Palladium or platinum complex catalysed reactions of carbonyl and imine compounds with disilanes †

Neil A. Williams,*[a] Yuko Uchimaru[b] and Masato Tanaka *[b,c]

[a] School of Chemical and Pharmaceutical Sciences, Kingston University,
   Kingston upon Thames, UK KT1 2EE
[b] National Institute of Advanced Industrial Science and Technology, Tsukuba Central 5,
   Ibaraki 305-8565, Japan
[c] Chemical Resources Laboratory, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku,
   Yokohama 226-8503, Japan

The transition metal catalysed reactions of benzaldehydes and benzylideneamines with disilanes have been investigated. Palladium phosphine complexes catalyse the double silylation of the C=O bond in benzaldehydes and the C=N bond in benzylideneamines with 1,2-difluoro-1,1,2,2-tetramethyldisilane to yield α-(fluorodimethylsilyl)-α-(fluorodimethylsiloxy)toluene and N-methyl-N-(fluorodimethylsilyl)-α-(fluorodimethylsilyl)benzylamine respectively. When less activated disilanes such as 1,2-dichloro- and 1,2-dimethoxy-1,1,2,2-tetramethyldisilane were employed, the palladium phosphine complexes were less active and selective, resulting in extensive side reactions inclusive of 1,2-disiloxy-1,2-diphenylethane formation. The reaction of benzophenone with the difluorodisilane formed 2,2-dimethyl-4,4,5,5-tetraphenyl-1,3-dioxa-2-silacyclopentane without affording the corresponding simple double silylation product. The formation of side products such as 1,2-disiloxy-1,2-diphenylethane in the reaction of benzaldehyde and 2,2-dimethyl-4,4,5,5-tetraphenyl-1,3-dioxa-2-silacyclopentane in the reaction of benzophenone appears to suggest intermediacy of radical and silylene species. Tris(dibenzylideneacetone)diplatinum–etpo (etpo = 4-ethyl-1-phospha-2,6,7-trioxabicyclo[2.2.2]octane catalyst system was more active for unactivated disilanes, catalysing double silylation of benzaldehydes with hexamethyldisilane. The same catalyst system was found to catalyse the ortho silylation of benzylideneamines with disilanes via intramolecular C–H activation; both mono- and bis-silylated products were obtained. Reaction rates and product distributions are rationalised in terms of the steric and electronic properties of the disilanes, substrates and the catalyst used.

Introduction

Organosilicon reagents have a diverse range of applications in organic synthesis.[1] Furthermore, they have important utilities in material applications as monomers in synthesis of silicon-containing functional polymers[2] and as coupling agents between organic polymers and inorganic surface modifiers.[3]

The transition metal catalysed double silylation of unsaturated hydrocarbons has been developed into a convenient and efficient method for synthesising organosilicon compounds.[4,5] Unsaturated carbon heteroatom linkages however have received much less attention.[6–8] Previously, we discovered the platinum complex catalysed dehydrogenative double silylation of aldehydes and ketones with o-bis(dimethylsilyl)benzene.[9] This prompted us to investigate the reactivity of disilanes towards C=O and C=N bonds in the presence of a palladium or platinum catalyst. To our knowledge, the only examples of transition metal catalysed double silylation of aldehydes with disilanes have involved the highly strained cyclic 3,4-benzo-1,1,2,2-tetraethyl-1,2-disilacyclobut-3-ene and 3,4-bis(alkylidene)-1,2-disilacyclobutanes.[10] The double silylation of imines has never been documented. The present paper reports successful double silylations of C=O and C=N bonds, inclusive of the unexpected o-silylation of imines via C–H activation[11] observed when the attempted double silylation reaction with hexamethyldisilane or 1,2-diphenyl-1,1,2,2-tetramethyldisilane was run in the presence of a catalyst comprising Pt$_2$(dba)$_3$ (dba = dibenzylideneacetone) and P(OCH$_2$)$_3$CEt (10/3 equivalents relative to Pt; this catalyst system will be abbreviated as the Pt–etpo system). Functionalisation of organic materials via catalytic C–H activation,[12,13] including silylation of aromatics with hydrosilanes,[14] is an extremely attractive synthetic strategy and is an area of great current interest. ortho-Functionalisation of aromatic imines has also been reported recently.[15]

Results

Palladium or platinum complex catalysed double silylation of benzaldehyde with disilanes

Table 1 summarises the results of the reaction of disilanes with benzaldehyde (Scheme 1).

(1) Reaction of benzaldehyde with 1,2-difluorotetramethyldisilane. Screening of catalysts has revealed that Pd(PPh$_3$)$_4$ is the catalyst of choice as far as 1,2-difluoro-1,1,2,2-tetramethyldisilane 1a is concerned. Thus, the reaction at 120 °C for 5 h
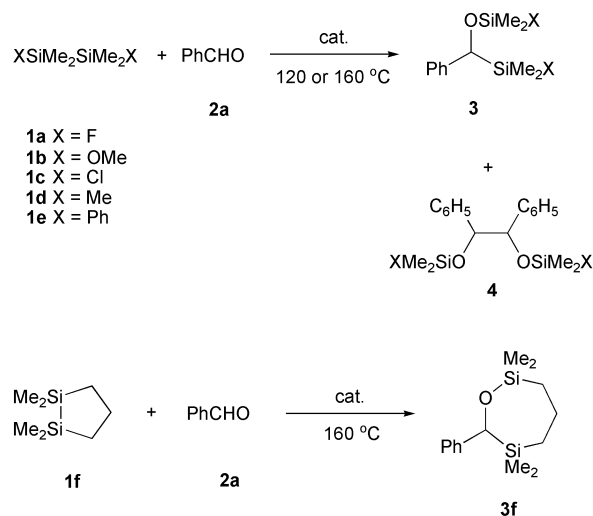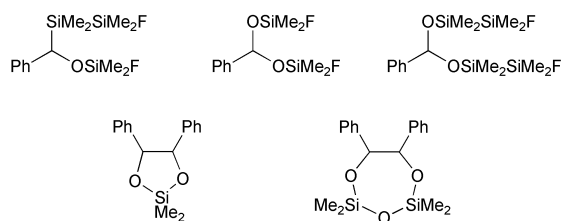

Scheme 1

† Electronic supplementary information (ESI) available: characterization data of the silicon-containing products obtained in the catalytic reactions. See http://www.rsc.org/suppdata/dt/b2/b207987a/

Table 1 Catalytic performance for double silylation of benzaldehyde[a]

Entry	Disilane	Catalyst	t/h	T/°C	Conversion of 2a (%)	Yield of 3 (%)[b]	Yield of 4 (%)[b]
1	**1a**	Pd(PPh$_3$)$_4$	5	120	100	**3a** 97	—
2	**1a**	Pd(PPh$_3$)$_2$Cl$_2$	5	120	90	**3a** 88	—
3	**1a**	Pd(PEt$_3$)$_2$Cl$_2$	5	120	95	**3a** 85	—
4	**1a**	Pd(PMe$_3$)$_2$Cl$_2$	5	120	100	**3a** 86	—
5	**1a**	Pd(dppb)Cl$_2$	5	120	70	**3a** 35[c]	—
6	**1a**	Pd(dppf)Cl$_2$	5	120	100	**3a** 30[c]	—
7	**1a**	Pd(dba)$_2$ + 2PPh$_3$	5	120	40	**3a** 38	—
8	**1a**	Ni(PEt$_3$)$_4$	5	120	100	**3a** 20[c]	—
9	**1b**	Pd(PPh$_3$)$_4$	5	120	60	**3b**[d] ~12	—
10	**1c**	Pd(PPh$_3$)$_4$	5	120	90	**3c**[d] ~20	—
11	**1d**	½ Pt$_2$(dba)$_3$ +5/3P(OCH$_2$)$_3$CEt	5	120	25	**3d** 9	**4d** 5
12	**1d**	½ Pt$_2$(dba)$_3$ +5/3P(OCH$_2$)$_3$CEt	20	160	100	**3d** 50	**4d** 35
13[e]	**1d**	½ Pt$_2$(dba)$_3$ +5/3P(OCH$_2$)$_3$CEt	120	160	90	**3d** 78	**4d** 10
14	**1e**	½ Pt$_2$(dba)$_3$ +5/3P(OCH$_2$)$_3$CEt	20	160	100	**3e** 75	**4e**[d] —
15	**1e**	Pt(PPh$_3$)$_4$	20	160	7	**3e** 7	—
16	**1f**	½ Pt$_2$(dba)$_3$ +5/3P(OCH$_2$)$_3$CEt	20	120	5	**3f** 5	—
17	**1f**	½ Pt$_2$(dba)$_3$ +5/3P(OCH$_2$)$_3$CEt	20	160	100	**3f** 90	—
18	**1f**	Pt(PPh$_3$)$_4$	20	160	95	**3f** 80	—

[a] Reaction conditions: benzaldehyde (0.5 mmol), disilane (0.5 mmol), catalyst 2 mol%, decane (30 µl) as internal standard, toluene (0.1 ml), under nitrogen. [b] Yields determined by GLC and based on the quantity of the aldehyde charged. [c] Many products were observed by GLC analysis. [d] Compound identified by GC/MS, but not isolated. [e] Reaction conditions: benzaldehyde (0.5 mmol), disilane (1.0 mmol).

gave the double silylated product α-(fluorodimethylsilyl)-α-(fluorodimethylsiloxy)toluene **3a** in 97% yield (entry 1). The next best set of catalysts are the bis(monodentate phosphine)-palladium(II) complexes (entries 2–4). The lower conversions, compared to the palladium(0) complex, may be attributed to the necessity of activation by reduction of palladium(II) to palladium(0) in order to generate the proposed active catalyst species or to the undesired interaction of the active palladium species with chlorofluorodimethylsilane generated in the reduction process (*vide infra*). Bidentate phosphine complexes Pd(dppb)Cl$_2$ [dppb = 1,4-bis(diphenylphosphino)butane] and Pd(dppf)Cl$_2$ [dppf = 1,1′-bis(diphenylphosphino)ferrocene] have been reported to exert high performance for the double silylation of 4-phenyl-3-buten-2-one with PhCl$_2$SiSiMe$_3$.[5g] In the present study however, these complexes were far less select-ive (entries 5–6). Undesired side products (Scheme 2), tenta-

Scheme 2

tively identified from GC and GC–MS analyses, include: PhCH(SiMe$_2$SiMe$_2$F)(OSiMe$_2$F) *m/z* (EI, 70 eV) 318 (M$^+$), [PhCH(OSiMe$_2$F)]$_2$ *m/z* 351 (M$^+$–Me), {PhCH(OSiMe$_2$Si-Me$_2$F)}$_2$ *m/z* (EI, 20 eV) 482 (M$^+$), 2,2-dimethyl-4,5-diphenyl-1,3-dioxa-2-silacyclopentane *m/z* (EI, 70 eV) 270 (M$^+$) and 2,2,4,4-tetramethyl-6,7-diphenyl-1,3,5-dioxa-2,4-disilacy-cloheptane *m/z* (EI, 70 eV) 344 (M$^+$). The formation of these compounds may be partially rationalised in terms of the gener-ation of silylene species, dimerisation of radicals produced by Pd–C bond homolysis (*vide infra*), and redistribution reaction of starting and resulting silane compounds.

Given that a bis(phosphine)palladium(0) species is the active species, Pd(dba)$_2$ + two equivalents of a phosphine ligand is expected to provide a good catalyst system. However, the con-version of benzaldehyde with the Pd(dba)$_2$ + 2PPh$_3$ system (entry 7) was much lower than that with Pd(PPh$_3$)$_2$Cl$_2$ or Pd(PPh$_3$)$_4$. Since dibenzylideneacetone is known to be a better ligand than PPh$_3$ to low ligated Pd(0) species,[16] the low

conversion is envisioned to be associated with lower concen-tration of active species as compared with the reaction using Pd(PPh$_3$)$_4$.

Use of Pd(dba)$_2$ or Pd(PhCN)$_2$Cl$_2$ without addition of any phosphine ligand was totally inactive. Pt(PPh$_3$)$_2$Cl$_2$, Pt(PEt$_3$)$_2$-Cl$_2$, Pt$_2$(dba)$_3$ and Ni(PEt$_3$)$_2$Cl$_2$ were also completely inactive. Ni(PEt$_3$)$_4$ catalysed the reaction (entry 8), but very many peaks were observed in GC analysis, 2,2,4,4-tetramethyl-6,7-di-phenyl-1,3,5-dioxa-2,4-disilacycloheptane being the major product (27%) and the selectivity for **3a** (20% yield) was much lower than that with the palladium-monophosphine systems. Pt(PPh$_3$)$_4$ catalysed reaction under similar conditions was even less selective.

(2) Reaction of benzaldehyde with other disilanes. The reaction of benzaldehyde with 1,2-dimethoxy-1,1,2,2-tetra-methyldisilane **1b** (entry 9) and 1,2-dichloro-1,1,2,2-tetramethyl-disilane **1c** (entry 10) was much less selective and gave only small yields of the anticipated double silylated product. A range of side products, inclusive of those similar to Scheme 2, appeared to have been formed, as judged on the basis of the GC-MS analysis.

In the reaction with hexamethyldisilane **1d**, Pd(PPh$_3$)$_4$, Pd(PEt$_3$)$_2$Cl$_2$ and Pd(PMe$_3$)$_2$Cl$_2$ did not show any catalytic activity, although these complexes have been revealed to be effective in the reaction of **1d** with α-diketones and an α-keto ester.[6] The Pd(dba)$_2$ + 2P(OCH$_2$)$_3$CEt system that exhibited high performance in the double silylation of acetylenes with **1d**[5d] was also inactive, even when the reaction was executed in the absence of any solvent. The analogous Pt–etpo system, which is effective in the double silylation of α-diketones,[6] catalysed double silylation with **1d** at 120 °C, albeit slowly (entry 11). The platinum catalyst system is more thermally stable than the palladium systems, allowing the reaction to be performed at 160 °C; the reaction was complete in 20 h. How-ever the selectivity for **3d** was poor (50% yield) and a consider-able amount of a double silylated, dimerisation product, 1,2-bis(trimethylsiloxy)-1,2-diphenylethane **4d** (35% yield) was also formed (entry 12). The selectivity for **3d** could be improved by using two equivalents (relative to benzaldehyde) of the disilane **1d**; this gave a yield of 78% of **3d** and 10% of **4d** (entry 13). The improvement may be rationalised in terms of disilane-assisted reductive elimination (*vide infra*).

The reaction with 1,2-diphenyl-1,1,2,2-tetramethyldisilane **1e** was also efficiently catalysed by the Pt–etpo system at 160 °C,

| Entry	Aldehyde	t/h	Conversion of **2** (%)[b]	Yield of **3** (%)[b]
1	**2a** Ar = Ph	1	46	44
2		5	100	97
3	**2g** Ar = *p*-MeO–Ph	1	23	21
4		10	100	92
5	**2h** Ar = *p*-Me–Ph	1	29	26
6		10	100	90
7	**2i** Ar = *p*-F–Ph	1	60	57
8		2.5	100	93
9	**2j** Ar = thienyl	2.5	65	45
10		10	100	58

[a] Reaction conditions: aldehyde (0.5 mmol), F(SiMe₂)₂F (0.5 mmol), Pd(PPh₃)₄ 2 mol%, decane (30 μl) as internal standard and toluene (0.1 ml), 120 °C, under N₂ (g). [b] Conversions and yields determined by GLC and based on the quantity of the aldehyde charged.

affording **3e** in 75% yield (entry 14). Pt(PPh₃)₄ gave only a trace of **3e** (entry 15), but Pt₂(dba)₃ was inactive. Pd(PPh₃)₄, Pd(PEt₂)₂Cl₂ and Pd(dba)₂–2P(OCH₂)₃CEt were also inactive at 120 °C.

The reaction with a cyclic disilane 1,1,2,2-tetramethyl-1,2-disilacyclopentane **1f** (entries 16–18) was catalysed by the Pt–etpo system to give the double silylation product **3f** in a high yield at 160 °C. Unlike the reaction with **1e** however, Pt(PPh₃)₄ also displayed high activity. This is presumably associated with the ring strain in the disilacyclopentane significantly weakening the Si–Si bond and the relatively small steric hindrance around the Si–Si bond as compared with **1e**.

Pd(PPh₃)₄-catalysed reaction of various aldehydes with 1a

A variety of *p*-substituted benzaldehydes reacted smoothly with **1a** catalysed by Pd(PPh₃)₄ to give the double silylated products (Scheme 3, Table 2). Regardless of the nature of the *p*-substitu-
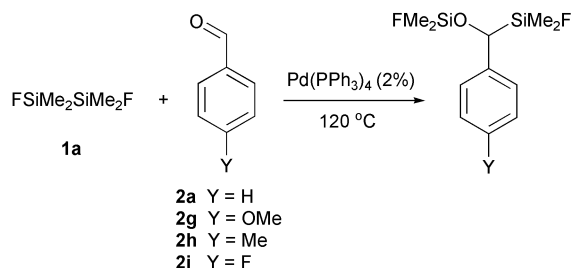
Scheme 3

ents, the selectivity did not vary significantly and was generally greater than 90%. Accordingly, if the reaction was continued sufficiently long (>2.5 h), the products could be obtained in excellent yields.

On the other hand, the reactivity of the aromatic aldehydes was dependent on the nature of substituents. To compare the reactivity, the reaction at 120 °C was discontinued after 1 h. The results illustrate that *p*-fluorobenzaldehyde **2i** reacted at a significantly faster rate than **2a**, whereas *p*-methoxybenzaldehyde **2g** and *p*-methylbenzaldehyde **2h** reacted at an appreciably slower rate (entries 1, 3, 5, 7). To compare the reactivities of **2g** and **2h** further a 1 : 1 mixture of these two aldehydes was subjected to a reaction that was discontinued after 2 h (otherwise the same conditions). The result revealed 48% conversion of **2h** and 34% conversion of **2g**. Thus benzaldehydes with electron withdrawing *para* substituents react at a faster rate than those with *para* donor substituents. The results suggest that the aldehyde is involved in the rate-determining step as far as 1,2-difluorodisilane is concerned.

2-Thiophenecarboaldehyde also reacted with **1a** smoothly but somewhat slowly to furnish the corresponding double silylated product (entries 9–10). The selectively was less satisfactory.

As is anticipated on the basis of the electronic effect of the *para* substituent of the aromatic aldehydes, aliphatic aldehydes exhibited very low reactivity with **1a** under the same conditions. Even when the reaction of n-hexanal was continued for 40 h, only 10% of the aldehyde was consumed; several products were found by GC analysis to have been formed.

**Pd(PPh₃)₄-catalysed reaction of benzophenone with 1a**

The Pd(PPh₃)₄ catalysed reaction of benzophenone with **1a** differs considerably from that of benzaldehyde (Scheme 4). The
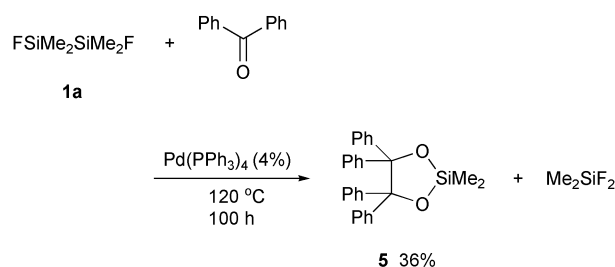
Scheme 4

major product formed after heating at 120 °C for 100 h was 2,2-dimethyl-4,4,5,5-tetraphenyl-1,3-dioxa-2-silacyclopentane **5** (36% ¹H NMR yield); the formation of SiMe₂F₂ was also evident by the NMR analysis, but there was no trace of the corresponding simple double silylated adduct. No reaction was observed when **1b** was employed instead of **1a**.

The double silylation of the C=N bond in *N*-benzylidenemethylamine

As the combination of 1,2-difluoro-1,1,2,2-tetramethyldisilane **1a** and Pd(PPh₃)₄ was most effective in the catalysed double silylation of benzaldehydes, the same procedure was applied to *N*-benzylidenemethylamine **6a** (Table 3, Scheme 5). On heating
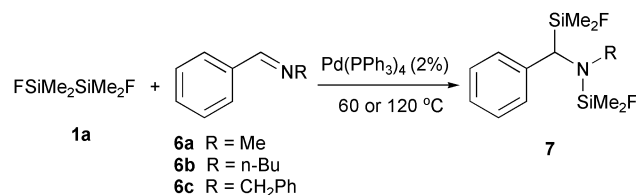
Scheme 5

a toluene solution of **1a** (0.5 mmol) and **6a** (0.5 mmol) with Pd(PPh₃)₄ (0.01 mmol) in a sealed tube at 120 °C for 5 h, double silylation of the C=N bond proceeded quantitatively to give *N*-methyl-*N*-(fluorodimethylsilyl)-α-(fluorodimethylsilyl)-benzylamine **7a** (entry 1).

Palladium(ɪɪ) phosphine complexes were also efficacious towards the double silylation; both Pd(PPh₃)₂Cl₂ and Pd(PMe₃)₂-

| Entry	Imine	Catalyst	t/h	T/°C	Conversion of 6 (%)[b]	Yield of 7 (%)[b]
1	**6a**	Pd(PPh$_3$)$_4$	5	120	100	**7a** 99
2	**6a**	Pd(PPh$_3$)$_2$Cl$_2$	5	120	100	**7a** 98
3	**6a**	Pd(PMe$_3$)$_2$Cl$_2$	5	120	100	**7a** 98
4	**6a**	Pd(dba)$_2$ + 2PPh$_3$	5	120	76	**7a** 70
5	**6a**	Pd(PMe$_3$)$_2$Cl$_2$	70	60	68	**7a** 66
6	**6a**	Pd(PPh$_3$)$_4$	70	60	42	**7a** 40
7	**6b**	Pd(PMe$_3$)$_2$Cl$_2$	20	120	85	**7b** 82
8	**6b**	Pd(PPh$_3$)$_4$	20	120	65	**7b** 62

Cl$_2$ gave **7a** in 98% yield under the standard conditions (entries 2, 3). A combination of Pd(dba)$_2$ and two equivalents of PPh$_3$ was less active giving **7a** in 70% yield under identical conditions (entry 4) and phosphine free complexes Pd(PhCN)$_2$Cl$_2$ and Pd(dba)$_2$ were totally inactive. The double silylation of benzylidenemethylamine proceeded even 60 °C, albeit more slowly (entries 5, 6).

N-benzylidenebutylamine **6b** also undergoes selective double silylation with **1a** in the presence of Pd(PMe$_3$)$_2$Cl$_2$ or Pd(PPh$_3$)$_4$ to give the double silylated product **7b** (entries 7, 8). *N*-Benzylidenebenzylamine **6c** gave a mixture of products that could not be separated or characterised. Other disilanes such as **1c** and **1d** were completely unreactive towards **6a** in the presence of Pd(PPh$_3$)$_4$.

The platinum catalysed *ortho*-silylation of benzylideneamines with disilanes

In our investigations on the double silylation of benzaldehyde we observed that whereas Pd(PPh$_3$)$_4$ was very effective in conjunction with **1a**, no reaction was observed with unactivated disilanes such as **1d**. However the Pt–etpo system did catalyse the double silylation with **1d**. This prompted us to try the same catalyst for the reaction between **6a** and **1d**.

Remarkably, the Pt–etpo system catalysed the regioselective *ortho*-silylation of **6a** with **1d**, giving the mono- and bis-silylated products in high yields (Scheme 6, Table 4). For
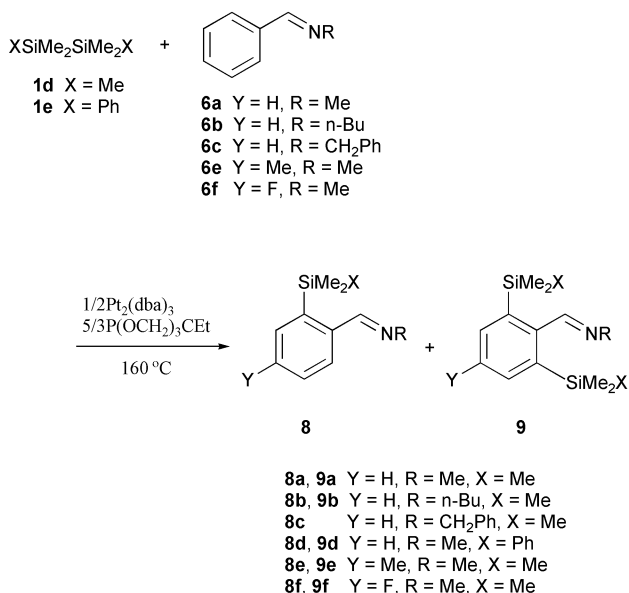
instance, heating a toluene solution of **6a** (0.5 mmol) and **1d** (0.5 mmol) in the presence of the Pt–etpo catalyst system (0.01 mmol Pt) at 160 °C for 120 h gave *N*-[(2-trimethylsilyl)benzylidene]methylamine **8a** in 38% yield and *N*-[2,6-bis(trimethyl-

silyl)benzylidene]methylamine **9a** in 54% yield based on the disilane charged (yield of **9a** based on the imine is 27%; entry 1). ^{1}H NMR analysis of a separate experiment run in a sealed NMR tube revealed that a small amount of trimethylsilane (δ 0.02, d, ^3J(H–H) = 3.6 Hz) was formed as a co-product although its quantitative analysis was not possible in this particular case due to its gaseous nature. Hydrosilylation products that could arise from trimethylsilane and the starting and resulting imines were not detected in the reaction mixture. Selectivity towards **8a** could be enhanced by employing an excess of the imine (entry 2) and conversely a higher yield of **9a** was achieved with excess hexamethyldisilane (entry 3).

The reaction also proceeded with other aldimines. *N*-Benzylidenebutylamine **6b** slowly reacted to give the mono-silylated **8b** in only 19% yield even after 120 h (entry 4). Approximately 3% of **9b** was also identified by GC and GC/MS. *N*-Benzylidenebenzylamine **6c** was even less reactive under the same conditions: GC and GC/MS analyses indicated that mono-silylated product **8c** was formed in approximately 3% yield.

In the reaction between 1,2-diphenyl-1,1,2,2-tetramethyldisilane **1e** and **6a**, mono-silylated product **8d** was formed in 15% yield while only a slight trace of the bis-*ortho*-silylated product **9d** was detected by GC/MS (entry 7). GC analysis indicated that an equimolar amount of phenyldimethylsilane was produced. The hydrosilane does not appear to play further role; in an attempted hydrosilylation of **6a** with phenyldimethylsilane in the presence of the Pt–etpo system, **6a** was completely recovered unchanged after heating at 160 °C for 48 h.

The lower yields of **8** and **9** in the reactions involving **6b**, **6c** and **1e** can presumably be attributed to steric hindrance.

In the study to determine the mechanism involved in the production of the *ortho*-silylated products, reactions were performed with *para*-substituted aromatic imines (entries 8~10). If the mechanism is to be considered in terms of electrophilic C–H activation, the usual reaction mode for palladium(II) and platinum(II) species, the results are opposite to what would be anticipated; the electron-donating methyl group (**6e**) retarded the reaction, whereas the withdrawing fluorine substituent (**6f**) accelerated it, to realise a combined yield of nearly 90% for the mono- and bis-silylated products, under identical conditions.

Discussion

Mechanism for the reaction between disilanes and benzaldehyde

The formation of the double silylated adduct and others can be explained by the mechanism illustrated in Scheme 7, which is analogous, in part, to that postulated for the double silylation of other carbon unsaturated molecules.[4,5] The catalytic cycle comprises of oxidative addition of the Si–Si bond to the active catalyst species, insertion of the carbonyl group into the silicon–metal bond to form an α-siloxybenzyl–metal species **11** and the reductive elimination. Depending on the structure of the precursor complex, generation of the active species must precede the catalysis.

XSiMe$_2$SiMe$_2$X +

1d X = Me
1e X = Ph

6a Y = H, R = Me
6b Y = H, R = n-Bu
6c Y = H, R = CH$_2$Ph
6e Y = Me, R = Me
6f Y = F, R = Me

1/2Pt$_2$(dba)$_3$
5/3P(OCH$_2$)$_3$CEt
160 °C

8   **9**

8a, 9a Y = H, R = Me, X = Me
8b, 9b Y = H, R = n-Bu, X = Me
8c Y = H, R = CH$_2$Ph, X = Me
8d, 9d Y = H, R = Me, X = Ph
8e, 9e Y = Me, R = Me, X = Me
8f, 9f Y = F, R = Me, X = Me

Scheme 6

Table 4 Platinum catalysed *ortho*-silylation of benzylideneamines[a]

Entry	Imine	Disilane	Imine-to-disilane ratio	Imine conversion (%)	Reaction time/h	Yield of **8** (%)[b]	Yield of **9** (%)[b]
1	**6a**	**1d**	1 : 1	64	120	**8a** 38	**9a** 27[c]
2	**6a**	**1d**	4 : 1	—	120	**8a** 82[d]	**9a** 9[d]
3	**6a**	**1d**	1 : 4	—	120	**8a** 23	**9a** 52
4	**6b**	**1d**	1 : 1	—	120	**8b** 19	**9b**[e] ~3
5	**6c**	**1d**	1 : 1	15	120	**8c**[e] ~3	—
6	**6f**	**1d**	1 : 1	71	120	**8f** 42	**9f** 29
7	**6a**	**1e**	1 : 1	—	120	**8d** 15[f]	**9d** trace
8	**6a**	**1d**	1 : 2	69	20	**8a** 31	**9a** 38
9	**6e**	**1d**	1 : 2	51	20	**8e** 29	**9e** 20
10	**6f**	**1d**	1 : 2	90	20	**8f** 23	**9f** 66

[a] Reaction conditions: benzylideneamine (0.5 mmol), disilane (0.5 mmol), Pt_2(dba)$_3$ (0.005 mmol), $P(OCH_2)_3CEt$ (0.0167 mmol), decane (20 µl) as internal standard, toluene (0.1 ml), 160 °C, under nitrogen. [b] Yields determined by GLC and unless stated differently, are based on the amount of imine charged. [c] 54% yield based on disilane. [d] Yields based on disilane charged. [e] GC and GC-MS analyses indicated an equimolar amount of $PhMe_2SiH$ was produced. [f] Identified by GC/MS but not isolated.
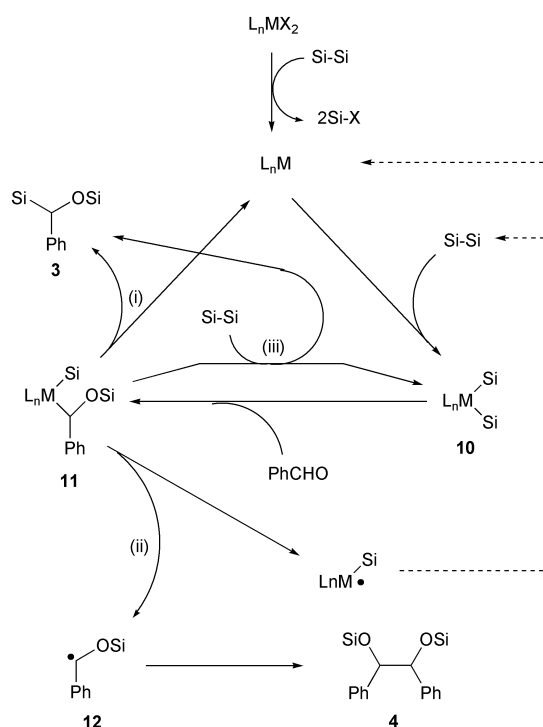
Scheme 7

The active species is thought to be a bis(phosphine)-palladium(0) complex; if a dichloropalladium(II) complex is used as precursor, reduction to palladium(0) is envisioned to be effected by interaction with a disilane molecule. Indeed, treatment of $Pd(PPh_3)_2Cl_2$ with octamethyl-1,2-disilacyclobutane forms 1,4-dichloro-1,4-disilaoctamethylbutane.[17] The reduced metal species, which is supposed to carry the double silylation catalysis, is reported to be reactive towards chlorosilanes.[18] Accordingly, the chlorosilane generated in the reduction of the precursor complex may interact under the catalytic conditions with the catalytically active species, resulting catalytic activity being lowered as compared with its intrinsic activity observed in the absence of the chlorosilane. The observation that the catalysis by the species generated from the palladium(II) complex precursors was less active than that where preformed palladium(0) complex was used is presumably associated with this "poisoning" by the chlorosilane.

A number of bis(silyl)-palladium and -platinum species have been synthesised and their roles in the double silylation of unsaturated compounds is well documented.[19] In general, disilanes substituted by more electro-negative groups like fluorine readily react with low valent transition metal complexes *via* oxidative addition to form more stable bis(silyl)metal species. This means that intermediate **10** is smoothly generated for the reaction of **1a** to proceed briskly. The next insertion process into silyl–metal species has also been documented for late transition metal complexes.[20] The insertion of carbonyl compounds into silicon–manganese bonds affording α-siloxybenzyl-manganese complex has also been demonstrated.[21] The last elemental process to conclude the catalytic cycle is the reductive elimination from the (silyl)(alkyl)metal intermediate **11** [path (i)],[22] a common process involved in all the other double silylation reactions catalysed by metal complexes. Thus, the observations made in the palladium-catalysed catalytic double silylation reactions with **1a** are mostly in consistent with these precedents, which are accommodated in Scheme 7. A minor aspect that is apparently inconsistent is the effect of the substituent bound to the aldehyde. In the insertion reaction with the Mn–$SiMe_3$ complex, the reactivity trend is reported to be *p*-NMe_2 > *p*-OMe > *p*-H.[21] On the other hand, the reactivity trend was *p*-F > *p*-H > *p*-Me > *p*-OMe in our palladium catalysed reaction with **1a**. We speculate that the fluorine substituent bound to the silicon effectively reduces the intrinsic electro-positive nature of the silyl group, which in turn enhances the electrophilic reactivity towards the carbonyl oxygen. In addition, more electron-deficient carbonyl compounds may interact more strongly with the palladium centre.

On the other hand, the Pt–etpo catalysed double silylation with unactivated **1d** appears somewhat different in terms of the formation of **4** from the palladium-catalysed reaction with **1a**. The intermediate **11**, leading to product **3** if reductive elimination follows, can react in an alternative direction [path (ii)], which is the homolysis of the metal–carbon bond to generate a benzylic radical (**12**);[23] subsequent homo-coupling of **12** would give the side product **4d**. Gladysz *et al.*[21] have reported for their Mn–Si systems that heating $Me_3SiO(Ph)CHMn(CO)_5$ indeed gave **4d** in high yields, presumably *via* homolysis of the metal–carbon bond and coupling of the benzylic radicals.

The quantity of **4d** formed in the catalysis could be suppressed when a two fold excess of **1d** was used. We have recently found that formal high valent species can be generated when silyl ligands are bound to the metal centre. If we assume a high valent species or σ-bond metathesis in the interaction of a disilane molecule with the intermediate **11**, the disilane-assisted reductive elimination [path (iii)] can be envisioned to take place, which rationalises the increased selectivity for **3d** achieved in the presence of excess **1d**.

The mechanism of the double silylation of imine is presumably similar to the aldehyde reaction and will not be discussed.

Mechanism for the reaction between disilane and benzophenone

The mechanistic key feature of the reaction of benzophenone lies in the formal involvement of silylene species, which is
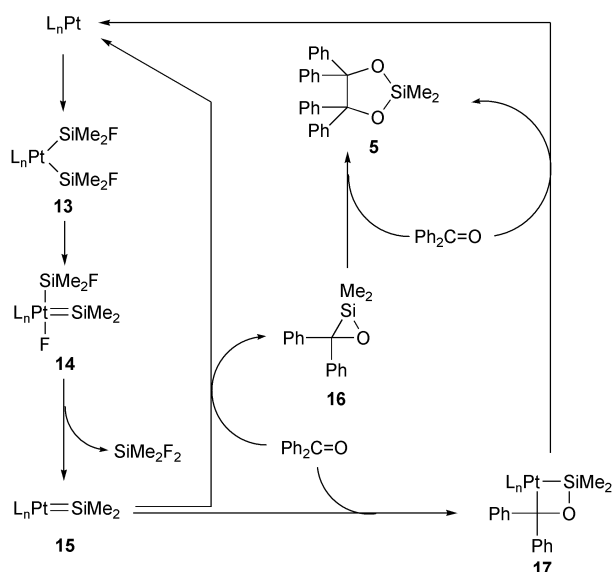
Scheme 8

Scheme 9

evident in the structure of **5**. The formation of **5** is best explained as illustrated in Scheme 8, which comprises of silylene and oxasilacyclopropane intermediates **14–16**. Since the reactivity of benzophenone was low as compared with aldehyde, the reaction was run at a relatively high temperature. Under the conditions, the intermediate **13** is likely to undergo α-migration of the fluorine attached to the silicon to the platinum centre, generating silylene species **14**. Subsequent reductive elimination from **14** would give Me_2SiF_2. The difluorosilane was actually detected in the reaction mixture by NMR spectroscopy. There are a number of reports of silylene species being generated from transition metal silyl species.[24] For instance, Rich noted the formation 2,2-dimethyl-4,5-diphenyl-1,3-dioxa-2-silacyclopentene in the palladium catalysed reaction of benzil with **1b**, presumably *via* silylene formation.[24e] One of us also encountered similar silylene generation and its reaction with acetylenes forming 1,4-disilacyclohexadienes.[24d]

Evidence of the generation of oxasilacyclopropane species from the reaction of a silylene species with benzophenone has appeared in the literature.[25] It has also been postulated that the reaction between di(t-butyl)silylene and ketones goes through oxasilacyclopropane intermediates before forming silyl enol ethers.[26] In addition, a crystalline oxasilacyclopropane has been isolated from the reaction of photochemically generated dimesitylsilylene with 1,1,3,3-tetramethyl-2-indanone.[27] The addition reactions of thermally stable bis(amino)silylenes to the C=O bond reported by Lappert and co-workers also lend support.[28]

At the moment we are unable to exclude the possibility that intermediate **14** reacts with benzophenone, forming **16** and a fluoro(fluorodimethylsilyl)platinum intermediate, the latter of which then reductively eliminates difluorodimethylsilane.
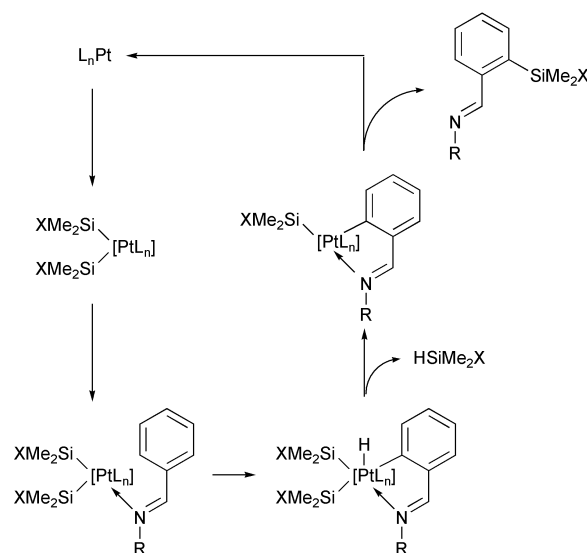
As for the final process forming the product **5**, there are also precedents, in which oxasilacyclopropane species react with another ketone molecule, giving 1,3-dioxa-2-silacyclopentane compounds.[25b]

Alternatively, complex **15** may interact as such with benzophenone to furnish intermediate **17**, which undergoes insertion of benzophenone at the Pt–Si bond. Reductive elimination from the resulting species can afford product **5**.

Reaction mechanism for *ortho*-silylation of benzylideneamines

As already mentioned, the oxidative addition of disilanes to platinum yielding bis(silyl)platinum species[19] and the catalytic activity of the Pt catalyst system for the double silylation with the unactivated hexamethyldisilane have been demonstrated.[5f] Cyclometallation of benzylideneamines with platinum and

palladium is also well known.[29] Accordingly one can imagine a mechanism that involves *ortho*-metallation of an imine with a $Pt(SiMe_3)_2$ species generating a Pt(IV) species, reductive elimination of a hydrosilane and further reductive elimination of a silylated imine, as depicted in Scheme 9.

In the closely related stoichiometric reaction reported by Puddephatt *et al.*[29] $Me_2Pt(II)$ sulfide complexes react with aromatic imines *via* a platinum(IV) species to give *ortho*-metallated MePt(II) complexes with extrusion of a methane molecule. Oxidative addition of the C–H bond as opposed to electrophilic substitution was proposed for this C–H cleavage mechanism, which was supported by the observation that electron-withdrawing fluorine substituents promoted this transformation. In our *ortho*-silylation, hydrosilane was extruded and the *p*-fluorine substitutent in the imine molecule facilitated the reaction. Thus the proposed catalytic cycle illustrated in Scheme 9 is in full agreement with the Pudephatt's observations.

Reductive elimination followed by decomplexation of the mono-silylated imine regenerates the active catalyst species, which re-enters the catalytic cycle to undertake the second *ortho*-silylation at the *o′*-position to form the bis-silylated imine. Alternatively, analogous to Murai's postulated mechanism[13] one can envision the second silylation occurring whilst the imine remains co-ordinated to the platinum.

The remaining observation that merits further consideration is the *para* substituent effect. There are two possibilities for *ortho* C–H activation: electrophilic substitution by an electron deficient platinum and oxidative addition of the C–H bond to an electron rich metal centre. In related reactions, such as the ruthenium catalysed *ortho*-alkylation of aromatic ketones and imines with alkenes, oxidative addition of aryl C–H bond to an electron-rich ruthenium(0) centre is the generally accepted mechanism for C–H activation. However, an alternative mechanism consisting of the addition of the ruthenium species at the *ortho*-position, followed by a 1,2-hydrogen migration to give a ruthenium hydride intermediate has been suggested by Murai. Murai observed that the *ortho*-alkylation of aromatic ketones was accelerated by electron donating groups at the *para*-position.[30] This is the reactivity trend that would be expected if electrophilic substitution was involved and hence lends credence to the latter mechanism. In the Pt catalysed *ortho*-silylation of benzylideneamines we observed the opposite trend; electron-withdrawing groups at the *para*-position increased the rate of reaction, which suggests that oxidative addition of C–H bond is involved. Recently, Jun *et al.* have reported that electron-withdrawing substituents enhanced the rate of rhodium catalysed *ortho*-alkylation of *para*-substituted ketimines.[15a] This

was interpreted as supporting oxidative addition of the *ortho*-C–H bond to the electron rich Rh(I) centre. In the Pt catalysed *ortho*-silylation of benzylideneamines C–H activation is effected most likely by $(Me_3Si)_2Pt(II)$ species. Generally, aromatic C–H activation with platinum(II) species has been assumed to involve electrophilic substitution. Numerous examples indicate that this supposition is reasonable for species like $[PtCl_4]^{2-}$ as the platinum is considerably electron deficient.[31] This is not necessarily true for $(Me_3Si)_2Pt$ bis(phosphine) species, where the silyl groups are electron-donating in nature. The platinum centre is envisioned to be much more electron rich than the formal oxidation state; this is supported by theoretical calculations.[32] In addition, intermolecular aromatic C–H activation is observed with Ta–Si complexes, but not with the analogous tantalum methyl species.[33] This is rationalised in terms of the superior electron-donation from silyl groups facilitating oxidation addition of C–H bond to electron rich metal centre. In our own work, it seemed apparent that a bis(silyl)-platinum species was the active complex in the coupling of an aryl C–H with *o*-bis(dimethylsilyl)benzene.[14b] The feasibility of oxidative addition to bis(silyl)Pt(II) and Pd(II) species has been further exemplified by the isolation of unusually stable Pt(IV) and Pd(IV) species.[34] There are other examples of oxidative addition of C–H to platinum(II) species in the literature.[35] Accordingly, the substituent effect in the present *ortho*-silylation catalysis, which is apparently unusual for Pt(II) species, can be attributed to oxidative addition with the "electron-rich" $(Me_3Si)_2Pt(II)$ species. An alternative possibility that we are unable to rigorously exclude is the *ortho*-metallation taking place between Pt(0) species and the imine before interaction with a disilane molecule.

The factor that differentiates double silylation and *ortho*-silylation of aromatic imines

The double silylation of aromatic imines proceeds when **1a** was used in the presence of palladium catalyst. On the other hand, the *ortho*-silylation takes place with **1d**, catalysed by the Pt–etpo system. As already mentioned, the fluorosilyl group ligated to the metal centre is envisioned to be sufficiently electrophilic due to the fluorine. In addition, it is less sterically demanding than Me_3Si. These structural features of the Me_2FSi ligand allow insertion of the imine linkage to the silicon–palladium bond at a relatively low temperature, leading to the double silylation. In the Pt–etpo catalysed reaction, the Me_3Si ligand in the postulated intermediate is less electrophilic and sterically more demanding, which hampers the insertion. Only when the reaction was run at a higher temperature (160 °C), a reaction can proceed, but in a different direction, leading to the *ortho*-silylation. The high performance of the Pt–etpo system in the present catalysis as well as in other double silylation reactions with **1d** is also envisaged to be associated with the steric factor of etpo, which is a quite small-sized ligand due to its cage structure. Since the aldimine substrate is a trisubstituted unsaturated compound, its double bond is rather congested and the insertion into the silicon–metal bond is not possible, prohibiting the double silylation with **1d** to occur. However, aldehydes, disubstituted unsaturated compounds, did undergo double silylation, albeit reluctantly. It is interesting to note that acetophenone, more congested than aldehydes, when treated with **1a** at 160 °C for 120 h in the presence of the Pt–etpo system, gave *o*-trimethylsilylacetophenone (~4% yield) *m/z* (EI, 70 eV) 192 (M⁺) and *o,o′*-bis(trimethylsilyl)acetophenone (~5% yield) *m/z* (EI, 70 eV) 264 (M⁺).[36] Thus, both electronic and steric factors play important roles in differentiation of the reaction pathways. In conclusion it can be seen that in the palladium and platinum catalysed reaction of disilanes with unsaturated carbon–heteroatom systems the reaction pathway is very sensitive to the nature of the metal, ligand, disilane and the organic substrate employed.

Experimental

General comments

All manipulations were performed under a nitrogen atmosphere. ¹H (300 MHz), ¹³C (75 MHz) and ²⁹Si (59.7 MHz) NMR spectra were recorded in C_6D_6 on a Bruker ARX 300 (300 MHz) machine. The spectra were referenced internally using the signal from the residual protio-solvent (¹H) or the signals of the solvent (¹³C). Infrared spectra were measured on a JASCO FT/IR 5000 spectrometer. Mass spectra (EI) were recorded on Shimadzu QP-5000 and JEOL JMS-DX303 spectrometers. Solvents were dried over sodium wire and distilled under nitrogen. Other organic liquids were dried over 4 Å molecular sieves and distilled before use. The following starting materials were prepared by literature methods: $Pd(PPh_3)_4$,[37] $Pd(PMe_3)_2Cl_2$,[38] $Pd(PEt_3)_2Cl_2$,[39] $Pd(PPh_3)_2Cl_2$,[40] $Pd(dppf)Cl_2$,[41] $Pd(dppb)Cl_2$,[42] $Pd(dba)_2$,[43] $Pt_2(dba)_3$,[44] $Pt(PPh)_4$,[45] $Pt(PPh_3)_2Cl_2$,[46] $Pt(CH_2=CH_2)(PPh_3)_2$,[47] $Ni(PEt_3)_2Cl_2$,[48] $Ni(PEt_3)_4$,[49] 1,2-difluoro-1,1,2,2-tetramethyldisilane[50] and 1,1,2,2-tetramethyl-1,2-disilacyclopentane.[51]

Representative procedure for the double silylation: the reaction of benzaldehyde with 1f

A mixture of 1,1,2,2-tetramethyl-1,2-disilacyclopentane **1f** (0.5 mmol, 71 µl), benzaldehyde **2a** (0.5 mmol, 51 µl), $Pt_2(dba)_3$ 0.005 mmol; 2 mol% Pt relative to **1f**), $P(OCH_2)_3CEt$ (0.0166 mmol), decane (30 µl) as an internal GC standard and toluene (100 µl) were sealed in a reaction tube under an atmosphere of nitrogen. The tube was heated at 160 °C for 20 h. GLC analysis (OV-17 column) showed **3f** was formed in 90% yield. The product was obtained by Kugelrohr distillation at 85 °C (1 mm Hg) in 81% yield. Analytically pure samples of compounds containing fluorine were obtained by preparative GC.

General procedure for the *ortho*-silylation: the reaction of benzylidenemethylamine 6a with hexamethyldisilane 1d

A mixture of **6a** (0.5 mmol, 61 µl), **1d** (0.5 mmol, 102 µl), $Pt_2(dba)_3$ (0.005 mmol, 5.35mg), $P(OCH_2)_3CEt$ (0.0167 mmol, 2.65 mg), decane (20 µl) as an internal standard and toluene (100 µl) were sealed in a glass reaction tube under an atmosphere of nitrogen. The tube was heated at 160 °C for 120 h. GLC analysis (OV-17 column) showed **8a** and **9a** were formed in 38 and 27% yields respectively, based on imine charged. The yield of **9a** corresponds to 54% yield based on disilane charged.

References

1 Z. Rappoport and Y. Apeloig, *Chemistry of Organosilicon Compounds*, John Wiley and Sons, New York, 2001, vol. 3; M. A. Brook, *Silicon in Organic, Organometallic and Polymer Chemistry*, John Wiley and Sons, New York, 2000; U. Schubert, *Silicon Chemistry*, Springer-Verlag, Vienna, 1999; E. R. Corey, J. Y. Corey and P. P. Gaspar, *Silicon Chemistry*, Ellis Horwood, Chichester, 1988.
2 R.G. Jones, W. Ando and J. Chojnowski, *Silicon-Containing Polymers*, Kluwer Academic, Dordrecht, 2000; J. M. Zeigler and F. W. G. Fearon, *Silicon-Based Polymer Science*, Advances in Chemistry Series 224, American Chemical Society, Washington, DC, 1990.
3 E. P. Pleuddemann, *Silane Coupling Agents*, Plenum, New York, 1991.
4 J. A. Reichl and D. H. Berry, *Adv. Organomet. Chem.*, 1999, **43**, 197; I. Beletskaya and C. Moberg, *Chem. Rev.*, 1999, **99**, 3435; K. Horn, *Chem. Rev.*, 1995, **95**, 1317; H. K. Sharma and K. H. Pannell, *Chem. Rev.*, 1995, **95**, 1351.
5 (*a*) A. Naka and M. Ishikawa, *Organometallics*, 2001, **20**, 1695;

(*b*) F. Ozawa and J. Kamite, *Organometallics*, 1998, **17**, 5630; (*c*) Y. Tsuji, R. M. Lago, S. Tomohiro and H. Tsuneishi, *Organometallics*, 1992, **11**, 2353; (*d*) H. Yamashita, M. Catellani and M. Tanaka, *Chem. Lett.*, 1991, 241; (*e*) T. Hayashi, A. Kawamoto, T. Kobayashi and M. Tanaka, *J. Chem. Soc., Chem. Commun.*, 1990, 563; (*f*) T. Hayashi, A. M. Kawamoto, T. Kobayashi, H. Yamashita and M. Tanaka, *Organometallics*, 1990, **9**, 280; (*g*) T. Hayashi, Y. Matsumoto and Y. Ito, *J. Am. Chem. Soc.*, 1988, **110**, 5579; (*h*) H. Watanabe, M. Saito, M. Sutou, K. Kishimoto, J. Inose and Y. Nagai, *J. Chem. Soc., Chem. Commun.*, 1981, 617; (*i*) H. Watanabe, M. Kobayashi, M. Saito and Y. Nagai, *J. Organomet. Chem.*, 1981, **216**, 149; (*j*) A. Wada, I. Matsubara, H. Watanabe and Y. Nagai, *J. Organomet. Chem.*, 1980, **199**, 185; (*k*) K. Tamao, S. Okazaki and M. Kumada, *J. Organomet. Chem.*, 1978, **146**, 87; (*l*) K. Tamao, S. Okazaki and M. Kumada, *J. Organomet. Chem.*, 1978, **146**, 87; (*m*) H. Sakurai, Y. Kamiyama and Y. Nakadaira, *J. Am. Chem. Soc.*, 1975, **97**, 931; (*n*) K. Tamao, T. Hayashi and M. Kumada, *J. Organomet. Chem.*, 1976, **114**, C19; (*o*) H. Matsumoto, K. Shono, H. Okinoshima, K. Yamamoto and M. Kumada, *J. Am. Chem. Soc.*, 1972, **94**, 9263.

6 H. Yamashita, N. P. Reddy and M. Tanaka, *Chem. Lett.*, 1993, 315.

7 N. P. Reddy, H. Yamashita and M. Tanaka, *J. Am. Chem. Soc.*, 1992, **114**, 6596; H. Yamashita, N. P. Reddy and M. Tanaka, *Organometallics*, 1997, **16**, 5223.

8 Y. Ito, T. Matsuura and M. Murakami, *J. Am. Chem. Soc.*, 1988, **110**, 3692.

9 Y. Uchimaru, H.-J. Lautenschlager, A. J. Wynd, M. Tanaka and M. Goto, *Organometallics*, 1992, **11**, 263.

10 M. Ishikawa, H. Sakamoto and T. Tabuchi, *Organometallics*, 1991, **10**, 3173; M. Ishikawa, A. Naka, S. Okazaki and H. Sakamoto, *Organometallics*, 1993, **12**, 87; T. Kusukawa, Y. Kabe and W. Ando, *Chem. Lett.*, 1993, 985.

11 A preliminary communication has appeared, see N. A. Williams, Y. Uchimaru and M. Tanaka, *J. Chem. Soc., Chem. Commun.*, 1995, 1129.

12 J.-Y. Cho, M. K. Tse, D. Holmes, R. E. Maleczka, Jr. and M. R. Smith III, *Science*, 2002, **295**, 305; H. Chen, S. Schlecht, T. C. Semple and J. F. Hartwig, *Science*, 2000, **287**, 1995; Y. Guari, S. Sabo-Etienne and B. Chaudret, *Eur. J. Inorg. Chem.*, 1999, 1047; G. Dyker, *Angew. Chem., Int. Ed.*, 1999, **38**, 1698; C. Jia, D. Piao, J. Oyamada, W. Lu, T. Kitamura and Y. Fujiwara, *Science*, 2000, **287**, 1992; C. Jia, W. Lu, T. Kitamura and Y. Fujiwara, *Org. Lett.*, 1999, **1**, 2097; K. L. Tan, R. G. Bergman and J. A. Ellman, *J. Am. Chem. Soc.*, 2001, **123**, 2685; C. P. Lenges and M. Brookhart, *J. Am. Chem. Soc.*, 1999, **121**, 6616; P. W. R. Harris, C. E. F. Rickard and P. D. Woodgate, *J. Organomet. Chem.*, 1999, **589**, 168; Y.-G. Lim, J.-B. Kang and Y. H. Kim, *J. Chem. Soc., Perkin Trans.*, 1998, 699; R. Grigg and V. Savic, *Tetrahedron Lett.*, 1997, **38**, 5737; G. Halbritter, F. Knoch, A. Wolski and H. Kisch, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 1603.

13 S. Murai, F. Kakiuchi, S. Sekine, Y. Tanaka, A. Kamatani, M. Sonoda and N. Chatani, *Nature*, 1993, **366**, 529; S. Murai, F. Kakiuchi, S. Sekine, Y. Tanaka, A. Kamatani, M. Sonoda and N. Chatani, *Pure Appl. Chem.*, 1994, **66**, 1527; F. Kakiuchi, S. Sekine, Y. Tanaka, A. Kamatani, M. Sonoda, N. Chatani and S. Murai, *Bull. Chem. Soc. Jpn.*, 1995, **68**, 62; N. Chatani, T. Asaumi, S. Yorimitsu, T. Ikeda, F. Kakiuchi and S. Murai, *J. Am. Chem. Soc.*, 2001, **123**, 10935; F. Kakiuchi, T. Sato, K. Igi, N. Chatani and S. Murai, *Chem. Lett.*, 2001, 422; F. Kakiuchi, T. Sato, K. Igi, N. Chatani and S. Murai, *Chem. Lett.*, 2001, 386; F. Kakiuchi, M. Matsumoto, M. Sonoda, T. Fukuyama, N. Chatani and S. Murai, *Chem. Lett.*, 2000, 750; F. Kakiuchi, T. Sato, M. Yamauchi, N. Chatani and S. Murai, *Chem. Lett.*, 1999, 19; F. Kakiuchi, T. Sato, T. Tsujimoto, M. Yamauchi, N. Chatani and S. Murai, *Chem. Lett.*, 1998, 1053.

14 (*a*) T. Sakakura, Y. Tokunaga, T. Sodeyama and M. Tanaka, *Chem. Lett.*, 1987, 2375; (*b*) Y. Uchimaru, A. M. M. El-Sayed and M. Tanaka, *Organometallics*, 1993, **12**, 2065; (*c*) K. Ezbiansky, P. I. Djurovich, M. LaForest, D. J. Sinning, R. Zayes and D. H. Berry, *Organometallics*, 1998, **17**, 1455.

15 (*a*) C.-H. Jun, J.-B. Hong, Y.-H. Kim and K.-Y. Chung, *Angew. Chem., Int. Ed.*, 2000, **39**, 3440; (*b*) Y. Ie, N. Chatani, T. Ogo, D. R. Marshall, T. Fukuyama, F. Kakiuchi and S. Murai, *J. Org. Chem.*, 2000, **65**, 1475–1488.

16 C. Amatore, A. Jutand, F. Khalil, M. A. M'Barki and L. Mottier, *Organometallics*, 1993, **12**, 3168.

17 D. Seyferth, E. W. Goldman and J. Escudie, *J. Organomet. Chem.*, 1984, **271**, 337.

18 H. Yamashita, M. Goto and M. Tanaka, *Organometallics*, 1997, **16**, 4696.

19 M. Suginome, H. Oike, P. H. Schuff and Y. Ito, *Bull. Chem. Soc. Jpn.*, 1996, **69**, 289; M. Suginome, H. Oike, P. H. Schuff and Y. Ito,

Organometallics, 1996, **15**, 2170; M. Murakami, T. Yoshida and Y. Ito, *Organometallics*, 1994, **13**, 2900; H. Yamashita, M. Tanaka and M. Goto, *Organometallics*, 1992, **11**, 3232; Y. Pan, J. T. Mague and M. J. Fink, *Organometallics*, 1992, **11**, 3495; M. Tanaka, Y. Uchimaru and H.-J. Lautenschlager, *Organometallics*, 1991, **10**, 16; H. Yamashita, T.-a. Kobayashi, T. Hayashi and M. Tanaka, *Chem. Lett.*, 1990, 1447; T.-A. Kobayashi, T. Hayashi, H. Yamashita and M. Tanaka, *Chem. Lett.*, 1989, 467.

20 Ozawa and J. Kamite, *Organometallics*, 1998, **17**, 5630; H. Yamashita, M. Tanaka and M. Goto, *Organometallics*, 1992, **11**, 3232.

21 L. Johnson and J. A. Gladysz, *Inorg. Chem.*, 1981, **20**, 2508; J. A. Gladysz, *Acc. Chem. Res.*, 1984, **17**, 326.

22 (*a*) K. Hasabe, J. Kamite, T. Mori, H. Katayama and F. Ozawa, *Organometallics*, 2000, **19**, 2022 and the references cited therein; (*b*) Y. Tanaka, H. Yamashita, S. Shimada and M. Tanaka, *Organometallics*, 1997, **16**, 3246.

23 For homolytic cleavage of benzylic metal species, see D. H. Hill, M. A. Parvez and A. Sen, *J. Am. Chem. Soc.*, 1994, **116**, 2889.

24 (*a*) K. H. Pannell and H. Sharma, *Organometallics*, 1991, **10**, 954; (*b*) K. Tamao, Y. Tarao, Y. Nakagawa, K. Nagata and Y. Ito, *Organometallics*, 1993, **12**, 1113; (*c*) H. Yamashita, M. Tanaka and M. Goto, *Organometallics*, 1992, **11**, 3227; (*d*) Y. Tanaka, H. Yamashita and M. Tanaka, *Organometallics*, 1995, **14**, 530; (*e*) J. D. Rich, *J. Am. Chem. Soc.*, 1989, **111**, 5886.

25 (*a*) W. Ando, M. Ikeno and A. Sekiguchi, *J. Am. Chem. Soc.*, 1977, **99**, 6447; (*b*) W. Ando, M. Ikeno and A. Sekiguchi, *J. Am. Chem. Soc.*, 1978, **100**, 3613.

26 A. Schafer, M. Weidenbruch and S. Pohl, *J. Organomet. Chem.*, 1985, **282**, 305.

27 W. Ando, Y. Hamada, A. Sekiguchi and K. Ueno, *Tetrahedron Lett.*, 1982, **23**, 5323.

28 B. Gehrhus, P. B. Hitchcock and M. F. Lappert, *Organometallics*, 1997, **16**, 4861.

29 C. M. Anderson, R. J. Puddephatt, G. Ferguson and A. J. Lough, *J. Chem. Soc., Chem. Commun.*, 1989, 1297; C. M. Anderson, M. Crespo, M. C. Jennings, A. J. Lough, G. Ferguson and R. J. Puddephatt, *Organometallics*, 1991, **10**, 2672; M. Crespo, M. Martinez, J. Sales, X. F. Solans and M. Font-Bardia, *Organometallics*, 1992, **11**, 1288; M. Crespo, M. Martinez and J. Sales, *J. Chem. Soc., Chem. Commun.*, 1993, 822; M. Crespo, M. Martinez and J. Sales, *Organometallics*, 1993, **12**, 4297.

30 Sonoda, N. Kakiuchi, N. Chatani and S. Murai, *Bull. Chem. Soc. Jpn.*, 1997, **70**, 3117.

31 R. H. Crabtree, *Chem. Rev.*, 1985, **85**, 245.

32 S. Sakaki and M. Ieki, *J. Am. Chem. Soc.*, 1993, **115**, 2373.

33 Q. Jiang, D. C. Pestana, P. J. Carroll and D. H. Berry, *Organometallics*, 1994, **13**, 3679.

34 W. Chen, S. Shimada and M. Tanaka, *Science*, 2002, **295**, 308; S. Shimada, M. Tanaka and M. L. N. Rao, *Organometallics*, 1999, **18**, 291; S. Shimada, M. Tanaka and K. Honda, *J. Am. Chem. Soc.*, 1995, **117**, 8289; S. Shimada, M. Tanaka and M. Shiro, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 1856.

35 P. Caston, J. Laud, N. P. Johnson and R. Souls, *J. Am. Chem. Soc.*, 1985, **107**, 5011.

36 The major product appeared to be α-trimethylsilylstyrene. The details will be reported separately.

37 D. R. Coulson, *Inorg. Synth.*, 1972, **13**, 121.

38 J. G. Evans, P. L. Goggin, R. L. Goodfellow and J. G. Smith, *J. Chem. Soc. A*, 1968, 464.

39 F. G. Mann and D. Puride, *J. Chem. Soc.*, 1935, 1549.

40 A. O. King, E. Negishi, F. J. Villani Jr. and A. Silveira Jr., *J. Org. Chem.*, 1978, **43**, 358.

41 T. Hayashi, M. Konishi and M. Kumada, *Tetrahedron Lett.*, 1979, 1871.

42 M. Tanaka, T.-a. Kobayashi and T. Sakakura, *Nippon Kagaku Kaishi*, 1985, 537.

43 Y. Takahashi, T. Ito, S. Sakai and Y. Ishii, *J. Chem. Soc., Chem. Commun.*, 1970, 1065.

44 K. Moseley and P. M. Maitlis, *J. Chem. Soc., Dalton Trans.*, 1974, 169; A. Keasey, B. E. Mann, A. Yates and P. M. Maitlis, *J. Organomet. Chem.*, 1978, **152**, 117.

45 R. Ugo, F. Cariati and G. La Monica, *Inorg. Synth.*, 1968, **11**, 105.

46 K. A. Jensen, *Z. Anorg. Chem.*, 1936, **229**, 225.

47 C. D. Cook and G. S. Jauhal, *J. Am. Chem. Soc.*, 1968, **90**, 1467.

48 M. L. H. Green, H. Murakata and T. Saito, *J. Chem. Soc. A*, 1971, 468.

49 R. A. Schunn, *Inorg. Synth.*, 1974, **15**, 5.

50 M. Kumada, M. Yamaguchi, Y. Yamamoto, J. Nakajima and K. Shiina, *J. Org. Chem.*, 1956, **21**, 1264.

51 M. Kumada, K. Tamao, T. Takabo and M. Ishikawa, *J. Organomet. Chem.*, 1967, **9**, 43.