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Conversion of Disilanes to Functional Monosilanes. XIII.[1] The Palladium Catalyzed Reductive Coupling of Benzylidene Dichlorides and Benzylidyne Trichlorides Using Disilanes as Reducing Agents

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The reaction of benzylidene dichlorides or benzylidyne trichlorides with 1,2-dichloro-1,1,2,2-tetramethyldisilane or hexamethyldisilane proceeded smoothly in the presence of a catalytic amount of $Pd(PPh_3)_4$ to give (*E*)-stilbenes or (*E*)- and (*Z*)-α,β-dichlorostilbenes in high yields, respectively. Also, in the presence of the palladium(0) catalyst, α,α-dichlorobenzyltrimethylsilanes reacted with hexamethyldisilane yielding (*E*)-α,β-bis(trimethylsilyl)stilbenes in quantitative yield.

The reductive coupling of benzylidene dichlorides and benzylidyne trichlorides has been studied extensively and previous work employed active metal agents in low-oxidation state such as zero-valent titanium, iron, cobalt, and nickel compounds or slurries[2] as well as copper(I), titanium(II), vanadium(II), chromium(II), iron(II), cobalt(I), and cobalt(II) species.[3]

In connection with our continuing interest in the Si–Si cleavage of disilanes by organic halides,[1,4] we examined the interaction of benzylidene dichloride with methylchlorodisilanes, *e.g.*, 1,2-dichloro-1,1,2,2-tetramethyldisilane, in the presence of $Pd(PPh_3)_4$.[5] The reaction afforded the coupling products of the *gem*-dichlorides, stilbenes, in good yields. The result in this preliminary investigation demonstrates that such methylchlorodisilanes, formally tetravalent silicon species, can be effectively used for the coupling reaction as reducing agents. We have now extended this approach to use of other active *gem*-polychloro compounds such as benzylidyne trichlorides and α,α-dichlorobenzyltrimethylsilanes. The present paper is intended to summarize our work on this palladium(0) complex-catalyzed reductive coupling reaction.

Results and Discussion

Results for the reaction of benzylidene dichloride and benzylidyne trichloride with methylchlorodisilanes, $Me_{6-n}Si_2Cl_n$ (n=0, 2, 4), are given in Tables 1 and 2.

As shown in the tables, both hexamethyldisilane and 1,2-dichloro-1,1,2,2-tetramethyldisilane can bring about the coupling reaction. However, there is somewhat a puzzling difference in the effectiveness of these disilanes and choice of disilane depends upon the nature of the polychloromethylbenzene. The dichlorotetramethyldisilane is much more effective for converting benzylidene dichloride to (*E*)-stilbene than hexamethyldisilane, and optimum yield is obtained at initial disilane/substrate molar ratio of 2. On the other hand, the coupling of benzylidyne trichloride can be achieved smoothly with the permethyldisilane rather than with the dichlorotetramethyldisilane. The observed trend seems to reflect a compromise of the controlling factors in the sequence of the steps involved in the present catalytic reaction.

These reactions were run at 130 °C in a refluxing system. However, we note that the coupling can be also achieved at lower temperatures. For example, benzylidyne trichloride reacted with the permethyldisilane at 100 °C to give α,β-dichlorostilbene in 97% yield after 10 h.

In contrast with the case of these disilanes, the reaction of 1,1,2,2-tetrachloro-1,2-dimethyldisilane with benzylidene dichloride and benzylidyne trichloride afforded a complex mixture of products involving polysilanes due to the competitive disproportionation of the disilane itself.

The fact that the product ratio [PhCClXCClXPh: PhCX=CXPh (X=H, Cl)] is markedly affected by the ratio of the reactants (Tables 1 and 2) suggests that the formation of PhCX=CXPh occurs by a two-step process, Eqs. 1 and 2. This is further confirmed by the time-concentration profiles for the coupling of $PhCCl_2X$, indicating the initial formation of the dichlorodiphenylethane (**2**) followed by conversion of **2** to the

Table 1. Reaction of benzylidene dichloride with methylchlorodisilanes in the presence of $Pd(PPh_3)_4$[a]

Disilane	$PhCHCl_2$: Disilane	Time / h	Yield[b]/% PhCHClCHClPh	PhCH=CHPh	(*E*)/(*Z*)[c]
Me_6Si_2	1 : 2	6	51	4	—
$Me_4Si_2Cl_2$[d]	1 : 2	3	0	78[e]	100/0
$Me_4Si_2Cl_2$	1 : 1	3	65	18	100/0
$Me_4Si_2Cl_2$	2 : 1	3	44	5	—
$Me_2Si_2Cl_4$[f,g]	1 : 2	2	4	35	100/0

a) Carried out at 130 °C in mesitylene. The catalyst concentration was 1 mol % based on $PhCHCl_2$ charged. b) Based on $PhCHCl_2$ charged and determined by GLC. c) Determined by GLC. d) 1,2-Dichloro-1,1,2,2-tetramethyldisilane. e) $PhCH(SiMe_2Cl)_2$ was also formed in 22 % yield. f) 1,1,2,2-Tetrachloro-1,2-dimethyldisilane. g) In this run the disilane was completely consumed.

TABLE 2. REACTION OF BENZYLIDYNE TRICHLORIDE WITH METHYLCHLORODISILANES IN THE PRESENCE OF $Pd(PPh_3)_4$[a)]

Disilane	$PhCCl_3$: Disilane	Time / h	Yield[b)]/% $PhCCl_2CCl_2Ph$	$PhCCl=CClPh$	(*E*)/(*Z*)[c)]
Me_6Si_2	1 : 2	2	0	quant.	30/70
Me_6Si_2	1 : 1	6	4	81	30/70
Me_6Si_2	2 : 1	12	50	0	—
$Me_4Si_2Cl_2$[d)]	1 : 2	6	49	45	30/70
$Me_2Si_2Cl_4$[e),f)]	1 : 2	2	0	15	—

a—d) See the corresponding footnotes in Table 1. e) 1,1,2,2-Tetrachloro-1,2-dimethyldisilane. f) In this run the disilane was completely consumed.

TABLE 3. REACTION OF $ArCCl_2X$ WITH METHYLCHLORODISILANES IN THE PRESENCE OF $Pd(PPh_3)_4$[a)]

Substrate Ar	X	Disilane	Time / h	Yield[b)] of ArCX=CXAr/%	(*E*)/(*Z*)[c)]
$2\text{-}ClC_6H_4$	H	$Me_4Si_2Cl_2$	0.5	94	100/0
$4\text{-}ClC_6H_4$	H	$Me_4Si_2Cl_2$	0.5	quant.	100/0
$2,4\text{-}Cl_2C_6H_3$	H	$Me_4Si_2Cl_2$	3	95	100/0
$2\text{-}ClC_6H_4$	Cl	Me_6Si_2	2	96	40/60
$4\text{-}ClC_6H_4$	Cl	Me_6Si_2	2	79	30/70
$2,4\text{-}Cl_2C_6H_3$	Cl	Me_6Si_2	2	86	48/52
C_6H_5	C_6H_5	Me_6Si_2	10	90[d)]	—

a) $[ArCCl_2X]/[disilane]/[Pd(0)] = 1/2/0.01$; at 130 °C in mesitylene. b) Based on $ArCCl_2X$ charged and determined by GLC unless otherwise stated. c) Determined by GLC. d) Isolated yield.

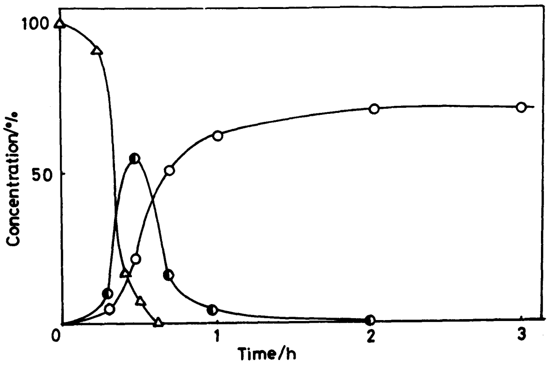


Fig. 1. Time-concentration profiles for the reaction of $PhCHCl_2$ with $ClMe_2SiSiMe_2Cl$ in the presence of $Pd(PPh_3)_4$ at 130 °C.
△: $PhCHCl_2$, ◐: PhCHClCHClPh, ○: (*E*)-PhCH=CHPh.

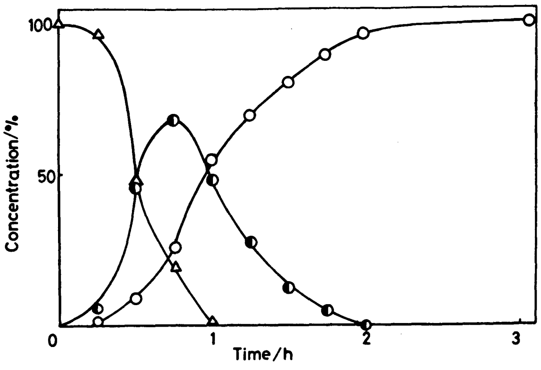


Fig. 2. Time-concentration profiles for the reaction of $PhCCl_3$ with $Me_3SiSiMe_3$ in the presence of $Pd(PPh_3)_4$ at 130 °C.
△: $PhCCl_3$, ◐: $PhCCl_2CCl_2Ph$, ○: (*E*)- and (*Z*)-PhCCl=CClPh.

$$\underset{\mathbf{1}}{2PhCCl_2X + YMe_2SiSiMe_2Y} \xrightarrow{[Pd]} \underset{\mathbf{2}}{PhCClXCClXPh} + 2Me_2SiClY \qquad (1)$$

$$\mathbf{1} + \mathbf{2} \xrightarrow{[Pd]} PhCX{=}CXPh + 2Me_2SiClY \qquad (2)$$

$$(X{=}H, Cl;\ Y{=}Cl, Me)$$

corresponding stilbenes (Figs. 1 and 2).

Under optimum conditions, the coupling of substituted benzylidene dichlorides and benzylidyne trichlorides was achieved in high yields by the reaction with the dichloroteramethyldisilane or with the permethyldisilane. As shown in Table 3, (*E*)-stilbenes are only coupled products obtained by the reaction with the dichlorides, whereas a mixture of (*E*)- and (*Z*)-isomers is obtained from the trichlorides.[6)] The geometrical isomerism for previously unreported stilbenes, *e.g.*, *α*,*β*,-2,2′-tetrachlorostilbene and *α*,*β*,2,2′,4,4′-hexachlorostilbene, was assigned based on differences in the physical properties of these isomers: (i) in ^1H NMR spectra, the phenyl proton signals in the (*E*)-isomers appear at lower fields compared to those on the (*Z*)-isomers. ii) In IR spectra, the C=C stretching frequences around 1600 cm^{-1} of the (*E*)-isomers are very weak and broad, due to their symmetrical structures, while those of the (*Z*)-isomers are relatively strong and sharp. (iii) The conjugation bands of the UV spectra for the (*E*)-isomers occur at shorter wave length than those of the (*Z*)-isomers. (iv) The melting points of the (*E*)-isomers are

Table 4. Effect of some other common group VIII metal complexes on the reaction of $PhCHCl_2$ with $ClMe_2SiSiMe_2Cl$[a]

Complex	Time h	Yield[b]/% PhCHClCHClPh	Yield[b]/% PhCH=CHPh
$PdCl_2L_2$	2	0	59[c]
PtL_4	2	28	19
$PtCl_2L_2$	2	25	12
$RhClL_3$	2	16	15
$NiCl_2L_2$	5	1	1

a) $[PhCHCl_2]/[disilane]/[Pd(0)] = 1/2/0.01$; at 130 °C in mesitylene. b) Determined by GLC. c) $PhCH(SiMe_2Cl)_2$ was also produced in 40% yield.

higher than those of the (*Z*)-isomers. Similar observations have been made in such pairs of the geometrical isomers of α,β-dichlorostilbene and α,β,4,4′-tetrachlorostilbene.[2,3,7)]

The data accumulated in Tables 1-3 clearly reveal that the present system provides a workable procedure for the selective coupling of these polychloromethylbenzenes to the stilbenes. This has advantages: (i) the methylchlorodisilanes employed are readily available in large quantities.[8)] (ii) Removal of the counter products, Me_2SiCl_2 (bp 70 °C) and Me_3SiCl (bp 57 °C), can be easily achieved by evaporation. The formation of large amounts of nonvolatile and solid inorganic salts as oxidation products is the drawback of the conventional methods using stoichiometric amount of low-valent metals as reducing agents.[2,3)] Further, the fact that only catalytic amounts of the palladium(0) complex are required in the present reaction also increases the potential synthetic utility of our method.

Catalytic efficiency was tested briefly for other common group VIII metal–phosphine complexes using the reaction of benzylidene dichloride with 1,2-dichloro-1,1,2,2-tetramethyldisilane as a standard. As shown in Table 4, $PdCl_2(PPh_3)_2$ showed the catalytic activity for the coupling. However, the reaction was less selective compared to that in the presence of the palladium(0) complex and gave a considerable amount of $PhCH(SiMe_2Cl)_2$ as well as (*E*)-stilbene. The complexes $Pt(PPh_3)_4$, $PtCl_2(PPh_3)_2$, and $RhCl(PPh_3)_3$ also induced the reaction, but their catalytic ability was much lower. $NiCl_2(PPh_3)_2$ failed to effect the expected reaction to any appreciable extent.

$ArCHCl_2 + ClMe_2SiSiMe_2Cl$

a $\downarrow$ [Pd]

$ArCHClSiMe_2Cl$ (**3**) + Me_2SiCl_2

b $\downarrow$ $ArCHCl_2$/[Pd]

$ArCHClCHClAr + Me_2SiCl_2$

c $\downarrow$ $ClMe_2SiSiMe_2Cl$/[Pd]

$ArCHClCH(SiMe_2Cl)Ar$ (**4**) + Me_2SiCl_2

d $\downarrow$ Δ

(*E*)-ArCH=CHAr + Me_2SiCl_2

Scheme 1.

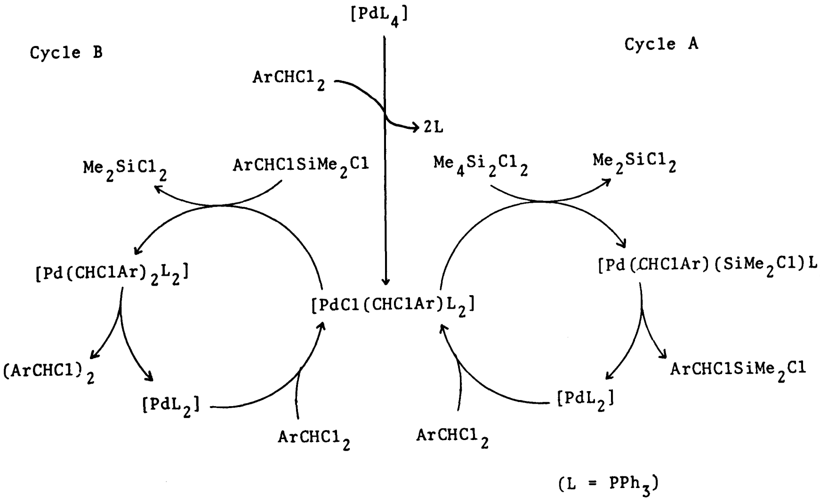
Mechanistically, the coupling reaction perhaps consists of several steps as shown in Scheme 1. This involves the palladium-catalyzed dechlorinative silylation of a benzylidene dichloride $ArCHCl_2$ with 1,2-dichloro-1,1,2,2-tetramethyldisilane to give the α-chlorobenzyldimethylchlorosilane (**3**) (path a), followed by the metathesis between **3** and $ArCHCl_2$ yielding a coupling product ArCHClCHClAr (path b). Support for the transient intermediate **3** was found in the reaction of $PhCHCl_2$ with excess of the dichlorotetramethyldisilane. The reaction afforded $PhCH(SiMe_2Cl)_2$, as a by-product, which should arise from **3** (Ar=Ph) by the reaction with the disilane (Table 1). Path b is the reminiscent of the palladium-catalyzed metathesis of allyltrimethylsilane with allyl bromide that gives 1,5-hexadiene together with trimethylbromosilane.[4c)] The reaction of ArCHClCHClAr with the dichlorotetramethyldisilane to give the 1-chloro-2-(dimethylchlorosilyl)-1,2-diarylethane **4** (path c), which releases spontaneously dimethyldichlorosilane *via* β-elimination[9)] resulting in the formation of (*E*)-ArCH=CHAr (path d), should be also involved. A similar mechanism may be given for the coupling of benzylidyne trichlorides.

Alternatively, a scheme might be proposed whereby the dichlorotetramethyldisilane as well as the permethyldisilane acts as reducing agents to regenerate the palladium(0) from the palladium(II) formed upon the coupling (Eqs. 3 and 4). This scheme, however, seems

$$ArCCl_2X + Pd(PPh_3)_4 \longrightarrow$$
$$ArCClXCClXAr + PdCl_2(PPh_3)_2 + 2PPh_3 \qquad (3)$$
$$PdCl_2(PPh_3)_2 + YMe_2SiSiMe_2Y \longrightarrow$$
$$Pd(PPh_3)_2 + 2MeSiClY \qquad (4)$$

to be unlikely, since vigorous conditions (*e.g.*, 160—200 °C) are generally required to bring about reduction of this type.[10)] Moreover, the recent finding by Stille and Lau,[11)] and Eaborn *et al.*[12)] that trimethylchlorosilane reacts with $Pd(PPh_3)_4$ to give hexamethyldisilane and $PdCl_2(PPh_3)_2$ strongly indicates that reaction 4 is much less favorable.

In consideration of the catalytic cycles for paths a and b in Scheme 1, it is likely that the cycles are initiated by the reaction of $ArCHCl_2$ with $Pd(PPh_3)_4$, since we found that such a reaction occurs rapidly at a room temperature, although an attempt to isolate the expected oxidative adduct, *e.g.*, $PdCl(CHClPh)(PPh_3)_2$, failed due to the instability of this complex. On the other hand, 1,2-dichloro-1,1,2,2-tetramethyldisilane is much less reactive toward the palladium(0) complex under comparable conditions.[1)] Thus, plausible catalytic cycles are shown in Scheme 2. Cycle A was inferred from the mechanism proposed for the palladium(0)-catalyzed metathesis between benzyl chlorides and the dichlorotetramethyldisilane to give benzyldimethylchlorosilanes.[1)] Cycle B involves the transmetallation of the palladium(II) complex, $PdCl(CHClAr)(PPh_3)_2$, with the α-chlorobenzyldimethylchlorosilane (**3**). Analogous transmetallation process has been proposed for the cleavage of silicon-alkyl and silicon-aryl bonds by palladium(II) compounds which takes places at 60—120 °C[13)] and also for the palladium-catalyzed coupling



Scheme 2.

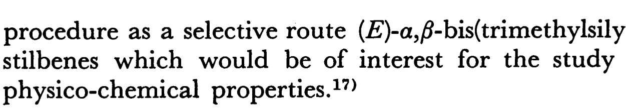
Table 5. Reaction of $ArCCl_2SiMe_3$ with $Me_3SiSiMe_3$ in the presence of $Pd(PPh_3)_4$[a]

Substrate Ar	Time h	Yield[b]/% ArCCl=CArSiMe3	Ar(Me3Si)C=C(SiMe3)Ar[c]
C_6H_5	2	42[d]	44[d]
C_6H_5	18	—	quant.
4-ClC_6H_4	24	—	quant.

a) [Substrate]/[disilane]/[Pd(0)] = 1/2/0.01; at 130 °C in mesitylene. b) Isolated yields unless otherwise stated. c) Only the (*E*)-isomers were formed. d) Determined by GLC.

of tetraorganotin compounds with aryl and benzyl halides.[14] Further, it has been found by Pitt *et al.*[15] that silicon-benzyl bond is cleaved by palladium under certain conditions.

In view of this proposed mechanism, it is expected that α,α-dichlorobenzyltrimethylsilanes could be readily enter into the coupling and this was found to be the case (Table 5). For example, $PhCCl_2SiMe_3$ reacted very smoothly with hexamethyldisilane in the presence of the palladium(0) catalyst to give (*E*)-α,β-bis(trimethylsilyl)stilbene together with α-chloro-β-(trimethylsilyl)-stilbene (presumably, (*E*)-isomer). Further, the bis(trimethylsilyl)stilbene could be obtained in quatitative yield by continuing the reaction until virtual disappearance of the monosilylstilbene. The formation of the bis(silyl)stilbene can be rationalized in terms of the palladium-catalyzed metathesis between the monosilylstilbene and the permethyldisilane (Eq. 5).[16] The results in the table again emphasize the utility of our



$$PhCCl{=}C(SiMe_3)Ph + Me_3SiSiMe_3 \xrightarrow{[Pd]} \begin{matrix}Ph\\Me_3Si\end{matrix}\!\!>C{=}C<\!\!\begin{matrix}SiMe_3\\Ph\end{matrix} + Me_3SiCl \qquad (5)$$

procedure as a selective route (*E*)-α,β-bis(trimethylsilyl)-stilbenes which would be of interest for the study of physico-chemical properties.[17]

Experimental

Melting points were uncorrected. IR spectra were taken on a JASCO A102 spectrophotometer. ^1H NMR spectra were obtained with a Varian EM-360 spectrometer using tetramethylsilane as an internal standard. UV spectra were taken on a Hitachi 200-10 spectrophotomter. Mass spectra were obtained with a JEOL JMS-07 spectrometer. GLC analyses were performed on an Ohkura GC-103 instrument with thermal conductivity detector using 0.4×100-200 cm Teflon and Pyrex glass columns packed with 10%SE-30, 10% DCQF-1, 10%KF-96, and 10%Carbowax 20M on Celite 545 (80—100 mesh). Corrections were made thermal conductivity of the various components.

Materials. Benzylidene dichloride was commercially available and used as received. Substituted benzylidene dichlorides were prepared by the benzoyl peroxide-catalyzed chlorination of the corresponding benzyl chlorides with sulfuryl chloride.[18] Benzylidyne trichlorides were commercially available and used as received. α,α-Dichlorobenzyltrimethylsilanes were prepared according to literature directions.[19] Hexamethyldisilane was commercially available and purified by distillation prior to use. 1,2-Dichloro-1,1,2,2-tetramethyldisilane[8f] and 1,1,2,2-tetrachloro-1,2-dimethyldisilane[8e] were prepared according to published procedures.

The complexes $Pd(PPh_3)_4$,[20] $PdCl_2(PPh_3)_2$,[21] $Pt(PPh_3)_4$,[22] $PtCl_2(PPh_3)_2$,[23] $RhCl(PPh_3)_3$,[24] and $NiCl_2(PPh_3)_2$[25] were prepared according to literature procedures.

Other organic reagents and solvents were commercially available and purified according to standard procedures.

Procedure for the Coupling of Benzylidene Dichlorides and Benzylidyne Trichlorides. All the reactions were carried out under nitrogen in a refluxing system and typical examples are described below.

(a) Reaction of 2-Chlorobenzylidene Dichloride with 1,2-Dichloro-1,1,2,2-tetramethyldisilane: A mixture of 1.98 g (10.2 mmol) of the dichloride, 3.75 g (20.0 mmol) of the disilane, 0.12 g (0.1 mmol) of $Pd(PPh_3)_4$, and 3 ml of mesitylene was heated at 130 °C for 0.5 h with stirring. GLC analysis showed that the dichloride had been completely consumed and that 2,2′-dichlorostilbene (4.7 mmol, 94% yield) had been produced. The reaction mixture was then diluted with 30 ml of pentanes to precipitate the catalyst which was removed by filtration. The filtrate was concentrated to yield 1.03 g (85% yield) of

stilbene as colorless crystals.

(b) Reaction of Benzylidyne Trichloride with Hexamethyldisilane: A mixture of 1.95 g (10.0 mmol) of the trichloride, 2.90 g (19.8 mmol) of the disilane, 0.12 g (0.1 mmol) of the palladium(0) complex, and 5 ml of mesitylene was heated at 130 °C for 2 h with stirring. GLC analysis showed that the reaction had given 5.0 mmol (100% yield) of *α,β*-dichlorostilbene as a 30 : 70 mixture of the (*E*)- and (*Z*)-isomers. Work-up as described above afforded 1.20 g (97% yield) of the product as colorless crystals.

The physical data of the products obtained are given below. PhCHClCHClPh: mp 176—190 °C (lit,[3a] *meso*, mp 191—193 °C; *dl*, 93—94 °C); NMR ($\mathrm{CCl_4}$) $\delta=5.05$ (s, 2H) and 7.31 (s, 10H). (*E*)-PhCH=CHPh: mp 123—124 °C (lit,[26] 124 °C); NMR ($\mathrm{CCl_4}$) $\delta=7.10$ (s, 2H) and 7.50 (m, 10H). $\mathrm{PhCH(SiMe_2Cl)_2}$: IR (neat) 1255 (s) cm^{-1}; NMR ($\mathrm{CCl_4}$) $\delta=0.46$ (s, 12H); 1.88 (s, 1H) and 7.12 (s, 5H); MS (30 eV), *m/e*, 276 (M$^+$). This compound gave a poor analytical result due to high susceptibility to hydrolysis. (*E*)-2-$\mathrm{ClC_6H_4CH{=}CHC_6H_4}$-2-Cl: mp 97—98 °C (lit,[26] 98—99 °C); NMR ($\mathrm{CCl_4}$) $\delta=6.98$ (s, 2H) and 7.53 (s, 8H). 4-$\mathrm{ClC_6H_4CH{=}CHC_6H_4}$-4-Cl: mp 174—176 °C (lit,[26] 176—176.5 °C); NMR ($\mathrm{CCl_4}$) $\delta=6.92$ (s, 2H) and 7.30 (s, 8H). (*E*)-2,4-$\mathrm{Cl_2C_6H_3CH{=}CHC_6H_3}$-2,4-$\mathrm{Cl_2}$: mp 159—161 °C (lit,[26] 161—161.5 °C); NMR ($\mathrm{CCl_4}$) $\delta=7.00$ (s, 2H) and 7.31 (m, 6H). $\mathrm{PhCCl_2CCl_2Ph}$: mp 166—167 °C (lit,[3b] 167 °C). (*E*)-PhCCl=CClPh: mp 139.5—140.5 °C (lit,[3c] 140 °C); IR (KBr disk) 1605 (vw) cm^{-1}; NMR ($\mathrm{CCl_4}$) $\delta=7.53$ (m). (*Z*)-PhCCl=CCl-Ph: mp 55—56 °C (lit,[3c] 62—64 °C); IR (KBr disk) 1615 (m) cm^{-1}; NMR ($\mathrm{CCl_4}$) $\delta=7.17$ (s). (*E*)-2-$\mathrm{ClC_6H_4CCl{=}CClC_6H_4}$-2-Cl: mp 170—170.5 °C; UV$_{\mathrm{max}}$ (heptane) 251 nm (ε 5100); IR (KBr disk) 1598 (vw) cm^{-1}; NMR ($\mathrm{CCl_4}$) $\delta=7.41$ (m); MS (30 eV), *m/e*, 316 (M$^+$). Found: C, 52.96; H, 2.55%. Calcd for $\mathrm{C_{14}H_8Cl_4}$: C, 52.87; H, 2.54%. (*Z*)-2-$\mathrm{ClC_6H_4CCl{=}CClC_6H_4}$-2-Cl: mp 133—133.5 °C; UV$_{\mathrm{max}}$ (heptane) 265 nm (ε 5140); IR (KBr disk) 1595 (m) cm^{-1}; NMR ($\mathrm{CCl_4}$) $\delta=7.16$ (m); MS (30 eV), *m/e*, 316 (M$^+$). Found: C, 52.95; H, 2.65%. Calcd for $\mathrm{C_{14}H_8Cl_4}$: C, 52.87; H, 2.54%. (*E*)-4-$\mathrm{ClC_6H_4CCl{=}CClC_6H_4}$-4-Cl: mp 163—165 °C (lit,[7a] 164—165 °C); IR (KBr disk) 1590 (vw) cm^{-1}; NMR ($\mathrm{CCl_4}$) $\delta=7.55$ (m). (*Z*)-4-$\mathrm{ClC_6H_4CCl{=}CClC_6H_4}$-4-Cl: mp 90—91 °C (lit,[7a] 85—86 °C); IR (KBr disk) 1590 (m) cm^{-1}; NMR ($\mathrm{CCl_4}$) $\delta=7.19$ (s). (*E*)-2,4-$\mathrm{Cl_2C_6H_3CCl{=}CClC_6H_3}$-2,4-$\mathrm{Cl_2}$: mp 171—172 °C; UV$_{\mathrm{max}}$ (heptane) 236 nm (ε 19300); IR (KBr disk) 1585 (vw) cm^{-1}; NMR ($\mathrm{CCl_4}$) $\delta=7.39$ (m, 4H) and 7.55 (m, 2H), MS (30 eV), *m/e*, 384 (M$^+$). Found: C, 43.75; H, 1.71%. Calcd for $\mathrm{C_{14}H_6Cl_6}$: C, 43.46; H, 1.71%. (*Z*)-2,4-$\mathrm{Cl_2C_6H_3CCl{=}CClC_6H_3}$-2,4-$\mathrm{Cl_2}$: mp 124—125 °C; UV$_{\mathrm{max}}$ (heptane) 266 nm (ε 6400); IR (KBr disk) 1580 (m) cm^{-1}; NMR ($\mathrm{CCl_4}$) $\delta=7.21$ (m, 4H) and 7.36 (m, 2H); MS (30 eV) *m/e* 384 (M$^+$). Found: C, 42.94; H, 1.62%. Calcd for $\mathrm{C_{14}H_6Cl_6}$: C, 43.46; H, 1.56%.

Time-concentration Profiles for the Coupling of Benzylidene Dichloride and Benzylidyne Trichloride. Typically, a mixture of 1.61 g (10.0 mmol) of benzylidene dichloride, 3.75 g (20.0 mmol) of 1,2-dichloro-1,1,2,2-tetramethyldisilane, 0.12 g (0.1 mmol) of the palladium(0) complex, 3 ml of mesitylene, and 0.488 g (2.00 mmol) of triphenylmethane as an internal standard was heated at 130 °C under nitrogen with stirring. The course of the reaction was monitored by GLC.

Effect of Some Common Group VIII Metal Complex on the Reaction of Benzylidene Dichloride with 1,2-Dichloro-1,1,2,2-tetramethyldisilane. A mixture of 1.61 g (10.0 mmol) of the dichloride, 3.75 g (20.0 mmol) of the disilane, 0.1 mmol of a complex, and 3 ml of mesitylene was heated at 130 °C under nitrogen with stirring. After 2—5 h, the resulting mixture was subjected to GLC analysis.

Reaction of α,α-Dichlorobenzyltrimethylsilane with Hexamethyldisilane. Typical examples are described below. *i)* A mixture of 2.34 g (10.0 mmol) of $\mathrm{PhCCl_2SiMe_3}$, 2.93 g (20.0 mmol) of hexamethyldisilane, 0.12 g (0.1 mmol) of the palladium(0) complex, and 5 ml of mesitylene was heated at 130 °C under nitrogen for 2 h. GLC analysis showed that the reaction had given *α,β*-bis(trimethylsilyl)stilbene in 44% yield together with a 42% yield of *α*-chloro-*β*-(trimethylsilyl)stilbene.

ii) A mixture of 1.34 g (5.0 mmol) of *α,α*,4-trichlorobenzyltrimethylsilane, 1.50 g (10.3 mmol) of the permethyldisilane, 0.058 g (0.05 mmol) of the palladium(0) complex, and 3 ml of mesitylene was heated at 130 °C for 24 h under nitrogen. The resulting mixture was diluted with 50 ml of pentanes and the precipitated catalyst was removed by filtration. The filtrate was concentrated to dryness under reduced pressure to yield 1.05 g (100% yield) of (*E*)-*α,β*-bis(trimethylsilyl)-4,4′-dichlorostilbene.

The physical data of the products obtained are given below. (*E*)-$\mathrm{Ph(Me_3Si)C{=}C(SiMe_3)Ph}$: mp 112 °C (lit,[17] 116 °C); IR (KBr disk) 1600 (vw) and 1248 (s) cm^{-1}; NMR ($\mathrm{CCl_4}$) $\delta=7.22$ (m, 10H) and -0.38 (s, 18H). $\mathrm{PhCCl{=}C(SiMe_3)Ph}$: mp 52—53 °C; IR (KBr disk) 1600 (vw) and 1250 (s) cm^{-1}; NMR ($\mathrm{CCl_4}$) $\delta=7.02$ (m, 10H) and 0.18 (s, 9H); MS (30 eV), *m/e* 286 (M$^+$). Found: C, 71.67; H, 6.25%. Calcd for $\mathrm{C_{17}H_{19}ClSi}$: C, 71.18; H, 6.68%. (*E*)-4-$\mathrm{ClC_6H_4(Me_3Si)C{=}C(SiMe_3)C_6H_4}$-4-Cl: mp 178—181 °C; IR (KBr disk) 1600 (vw) and 1252 (s) cm^{-1}; NMR ($\mathrm{CCl_4}$) $\delta=6.98$ (d, 2H, $J=7$ Hz), 7.12 (d, 2H, $J=7$ Hz) and -0.08 (s, 18H); MS (30 eV), *m/e*, 392 (M$^+$). Found: C, 60.89; H, 6.15%. Calcd for $\mathrm{C_{20}H_{26}Cl_2Si_2}$: C, 61.05; H, 6.61%.

Reaction of Benzylidene Dichloride with $\mathit{Pd(PPh_3)_4}$. To a solution of 0.23 g (0.20 mmol) of the palladium(0) complex in 5 ml of benzene was added 0.064 g (0.40 mmol) of the dichloride under nitrogen. The reaction mixture was stirred at a room temperature for 5 h and then diluted with 20 ml of pentanes. The yellow microcrystals that separated were filtered, washed with ether and dried *in vacuo*. IR spectrum of this product was in complete agreement with that of the complex $\mathrm{PdCl_2(PPh_3)_2}$; 0.083 g (64% yield). Further, GLC analysis of the filtrate showed the formation of (*E*)-stilbene (0.07 mmol) and 1,2-dichloro-1,2-diphenylethane (0.02mmol).

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