 : 1. However, the addition of a 1 : 4 molar mixture of *cis*-[PtMe<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>2</sub>] and Ph<sub>3</sub>SiH [reaction II] in benzene ultimately gave *cis*-[PtH(SiPh<sub>3</sub>)(PMe<sub>2</sub>Ph)<sub>2</sub>] (II), Ph<sub>3</sub>SiMe, CH<sub>4</sub> and a small amount of H<sub>2</sub>. The ratio of *cis*-[PtH(SiPh<sub>3</sub>)(PMe<sub>2</sub>Ph)<sub>2</sub>] : Ph<sub>3</sub>SiMe : unreacted Ph<sub>3</sub>SiH was found to be 1 : 1 : 0.3 based on the integral ratios of the underlined <sup>1</sup>H nmr resonances (as shown in the formula above) in the <sup>1</sup>H nmr spectrum. In another experiment, the <sup>31</sup>P-{'<sup>1</sup>H} nmr spectrum of the reaction mixture showed the presence of *cis*-[PtH(SiPh<sub>3</sub>)(PMe<sub>2</sub>Ph)<sub>2</sub>] (90%) and *cis*-[PtMe(SiPh<sub>3</sub>)(PMe<sub>2</sub>Ph)<sub>2</sub>] (10%) (See Table 1).

#### Reaction pathway

The two possible pathways (*i.e.* via route X and route Y) for the reactions of *cis*-[PtMe<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>2</sub>] with triarylsilanes (triphenylsilane and diphenylsilane) can be represented in Scheme 1. The detection of Ph<sub>2</sub>MeSiH and Ph<sub>3</sub>SiMe in reactions I and II strongly suggests that the reactions may

proceed *via* route X. The observed molar ratio of approximately 1 : 1 of  $\text{Ph}_3\text{Si} : \text{cis-}[\text{PtH}(\text{SiPh}_3)(\text{PMe}_2\text{Ph})_2]$  is also in accordance with the suggested route X. However, there is a need to account for the presence of  $\text{H}_2$  in reaction II. The most likely source of  $\text{H}_2$  would be from the catalytic disproportionation of  $\text{Ph}_3\text{SiH}$  by the Pt complex to form  $\text{Ph}_3\text{Si}_2$  and  $\text{H}_2$ . This would also explain the lower

observed ratio of unreacted  $\text{Ph}_3\text{SiH} : \text{cis-}[\text{PtH}(\text{SiPh}_3)(\text{PMe}_2\text{Ph})_2] : \text{Ph}_3\text{SiMe}$  (0.3 : 1 : 1) as compared to the theoretically calculated ratio of 2 : 1 : 1 based on

- (i) the initial quantity of reactants used, *i.e.* 1 : 4 molar ratio of *cis-}[\text{PtMe}\_2(\text{PMe}\_2\text{Ph})\_2] : \text{Ph}\_3\text{SiH}, and*
- (ii) the stoichiometry for reaction II which can be represented by the equation below :

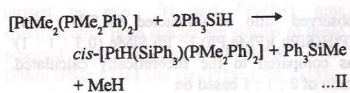
**Table 1 :** Reactions of  $\text{R}_3\text{SiH}$  with *cis-}[\text{PtMe}\_2(\text{PMe}\_2\text{Ph})\_2]*

$\text{R}_3\text{SiH}$	Product	IR (Nujol mull) $\text{cm}^{-1}$	$^{31}\text{P-}\{^1\text{H}\}\text{NMR}^a$	$^1\text{HNMR}^b$
$\text{Ph}_2\text{SiH}_2$	<i>cis-}[\text{Pt}(\text{SiPh}_2\text{H})_2(\text{PMe}_2\text{Ph})_2]</i>	$\nu(\text{SiH})$ 2000  2065  (2050)* (2095)* (2035)*	$\delta = 145.6$ ppm $^1\text{J} = 1687.0$ Hz	$\delta(\text{PMe})$ 1.10 ppm(t)(1.08)*, $^2\text{J}(\text{PH})$ 7.5 Hz $^3\text{J}(\text{PtPCH})$ 20.2 Hz, (20)* $\delta(\text{SiH})$ 5.68 ppm(t), (5.66)* $^1\text{J}(\text{SiH})$ 30.4 Hz, $^2\text{J}(\text{PtSiH})$ 74.9 Hz, (74)*
	$\text{Ph}_2\text{MeSiH}$			$\delta(\text{SiMe}) = 0.48$ ppm (d) $\delta(\text{SiH}) = 6.20$ ppm (br) $\delta(\text{SiH}) = 4.95$ ppm (s) excess
	$\text{Ph}_2\text{SiH}_2$ (excess)			
$\text{Ph}_3\text{SiH}$	<i>cis-}[\text{PtH}(\text{SiPh}_3)(\text{PMe}_2\text{Ph})_2]</i>	$\nu(\text{Pt-H})$ = 2040	$\delta = 143.9$ ppm $^1\text{J} = 1550.3$ Hz $\delta = 147.4$ ppm $^1\text{J} = 2294.9$ Hz $^2\text{J}(\text{PP}) = 19.5$ Hz $\delta = 145.1$ ppm $^1\text{J} = \text{not observed}$ $\delta = 151.8$ ppm $^1\text{J} = \text{not observed}$ $^2\text{J}(\text{PP}) = 19.5$ Hz	$\delta(\text{Me})$ 1.05 (d) (1.1)* 1.28 (d) $\delta(\text{PtH})$ -2.11 ppm (d of d) $^1\text{J}(\text{PtH})$ -041.9 $^2\text{J}(\text{HPtP}) = 158.7$ Hz <i>trans</i> $^2\text{J}(\text{MPtP}) = 20.5$ Hz <i>cis</i>  $\delta(\text{SiMe})$ 0.73 ppm (s) $\delta(\text{Si-H})$ 5.7 ppm (s)
	$\text{Ph}_3\text{SiMe}$ $\text{Ph}_3\text{SiH}$ (excess)			

**a** Spectra recorded in  $\text{C}_6\text{D}_6$ , negative values of  $\delta$  are to high field of TMS in  $\text{C}_6\text{D}_6$ .

**b** Spectra recorded in  $\text{C}_6\text{D}_6$ , referenced against TMS ( $\delta = 0$  ppm).

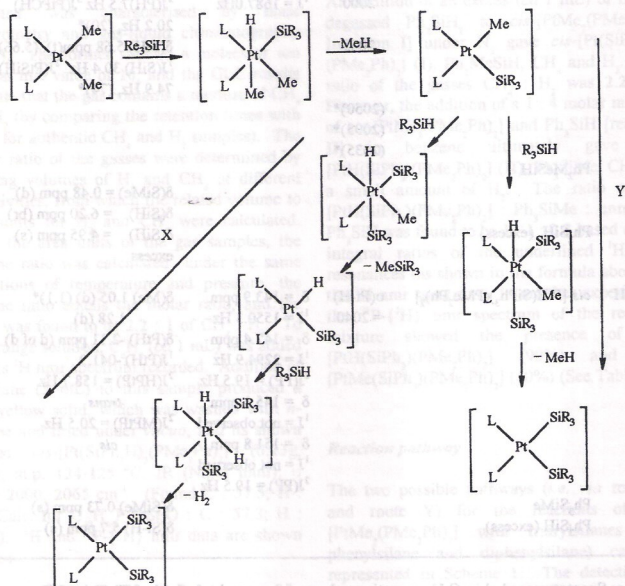
**c** Values in brackets with asterisks are from Ref. [7].



Recent works on the formation of Si-Si bond from Si-H bond in the presence of some hydrosilylation catalysts showed that most catalysts do not convert Et<sub>3</sub>SiH to disilane. However, Et<sub>6</sub>Si<sub>2</sub> could be observed among the products in the reactions containing [Pd(allyl)Cl]<sub>2</sub>; [PtCl<sub>2</sub>(COD)]; (COD = cyclooctadiene); [IrCl<sub>2</sub>(COD)] and [RhCO<sub>2</sub>Cl]<sub>2</sub> [6]. Thus a plausible explanation for the presence

of H<sub>2</sub> in reaction II is from the formation of Ph<sub>3</sub>Si-Si-Ph<sub>3</sub> bond from Ph<sub>3</sub>Si-H in the presence of a platinum catalyst, similar to the formation of Et<sub>6</sub>Si<sub>2</sub> from Et<sub>3</sub>SiH with the liberation of the H<sub>2</sub> gas. The detection of *cis*-[PtMe<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>2</sub>] from reaction II provides strong evidence for the involvement of the Pt(IV)-Si intermediate [PtMe<sub>2</sub>H(SiPh<sub>3</sub>)(PMe<sub>2</sub>Ph)<sub>2</sub>]. The corresponding species *cis*-[PtMe(SiPh<sub>2</sub>H)(PMe<sub>2</sub>Ph)<sub>2</sub>], from reaction I was never detected and this is presumably due to the strong tendency of the Si-H bond in Ph<sub>2</sub>SiH<sub>2</sub> to add very rapidly to Pt(II) to form the Pt(IV) intermediate, which then rapidly eliminates Ph<sub>2</sub>MeSiH.

Scheme I



While all results are in accordance with route X, the observed ratio of 2.2 : 1 for  $\text{CH}_4$  :  $\text{H}_2$  in reaction I appears inconsistent. The larger than the expected ratio of 1 : 1 of  $\text{CH}_4$  :  $\text{H}_2$  for route X could be due to the fact that  $\text{H}_2$  has a high diffusion coefficient and although the length of the tubing was kept to the minimum, some  $\text{H}_2$  may have escaped by diffusion.

## Conclusion

From the nature of the products obtained from both reactions I and II, it is clear that the oxidative-addition and reductive elimination step involves the liberation of  $\text{R}_3\text{MeSi}$ . This seems to substantiate the mode of reaction frequently postulated in the mechanism of homogeneously catalysed hydrosilylation of olefins where in both the Si and C ligands are believed to leave the Pt center in the Pt(IV) intermediate [5]. The detection of *cis*- $[\text{PtMe}(\text{SiPh}_3)(\text{PMe}_2\text{PH}_2)_2]$  from one of the reactions *i.e.* reaction II, provides a strong evidence for the intermediacy of the Pt(IV)-Si species,  $[\text{PtMe}_2\text{H}(\text{SiPh}_3)(\text{PMe}_2\text{Ph}_2)_2]$ .

The calculated ratios  $\text{SiMe} : \text{PMe}$  based on the integral of the methyl protons in  $^1\text{H}$  nmr spectra *i.e.* for the species  $\text{Ph}_2\text{SiMe} : \text{cis}-[\text{Pt}(\text{SiPh}_2\text{H})(\text{PMe}_2\text{Ph}_2)_2]$  [Reaction I] or  $\text{Ph}_3\text{SiMe} : \text{cis}-[\text{PtH}(\text{SiPh}_3)(\text{PMe}_2\text{Ph}_2)_2]$  [Reaction II] are consistent with route X. The  $\text{H}_2$

obtained from reaction II was most probably derived from the formation of  $\text{Ph}_3\text{Si-SiPh}_3$  bond from the  $\text{Ph}_3\text{Si-H}$  bond in the presence of a platinum catalyst.

## Acknowledgement

I would like to thank the University of Sussex, Brighton for providing the facilities. Financial support from the Public Services Department of Malaysia, and the University of Malaya are gratefully acknowledged.

## References

1. C. Eaborn, A. Pidcock and B. Ratcliff, *J. Organomet Chem*, 1974, **66**, 23.
2. A. J. Chalk and J. F. Harrod, *J. Amer. Chem. Soc. (A)*, 1965, **87**, 16.
3. J. D. Ruddick and B. L. Shaw, *J. Chem. Soc. (A)*, 1969, 2801.
4. R. J. Goodfellow, M. J. Hardy and B. E. Taylor, *J. Chem. Soc. (Dalton)*, 1973, 2450.
5. F. H. Allen and A. Pidcock, *J. Chem. Soc. (A)*, 1968, 2700.
6. Katherine A. Brown-Wensley, *Organometallics*, 1987, **6**, 1590.
7. C. S. Cundy, B. M. Kingston and M. F. Lappert, *Adv. Organomet. Chem.*, 1973, **11**, 253.