

Reductive Elimination of *sym*-Diphenyltetramethyldisilane from  
*cis*-Bis(phenyldimethylsilyl)bis(phosphine)platinum(II) Complexes

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Reductive elimination of *cis*-bis(phenyldimethylsilyl)bis-(phosphine)platinum(II) complexes was found to occur to give *sym*-diphenyltetramethyldisilane together with redistribution by-products. Addition of free phosphine was favorable for the reductive elimination, and the disilane was formed in more than 80% yields.

Reductive elimination leading to carbon-carbon bond formation is one of key elemental steps involved in transition metal complex-catalyzed organic synthesis. Hence, increasing attention has been paid to various aspects of reductive elimination of diorgano transition metal complexes.<sup>1)</sup> In striking contrast with this, reductive elimination process of bissilyl metal complexes seems to have been totally neglected. Although some isolated descriptions of the disilane formation encountered with some bissilyl iron<sup>2,3)</sup> and nickel<sup>4,5)</sup> complexes have appeared, the yields reported are usually very low. In the previous paper, we have reported the dehydrogenative dimerization of monohydrosilanes to disilanes in the presence of platinum complex catalysts.<sup>6)</sup> It seems to be quite reasonable to assume a bissilyl platinum(II) intermediate undergoing reductive elimination as the final step of the catalytic cycle to yield a disilane. Accordingly, we felt a considerable interest in thermolysis of bissilyl platinum(II) complexes. We now wish to report that the thermolysis offers the first examples of high yield formation of disilane via reductive elimination.

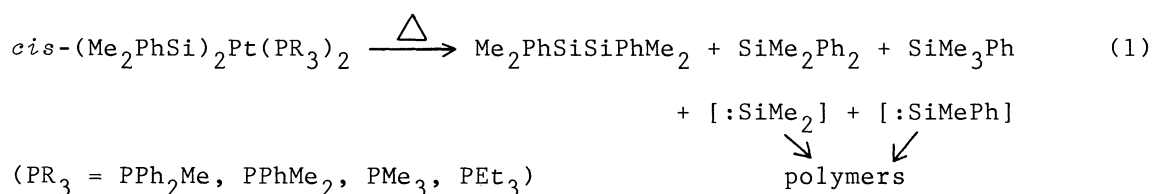
The bissilyl platinum(II) complexes were prepared by the reaction of *cis*-dichlorobis(phosphine)platinum(II), *cis*-Cl<sub>2</sub>Pt(PR<sub>3</sub>)<sub>2</sub>, with phenyldimethylsilyl lithium in tetrahydrofuran,<sup>7)</sup> and the *cis* configuration was confirmed by <sup>31</sup>P-NMR and <sup>1</sup>H-NMR.<sup>8-11)</sup> We also attempted to synthesize *cis*-(Me<sub>2</sub>PhSi)<sub>2</sub>Pt(PPh<sub>3</sub>)<sub>2</sub> to examine its reactivity. However, the attempt was unsuccessful owing to its thermal instability.

When a bissilyl platinum(II) complex (0.023 mmol) dissolved in benzene-d<sub>6</sub> (0.2 cm<sup>3</sup>) was heated in a sealed NMR tube at 80 °C for 40 h, *sym*-diphenyltetramethyldisilane and redistribution products (dimethyldiphenylsilane and/or trimethylphenylsilane) were found by <sup>1</sup>H-NMR spectroscopy to be formed as depicted in Eq. 1. Besides these products, polymeric materials also appeared to be formed as judged from the broad <sup>1</sup>H-NMR signal assignable to Me-Si species. The polymeric materials are also presumably due to the redistribution reaction (*vide infra*), but the identity is ambiguous at the moment. Since platinum complexes have been known to be capable catalysts for redistribution reactions,<sup>12)</sup>

Table 1. Thermolysis of *cis*-(Me<sub>2</sub>PhSi)<sub>2</sub>Pt(PR<sub>3</sub>)<sub>2</sub><sup>a)</sup>

| PR <sub>3</sub>     | Cone angle/° <sup>b)</sup> | Electronic parameter/cm <sup>-1</sup> <sup>b)</sup> | Conv. /% <sup>c)</sup> | Products and yields/% <sup>c)</sup>     |                                   |                      |
|---------------------|----------------------------|---|------------------------|---|-----------------------------------|----------------------|
|                     |                            |   |                        | Me <sub>2</sub> PhSiSiPhMe <sub>2</sub> | SiMe <sub>2</sub> Ph <sub>2</sub> | SiMe <sub>3</sub> Ph |
| PPh <sub>2</sub> Me | 136                        | 2067.0  | 100                    | 48.7 (48.7)                             | 28.6 (28.6)                       | 19.1 (19.1)          |
| PEt <sub>3</sub>    | 132                        | 2061.7  | 100                    | 24.1 (24.1)                             | 13.5 (13.5)                       | 42.4 (42.4)          |
| PPhMe <sub>2</sub>  | 122                        | 2065.3  | 32.9                   | 5.2 (15.8)                              | 0 (0)                             | 13.8 (41.9)          |
| PMe <sub>3</sub>    | 118                        | 2064.1  | 44.3                   | 2.6 (5.9)                               | 0 (0)                             | 17.2 (38.8)          |

a) *cis*-(Me<sub>2</sub>PhSi)<sub>2</sub>Pt(PR<sub>3</sub>)<sub>2</sub> 0.023 mmol, C<sub>6</sub>D<sub>6</sub> 0.2 cm<sup>3</sup>, 80 °C, 40 h. b) C. A. Tolman, Chem. Rev., 77, 313 (1977). c) Determined by <sup>1</sup>H-NMR. Numbers in parentheses are selectivities.



the formation of dimethyldiphenylsilane and trimethylphenylsilane (and the polymers) is not surprising.

The ligand effect on the thermolysis is summarized in Table 1. The data listed in Table 1 combined with the unsuccessful synthesis of *cis*-(Me<sub>2</sub>PhSi)<sub>2</sub>Pt-(PPh<sub>3</sub>)<sub>2</sub> suggest that a more electron-donating and/or less sterically-demanding ligand forms a more thermally-stable bis-silyl platinum(II) complex. The selectivity of the disilane resulting from reductive elimination decreased in the order of PPh<sub>2</sub>Me > PEt<sub>3</sub> > PPhMe<sub>2</sub> > PMe<sub>3</sub>. Thus, more sterically-congested and less basic phosphines are favorable for the formation of the disilane. However, it may be concluded that the steric nature is the dominant factor dictating the reactivity of the complexes, since PEt<sub>3</sub> which is more sterically-congested and more basic than PMe<sub>3</sub> gave a higher yield (and selectivity) of the disilane.

The observations described above clearly demonstrate the first examples of reductive elimination of disilane from the bis-silyl platinum(II) complex. However, owing to the undesired side reactions leading to the redistribution products, the selectivity of the reductive elimination which would be a key step in the catalytic dehydrogenative dimerization of monohydrosilanes is not very high as yet. Hence, we examined the effect of the extra phosphine added to the thermolysis reaction system of *cis*-(Me<sub>2</sub>PhSi)<sub>2</sub>Pt(PPh<sub>2</sub>Me)<sub>2</sub>. Table 2 shows that the extra free phosphine exerted a very favorable effect. Addition of 0.5 equiv. PPh<sub>2</sub>Me halved the formation of redistribution by-products. When the amount of the phosphine was increased to 2 equiv. or more, redistribution was completely suppressed, and the disilane could be formed in more than 80% yield.

A preliminary kinetic study has revealed that the reductive elimination in the presence of added phosphine obeys first-order kinetics, and that it does not depend on the concentration of the free phosphine. The results are compatible with a mechanism involving the concerted unimolecular reductive elimination taking place directly on the four coordinate complex without prior dissociation

Table 2. Effect of added phosphine in the thermolysis of *cis*-(Me<sub>2</sub>PhSi)<sub>2</sub>Pt(PPh<sub>2</sub>Me)<sub>2</sub><sup>a)</sup>

| Added PPh <sub>2</sub> Me<br>/Pt complex | Products and yields/% <sup>b)</sup>     |                                   |                      |
|--|---|-----------------------------------|----------------------|
|  | Me <sub>2</sub> PhSiSiPhMe <sub>2</sub> | SiMe <sub>2</sub> Ph <sub>2</sub> | SiMe <sub>3</sub> Ph |
| 0  | 50.3                                    | 27.2                              | 12.0                 |
| 0.5                                      | 65.6                                    | 12.6                              | 5.2                  |
| 2  | 81.3                                    | ≈0                                | ≈0                   |
| 8  | 82.9                                    | ≈0                                | ≈0                   |

a) *cis*-(Me<sub>2</sub>PhSi)<sub>2</sub>Pt(PPh<sub>2</sub>Me)<sub>2</sub> 0.023 mmol, C<sub>6</sub>D<sub>6</sub> 0.2 cm<sup>3</sup>, 80 °C, 40 h. b) Determined by GLC. Conversion 100% by <sup>1</sup>H-NMR.

or coordination of the phosphine. A similar conclusion has been made for the reductive elimination from *cis*-hydrido(2,2,2-trifluoroethyl)bis(triphenylphosphine)platinum(II) complex.<sup>13)</sup> Activation parameters obtained in the presence of 2 equiv. PPh<sub>2</sub>Me were E<sub>a</sub> = 131.8 kJ mol<sup>-1</sup>, ΔG<sup>‡</sup> = 120.5 kJ mol<sup>-1</sup>, ΔH<sup>‡</sup> = 129.3 kJ mol<sup>-1</sup>, and ΔS<sup>‡</sup> = 28.9 J K<sup>-1</sup> mol<sup>-1</sup> (at 80 °C). The latter two are in good agreement with the values (ΔH<sup>‡</sup> = 102.9 kJ mol<sup>-1</sup> and ΔS<sup>‡</sup> = 20.5 J K<sup>-1</sup> mol<sup>-1</sup> at 25 °C) reported for the hydrido(2,2,2-trifluoroethyl) complex.<sup>13)</sup>

Survey of literatures suggested a possibility that the redistribution reaction is triggered by the α-elimination of one of the groups attached to the silicon center, Eq. 2.<sup>12,14,15)</sup> The process would require an expansion of the



coordination number of the central metal or a dissociation of a ligand. The favorable effect of extra phosphine may be associated with the suppression of the α-elimination by preventing the ligand dissociation. In the catalytic dehydrogenative dimerization of monohydrosilane, we have reported that the catalyst performance is higher at PR<sub>3</sub>/Pt = 4 than at the ratio = 2. This is in complete agreement with the present results.

To summarize, reductive elimination of *cis*-(Me<sub>2</sub>PhSi)<sub>2</sub>Pt(PR<sub>3</sub>)<sub>2</sub> affords the disilane. In particular, the reaction proceeds cleanly in the presence of free phosphine. Studies on detailed mechanism and the reductive elimination of other complexes are under way

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- 8)  $^{31}\text{P}$ -195 $_{\text{Pt}}$  values (1648, 1521, 1499, 1622 Hz) of bis-silyl platinum(II) complexes ( $\text{PR}_3 = \text{PPh}_2\text{Me}$ ,  $\text{PPhMe}_2$ ,  $\text{PMe}_3$ ,  $\text{PEt}_3$ , respectively) were similar to the values (1613-1838 Hz) of *cis*- $\text{Pt}(\text{PPh}_2\text{CH}_2\text{CH}_2\text{SiR}^1\text{R}^2)_2$ ,<sup>9)</sup> and much smaller than 2622-2873 Hz reported for *trans*- $\text{PtCl}(\text{SiR}_3)(\text{PPhMe}_2)_2$  and than 2629 Hz for *trans*- $\text{Pt}(\text{GeMePh}_2)_2(\text{PPhMe}_2)_2$ .<sup>7)</sup> Analogous values were also observed in *cis*- and *trans*-diorgano platinum(II) complexes.<sup>10)</sup> In  $^1\text{H}$ -NMR, the coupling with  $^{31}\text{P}$  was observed as symmetrical doublet. The absence of virtual coupling characteristic to *trans*-H-C-P-Pt-P-C-H linkage was consistent with the assignment of *cis* configuration.<sup>11)</sup> Individual spectral and analytical data are shown below.
- $\text{PR}_3 = \text{PPh}_2\text{Me}$ : yellow powder, 35% yield; mp 140-145 °C (dec.) under  $\text{N}_2$ ;  $^1\text{H}$ -NMR ( $\text{C}_6\text{D}_6$ , TMS)  $\delta$  0.74 (broad s, 12H, SiMe, ( $J_{\text{Pt-H}} = 26.2$  Hz)), PMe(6H) signals were hidden in the range of 0.65-0.95 under SiMe, 6.9-7.4 (m, 26H, Ph), 7.65-7.9 (m, 4H, Ph);  $^{31}\text{P}$ -NMR ( $\text{C}_6\text{D}_6$ , 85% $\text{H}_3\text{PO}_4$ )  $\delta$  5.72. Anal. Found: C, 57.95; H, 5.53%. Calcd for  $\text{C}_{42}\text{H}_{48}\text{P}_2\text{PtSi}_2$ : C, 58.25; H, 5.59%.
- $\text{PPhMe}_2$ : yellow powder, 32% yield; mp 170-172 °C (dec.) under  $\text{N}_2$ ;  $^1\text{H}$ -NMR ( $\text{C}_6\text{D}_6$ , TMS)  $\delta$  0.70 (d,  $J_{\text{P-H}} = 7.6$  Hz, 12H, PMe, ( $J_{\text{Pt-H}} = 15.8$  Hz)), 0.90 (s, 12H, SiMe, ( $J_{\text{Pt-H}} = 27.0$  Hz)), 6.9-7.4 (m, 16H, Ph), 7.7-7.9 (m, 4H, Ph);  $^{31}\text{P}$ -NMR ( $\text{C}_6\text{D}_6$ , 85% $\text{H}_3\text{PO}_4$ )  $\delta$  -8.35. Anal. Found: C, 51.93; H, 5.94%. Calcd for  $\text{C}_{32}\text{H}_{44}\text{P}_2\text{PtSi}_2$ : C, 51.81; H, 5.98%.
- $\text{PMe}_3$ : yellow crystals, 16% yield; mp 115-125 °C (dec.) under  $\text{N}_2$ ;  $^1\text{H}$ -NMR ( $\text{C}_6\text{D}_6$ , TMS)  $\delta$  0.80 (d,  $J_{\text{P-H}} = 7.2$  Hz, 18H, PMe, ( $J_{\text{Pt-H}} = 17.4$  Hz)), 0.89 (s, 12H, SiMe, ( $J_{\text{Pt-H}} = 26.6$  Hz)), 7.1-7.4 (m, 6H, Ph), 7.7-7.9 (m, 4H, Ph);  $^{31}\text{P}$ -NMR ( $\text{C}_6\text{D}_6$ , 85% $\text{H}_3\text{PO}_4$ )  $\delta$  -16.02. Anal. Found: C, 43.07; H, 6.67%. Calcd for  $\text{C}_{22}\text{H}_{40}\text{P}_2\text{PtSi}_2$ : C, 42.77; H, 6.53%.
- $\text{PEt}_3$ : yellow needles, 21% yield; mp 110-116 °C (dec.) under  $\text{N}_2$ ;  $^1\text{H}$ -NMR ( $\text{C}_6\text{D}_6$ , TMS)  $\delta$  0.77 (dt,  $J_{\text{P-H}} = 13.8$  Hz,  $J = 6.9$  Hz, 18H,  $\text{CH}_3\text{-CH}_2$ ), 0.90 (s, 12H, SiMe, ( $J_{\text{Pt-H}} = 27.0$  Hz)), 1.35 (quintet,  $J_{\text{P-H}} = J = 6.9$  Hz, 12H,  $\text{CH}_2$ ), 7.1-7.4 (m, 6H, Ph), 7.7-7.9 (m, 4H, Ph);  $^{31}\text{P}$ -NMR ( $\text{C}_6\text{D}_6$ , 85% $\text{H}_3\text{PO}_4$ )  $\delta$  11.78. Anal. Found: C, 46.56; H, 7.29%. Calcd for  $\text{C}_{28}\text{H}_{52}\text{P}_2\text{PtSi}_2$ : C, 47.91; H, 7.47%.
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