The Reactions of cis-[PtMe2(PMe2Ph)2] with R3SiH (R3 = Ph3H and Ph2H) - A Reinvestigation

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Abstract - The reaction between cis-[PtMe2(PMe2Ph)2] and Ph3SiH at 70 °C gave cis-[PtH(SiPh3)(PMe2Ph)2] (II), Ph3SiMe, CH4 and a small quantity of H2. However, with Ph2SiH2, the reaction occurs much more readily to give cis-[Pt(SiPh3H)(PMe2Ph)2] (I), Ph2MeSiH, CH4 and H2. The observed molar ratio of the products formed indicate that the reactions most probably occur via the two/three oxidative-additions of R3SiH (R3 = Ph3H and Ph2H) to form (I) and (II) respectively, with the liberation of R3SiMe.

Abstrak - Tindak balas antara cis-[PtMe2(PMe2Ph)2] dengan Ph3SiH pada 70 °C menghasilkan cis-[PtH(SiPh3)(PMe2Ph)2] (II), Ph3SiMe, CH4 dan sedikit gas H2. Walau bagaimanapun, tindak balas dengan Ph2SiH2, berlaku dengan lebih cergas untuk menghasilkan cis-[Pt(SiPh2H)(PMe2Ph)2] (I), Ph2MeSiH, CH4 dan H2. Nisbah molar bagi bahan dan hasil tindak balas menunjukkan bahawa tindak balas tersebut mungkin berlaku melalui dua atau tiga penambahan-oksidasi R3SiH (R3 = Ph3H dan Ph2H) untuk membentuk masing-masing (I) dan (II) dan disertai dengan penghasilan R3SiMe.

Introduction

Eaborn and co-workers [1] have shown that the reactions of Ph3SiH (R3 = (p-FC6H4)3MePh2 and Ph2H) with cis-[PtMe2(PMe2Ph)2] gave either the hyridosilyl complexes, cis-[PtH(SiR2)(PMe2Ph)2] or the bis(silyl) species, cis-[Pt(SiR2)2(PMe2Ph)2]. 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-[PtMe2(PMe2Ph)2]) with Ph3SiH2, a silicon containing product, Ph2MeSiH, 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 H2PtCl6 [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

Ph3SiH2 was supplied by Prof. C. Eaborn and Ph2SiH2 was obtained commercially. The Pt complex, cis-[PtMe2(PMe2Ph)2] was prepared by treating cis-[PtCl2(PMe2Ph)2] with ethereal MeLi [3]. The title compound was charac-
terised by m.p., $^1$H and $^{31}$P-$^1$H nmr spectroscopy. Both spectra are similar to those reported for similar complexes, cis-
$[\text{PtMe}_2(\text{PMe}_3)_2]$ [4] and cis-
$[\text{PtMe}_2(\text{PET})_2]$ [5].

Reaction of cis-[PtMe$_2$(PMe$_2$Ph)$_2$] with Ph$_2$SiH$_2$ [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$_2$SiH$_2$ was put into a small tube, which was then placed in the flask containing cis-[PtMe$_2$(PMe$_2$Ph)$_2$] (0.2 g, 0.4 mmol). Vigorous gas evolution occurred as the two reactants were mixed, and the mixture 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$_4$ and H$_2$ (by comparing the retention times with those for authentic CH$_4$ and H$_2$ samples). The molar ratio of the gases were determined by running volumes of H$_2$ and CH$_4$ at different sensitivities, from which the related volume to area units for H$_2$ and CH$_4$ 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$_4$ : H$_2$. To the orange solution, C$_6$H$_6$ (ca 1 mL) was added and its $^1$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$_3$)$_3$(PMe$_2$Ph)$_2$] (0.23 g, 70%); m.p. 124-125 °C; IR (Nujol mull); ν (SiH) 2000, 2065 cm$^{-1}$. (Found C : 57.5; H : 4.7; Calc. for C$_{38}$H$_{32}$P$_4$Si$_2$O : C : 57.3; H : 5.3%). $^1$H and $^{31}$P-$^1$H nmr data are shown Table 1.

Results

An addition of an excess (ca 1 mL) of freshly degassed Ph$_2$SiH$_2$ to cis-[PtMe$_2$(PMe$_2$Ph)$_2$] [reaction I] under N$_2$ gave cis-[Pt(SiPh$_3$)$_3$(PMe$_2$Ph)$_2$] (I), Ph$_2$MeSiH, CH$_4$, and H$_2$. The ratio of the gasses CH$_4$ : H$_2$ was 2.2 : 1. However, the addition of a 1 : 4 molar mixture of cis-[PtMe$_2$(PMe$_2$Ph)$_2$] and Ph$_2$SiH [reaction II] in benzene ultimately gave cis-[Pt(SiPh$_3$)$_3$(PMe$_2$Ph)$_2$] (II), Ph$_2$SiMe, CH$_4$, and a small amount of H$_2$. The ratio of cis-[Pt(SiPh$_3$)$_3$(PMe$_2$Ph)$_2$] : Ph$_2$SiMe : unreacted Ph$_2$SiH was found to be 1 : 1 : 0.3 based on the integral ratios of the underlined $^1$H nmr resonances (as shown in the formula above) in the $^1$H nmr spectrum. In another experiment, the $^{31}$P-$^1$H nmr spectrum of the reaction mixture showed the presence of cis-[Pt(SiPh$_3$)$_3$(PMe$_2$Ph)$_2$] (90%) and cis-[PtMe$_2$(SiPh$_3$)$_3$(PMe$_2$Ph)$_2$] (10%) (See Table 1).

Reaction pathway

The two possible pathways (i.e. via route X and route Y) for the reactions of cis-[PtMe$_2$(PMe$_2$Ph)$_2$] with triarylsilanes (triphenylsilane and diphenylsilane) can be represented in Scheme 1. The detection of Ph$_2$MeSiH and Ph$_2$SiMe in reactions I and II strongly suggests that the reactions may
The observed molar ratio of approximately 1 : 1 of Ph₃SiH : cis-[PtH(SiPh₃)(PMe₂Ph)₂] is also in accordance with the suggested route X. However, there is a need to account for the presence of H in reaction II. The most likely source of H₂ would be from the catalytic disproportionation of Ph₃SiH by the Pt complex to form Ph₅Si₆ and H₂. This would also explain the lower observed ratio of unreacted Ph₃SiH : cis-[PtH(SiPh₃)(PMe₂Ph)₂] : Ph₃SiMe (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-[PtMe₂(PMe₂Ph)₂] : Ph₃SiH, and

(ii) the stoichiometry for reaction II which can be represented by the equation below:

Table 1: Reactions of R₃SiH with cis-[PtMe₂(PMe₂Ph)₂]

<table>
<thead>
<tr>
<th>R₃SiH</th>
<th>Product</th>
<th>IR (Nujol mull) cm⁻¹</th>
<th>¹H-{¹H}NMR a</th>
<th>¹H NMR b</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ph₃SiH</td>
<td>cis-[PtH(SiPh₃)(PMe₂Ph)₂] u(Pt-H) = 2040</td>
<td>δ = 143.9 ppm</td>
<td>δ(Me) 1.05 ppm</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>J = 1550.3 Hz</td>
<td>(1.1)*</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>δ = 147.4 ppm</td>
<td>1.28 (d)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>J = 2294.9 Hz</td>
<td>(d of d)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>²J(P₃) = 19.5 Hz</td>
<td>²J(P₃P) = 158.7 Hz</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>δ = 145.1 ppm</td>
<td>²J(MP₃P) = 20.5 Hz</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>J = not observed</td>
<td>cis</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>δ = 151.8 ppm</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>J = not observed</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>²J(P₃) = 19.5 Hz</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ph₃SiMe</td>
<td></td>
<td>δ(SiMe) 0.73 ppm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ph₃SiH (excess)</td>
<td>Ph₅Si₆</td>
<td>δ(Si-H) 5.7 ppm</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a Spectra recorded in C₆H₆, negative values of δ are to high field of TMP in C₆D₆.
b Spectra recorded in C₆H₆, referenced against TMS (δ = 0 ppm).
c Values in brackets with asterisks are from Ref. [7].
The Reactions of cis-[PtMe₂(PMe₂Ph)₂] with R₃SiH; R₃ = Ph₂H and Ph₃H - a reinvestigation

\[
\text{[PtMe}_2(\text{PMe}_2\text{Ph})_2] + 2\text{Ph}_3\text{SiH} \rightarrow \]
cis-[PtH(SiPh)(PMe₂Ph)₂] + Ph₃SiMe + MeH

...II

Recent works on the formation of Si-Si bond from Si-H bond in the presence of some hydroisilylation catalysts showed that most catalysts do not convert Et₃SiH to disilane. However, Et₅Si₂ could be observed among the products in the reactions containing [Pd(allyl)Cl₂]; [PtCl₂(COD)]; (COD = cyclooctadiene); [IrCl₂(COD)] and [RhCO₂Cl₂] [6]. Thus a plausible explanation for the presence of H₂ in reaction II is from the formation of Ph₃Si-SiPh₃ bond from Ph₃Si-H in the presence of a platinum catalyst, similar to the formation of Et₅Si₂ from Et₃SiH with the liberation of the H₂ gas. The detection of cis-[PtMe₂(PMe₂Ph)₂] from reaction II provides strong evidence for the involvement of the Pt(IV)-Si intermediate [PtMe₂H(SiPh)(PMe₂Ph)₂]. The corresponding species cis-[PtMe(SiPh₂H)(PMe₂Ph)₂], from reaction I was never detected and this is presumably due to the strong tendency of the Si-H bond in Ph₃SiH₂ to add very rapidly to Pt(II) to form the Pt(IV) intermediate, which then rapidly eliminates Ph₂MeSiH.

Scheme I

\[
(L = \text{PMe}_2\text{Ph} : \text{Me} = \text{CH}_3)
\]
While all results are in accordance with route X, the observed ratio of 2.2 : 1 for CH₄ : H₂ in reaction I appears inconsistent. The larger than the expected ratio of 1 : 1 of CH₄ : H₂ for route X could be due to the fact that H₂ has a high diffusion coefficient and although the length of the tubing was kept to the minimum, some H₂ 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 R₃MeSi. This seems to substantiate the mode of reaction frequently postulated in the mechanism of homogenously 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-[PtMe₂(SiPh₃)(PMe₂PH₂)] from one of the reactions i.e. reaction II, provides a strong evidence for the intermediacy of the Pt(IV)-Si species, [PtMe₂H(SiPh₃)(PMe₂Ph₂)].

The calculated ratios SiMe : PMe based on the integral of the methyl protons in H nmr spectra i.e. for the species Ph₂SiMe : cis-[Pt(SiPh₂H₂)(PMe₂Ph₂)] [Reaction I] or Ph₃SiMe : cis-[PtH(SiPh₃)(PMe₂Ph₂)] [Reaction II] are consistent with route X. The H₂ obtained from reaction II was most probably derived from the formation of Ph₃Si-SiPh₃ bond from the Ph₃Si-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