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

Toshi-aki KOBAYASHI, Teruyuki HAYASHI, Hiroshi YAMASHITA, and Masato TANAKA*
National Chemical Laboratory for Industry, Tsukuba, Ibaraki 305

Reductive elimination of *cis*-bis(phenyldimethylsilyl)bis-
(phosphine)platinum(II) complexes was found to occur to give *sym*-
diphenyltetramethyldisilane together with redistribution by-prod-
ucts. 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 synthe-
sis. Hence, increasing attention has been paid to various aspects of reductive
elimination of diorgano transition metal complexes.[1] 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[2,3] and nickel[4,5] 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.[6] It seems to be quite reasona-
ble to assume a bissilyl platinum(II) intermediate undergoing reductive elimina-
tion as the final step of the catalytic cycle to yield a disilane. Accordingly,
we felt a considerable interest in thermolysis of bissilyl platinum(II) com-
plexes. We now wish to report that the thermolysis offers the first examples of
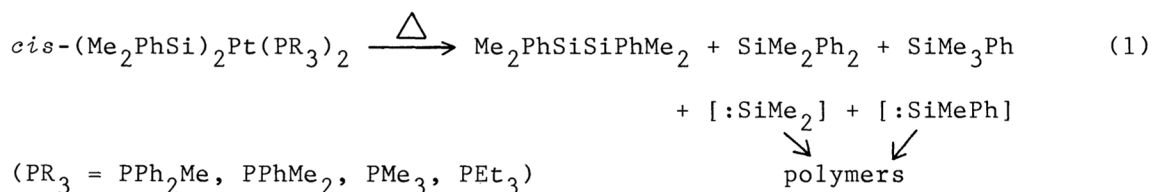high yield formation of disilane via reductive elimination.

The bissilyl platinum(II) complexes were prepared by the reaction of *cis*-
dichlorobis(phosphine)platinum(II), cis-$Cl_2Pt(PR_3)_2$, with phenyldimethylsilyl
lithium in tetrahydrofuran,[7] and the *cis* configuration was confirmed by ^{31}P-NMR
and ^{1}H-NMR.[8-11] We also attempted to synthesize cis-$(Me_2PhSi)_2Pt(PPh_3)_2$ to ex-
amine its reactivity. However, the attempt was unsuccessful owing to its ther-
mal instability.

When a bissilyl platinum(II) complex (0.023 mmol) dissolved in benzene-d_6
(0.2 cm^3) was heated in a sealed NMR tube at 80 °C for 40 h, *sym*-diphenyltetra-
methyldisilane and redistribution products (dimethyldiphenylsilane and/or tri-
methylphenylsilane) were found by ^{1}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 ^{1}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 com-
plexes have been known to be capable catalysts for redistribution reactions,[12]

Table 1. Thermolysis of cis-$(Me_2PhSi)_2Pt(PR_3)_2$[a)]

PR_3	Cone angle/°[b)]	Electronic parameter/cm[-1 b)]	Conv. /%[c)]	Products and yields/%[c)]		
				$Me_2PhSiSiPhMe_2$	$SiMe_2Ph_2$	$SiMe_3Ph$
PPh_2Me	136	2067.0	100	48.7 (48..7)	28.6 (28.6)	19.1 (19.1)
PEt_3	132	2061.7	100	24.1 (24.1)	13.5 (13.5)	42.4 (42.4)
$PPhMe_2$	122	2065.3	32.9	5.2 (15.8)	0 (0)	13.8 (41.9)
PMe_3	118	2064.1	44.3	2.6 (5.9)	0 (0)	17.2 (38.8)

a) cis-$(Me_2PhSi)_2Pt(PR_3)_2$ 0.023 mmol, C_6D_6 0.2 cm^3, 80 °C, 40 h. b) C. A. Tolman, Chem. Rev., 77, 313 (1977). c) Determined by ^{1}H-NMR. Numbers in parentheses are selectivities.

$$cis\text{-}(Me_2PhSi)_2Pt(PR_3)_2 \xrightarrow{\triangle} Me_2PhSiSiPhMe_2 + SiMe_2Ph_2 + SiMe_3Ph \qquad (1)$$

$$+ [:SiMe_2] + [:SiMePh]$$

$$(PR_3 = PPh_2Me, PPhMe_2, PMe_3, PEt_3) \qquad \qquad \searrow \quad \swarrow$$
$$polymers$$

the formation of dimethyldiphenylsilane and trimethylphenylsilane (and the poly-
mers) 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-$(Me_2PhSi)_2Pt$-
$(PPh_3)_2$ suggest that a more electron-donating and/or less sterically-demanding
ligand forms a more thermally-stable bissilyl platinum(II) complex. The selec-
tivity of the disilane resulting from reductive elimination decreased in the or-
der of $PPh_2Me > PEt_3 > PPhMe_2 > PMe_3$. 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_3 which is more sterically-congested and
more basic than PMe_3 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 bissilyl platinum(II) complex. How-
ever, owing to the undesired side reactions leading to the redistribution prod-
ucts, 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 ther-
molysis reaction system of cis-$(Me_2PhSi)_2Pt(PPh_2Me)_2$. Table 2 shows that the
extra free phosphine exerted a very favorable effect. Addition of 0.5 equiv.
PPh_2Me 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-$(Me_2PhSi)_2Pt(PPh_2Me)_2$ [a]

Added PPh$_2$Me	Products and yields/% [b]		
/Pt complex	Me$_2$PhSiSiPhMe$_2$	SiMe$_2$Ph$_2$	SiMe$_3$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-$(Me_2PhSi)_2Pt(PPh_2Me)_2$ 0.023 mmol, C_6D_6 0.2 cm^3,
80 °C, 40 h. b) Determined by GLC. Conversion 100% by
^{1}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(triphenylphos-
phine)platinum(II) complex.[13] Activation parameters obtained in the presence
of 2 equiv. PPh$_2$Me were E_a = 131.8 kJ mol^{-1}, $\Delta G^{\ddagger}$ = 120.5 kJ mol^{-1}, $\Delta H^{\ddagger}$ = 129.3
kJ mol^{-1}, and $\Delta S^{\ddagger}$ = 28.9 J K^{-1} mol^{-1} (at 80 °C). The latter two are in good agree-
ment with the values ($\Delta H^{\ddagger}$ = 102.9 kJ mol^{-1} and $\Delta S^{\ddagger}$ = 20.5 J K^{-1}mol^{-1} at 25 °C) re-
ported for the hydrido(2,2,2-trifluoroethyl) complex.[13]

Survey of literatures suggested a possibility that the redistribution re-
action is triggered by the α-elimination of one of the groups attached to the
silicon center, Eq. 2.[12,14,15] The process would require an expansion of the

$$M-SiR'_3 \longrightarrow \begin{array}{c} R' \\ | \\ M=SiR'_2 \end{array} \qquad (2)$$
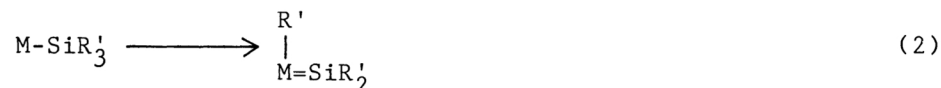
coordination number of the central metal or a dissociation of a ligand. The
favorable effect of extra phosphine may be associated with the suppression of
the α-elimination by preventing the ligand dissociation. In the catalytic dehy-
drogenative dimerization of monohydrosilane, we have reported that the catalyst
performance is higher at PR$_3$/Pt = 4 than at the ratio = 2. This is in complete
agreement with the present results.

To summarize, reductive elimination of cis-$(Me_2PhSi)_2Pt(PR_3)_2$ 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

References
1) J. P. Collman, L. S. Hegedus, J. R. Norton, and R. G. Finke, "Principles and
   Applications of Organotransition Metal Chemistry," University Science Books,
   Mill Valley (1987), p. 332.
2) R. V. Parish and B. F. Riley, J. Chem. Soc., Dalton Trans., 1979, 482.
3) H. Sakurai, K. Sakamoto, and M. Kira, Chem. Lett., 1987, 1075.
4) Y. Kiso, K. Tamao, and M. Kumada, J. Organomet. Chem., 76, 95 (1974).
5) T. J. Groshens and K. J. Klabunde, J. Organomet. Chem., 259, 337 (1983).

6) M. Tanaka, T. -a. Kobayashi, T. Hayashi, and T. Sakakura, Appl. Organomet. Chem., <u>2</u>, 91 (1988).

7) J. Chatt, C. Eaborn, S. D. Ibekwe, and P. N. Kapoor, J. Chem. Soc., A, <u>1970</u>, 1343.

8) $J_{31_P-195_{Pt}}$ values (1648, 1521, 1499, 1622 Hz) of bissilyl platinum(II) complexes (PR_3 = PPh_2Me, $PPhMe_2$, PMe_3, PEt_3, respectively) were similar to the values (1613-1838 Hz) of cis-Pt($PPh_2CH_2CH_2SiR^1R^2$)$_2$,[9] and much smaller than 2622-2873 Hz reported for $trans$-PtCl(SiR_3)($PPhMe_2$)$_2$ and than 2629 Hz for $trans$-Pt($GeMePh_2$)$_2$($PPhMe_2$)$_2$.[7] Analogous values were also observed in cis- and $trans$-diorgano platinum(II) complexes.[10] In ^{1}H-NMR, the coupling with ^{31}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.[11] Individual spectral and analytical data are shown below.

PR_3 = PPh_2Me: yellow powder, 35% yield; mp 140-145 °C (dec.) under N_2; ^{1}H-NMR (C_6D_6, TMS) δ 0.74 (broad s, 12H, SiMe, (J_{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}P-NMR (C_6D_6, 85%H_3PO_4) δ 5.72. Anal. Found: C, 57.95; H, 5.53%. Calcd for $C_{42}H_{48}P_2PtSi_2$: C, 58.25; H, 5.59%.

$PPhMe_2$: yellow powder, 32% yield; mp 170-172 °C (dec.) under N_2; ^{1}H-NMR (C_6D_6, TMS) δ 0.70 (d, J_{P-H} = 7.6 Hz, 12H, PMe, (J_{Pt-H} = 15.8 Hz)), 0.90 (s, 12H, SiMe, (J_{Pt-H} = 27.0 Hz)), 6.9-7.4 (m, 16H, Ph), 7.7-7.9 (m, 4H, Ph); ^{31}P-NMR (C_6D_6, 85%H_3PO_4) δ -8.35. Anal. Found: C, 51.93; H, 5.94%. Calcd for $C_{32}H_{44}P_2PtSi_2$: C, 51.81; H, 5.98%.

PMe_3: yellow crystals, 16% yield; mp 115-125 °C (dec.) under N_2; ^{1}H-NMR (C_6D_6, TMS) δ 0.80 (d, J_{P-H} = 7.2 Hz, 18H, PMe, (J_{Pt-H} = 17.4 Hz)), 0.89 (s, 12H, SiMe, (J_{Pt-H} = 26.6 Hz)), 7.1-7.4 (m, 6H, Ph), 7.7-7.9 (m, 4H, Ph); ^{31}P-NMR (C_6D_6, 85%H_3PO_4) δ -16.02. Anal. Found: C, 43.07; H, 6.67%. Calcd for $C_{22}H_{40}P_2PtSi_2$: C, 42.77; H, 6.53%.

PEt_3: yellow needles, 21% yield; mp 110-116 °C (dec.) under N_2; ^{1}H-NMR (C_6D_6, TMS) δ 0.77 (dt, J_{P-H} = 13.8 Hz, J = 6.9 Hz, 18H, <u>CH$_3$</u>-CH$_2$), 0.90 (s, 12H, SiMe, (J_{Pt-H} = 27.0 Hz)), 1.35 (quintet, J_{P-H} = J = 6.$\overline{9}$ Hz, 12H, CH$_2$), 7.1-7.4 (m, 6H, Ph), 7.7-7.9 (m, 4H, Ph); ^{31}P-NMR (C_6D_6, 85%H_3PO_4) δ 11.78. Anal. Found: C, 46.56; H, 7.29%. Calcd for $C_{28}H_{52}P_2PtSi_2$: C, 47.91; H, 7.47%.

9) R. D. Holmes-Smith, S. R. Stobart, T. S. Cameron, and K. Jochem, J. Chem. Soc., Chem. Commun., <u>1981</u>, 937.

10) B. T. Heaton and A. Pidcock, J. Organomet. Chem., <u>14</u>, 235 (1968).

11) F. Glockling and K. A. Hooton, J. Chem. Soc., A, <u>1967</u>, 1066.

12) M. D. Curtis and P. S. Epstein, Adv. Organomet. Chem., <u>19</u>, 213 (1981).

13) R. A. Michelin, S. Faglia, and P. Uguagliati, Inorg. Chem., <u>22</u>, 1831 (1983).

14) M. Auburn, M. Ciriano, J. A. K. Howard, M. Murray, N. J. Pugh, J. L. Spencer, F. G. A. Stone, and P. Woodward, J. Chem. Soc., Dalton Trans., <u>1980</u>, 659.

15) M. C. Baird, J. Inorg. Nucl. Chem., <u>29</u>, 367 (1967).