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FURTHER STUDIES ON REACTIONS OF ORGANIC HALIDES WITH DISILANES CATALYSED BY TRANSITION METAL COMPLEXES *

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Summary

The interaction of a range of organic halides with $(Cl_3Si)_2$ or $(Me_3Si)_2$ in the presence of a variety of transition metal catalysts (very predominantly Pd^0 or Pd^{II} complexes) have been examined. $PhSiMe_3$ was formed from PhCl [m.y., 15%] (m.y. = maximum yield), PhBr (m.y., 92%, with $[PdL_2Br_2]$ as catalyst ($L = PPh_3$)), and (contrary to earlier reports) PhI (m.y. 51%, with $[PdL_2I_2]$). $MeSiCl_3$ was formed from MeBr (m.y., 78% with $[PdL_4]$) and MeI (m.y., 91% with $[PdL_4]$), and $EtSiCl_3$ from EtBr (m.y., 49%, with $[PdL''_2Br_2]$; $L'' = P(C_6H_4OMe\text{-}p)_3$) and EtI (m.y. 45%, with $[PdL_4]$). Me_4Si was satisfactorily formed from MeBr (m.y. 42%, with $[PdL_4]$). Evidence was obtained for the formation of Me_3SiCF_3 from CF_3I. Very poor yields of $XC_6H_4CH_2SiMe_3$ were obtained from $XC_6H_4CH_2Br$ (X = H or *p*-Me) (with X = H some $PhSiMe_3$ was formed), but *p*-$O_2NC_6H_4CH_2SiMe_3$ was formed in 48% yield from *p*-$O_2NC_6H_4CH_2Cl$ with $[PdL''_4]$ as catalyst. $PhCOSiMe_3$ was formed from PhCOCl (m.y. 52% with $[PdL_2I_2]$). The nickel complex $[NiL_4]$ was moderately effective as a catalyst for reactions between $(Cl_3Si)_2$ and MeBr, EtBr, or $PhCH_2Br$. The new complex $[PdL_2(SiCl_3)_2]$ was prepared by treatment of $[PdL_4]$ with $(Cl_3Si)_2$ or Cl_3SiH, and shown to catalyse the reaction between MeBr and $(Cl_3Si)_2$.

Introduction

The most important method of forming Si—C bonds involves the reaction between organosilicon halides and organo-magnesium or -lithium reagents, on which very extensive and important developmental studies were made by Gilman and his coworkers [1]. Numerous other methods are now available, how-

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* Dedicated to Henry Gilman, in recognition of his outstanding contributions to organic and organometallic chemistry. (*Note by C.E.*: My wife and I have been privileged to enjoy the friendship of Henry and Ruth Gilman since we first met them in 1957, and I take special pride in having been chosen to deliver the Henry Gilman Lecture at Ames in 1978.)

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ever, and can be of value in special circumstances, and one such is based on the reaction between organic halides and disilanes in the presence of suitable transition metal complexes. This method was first described in a patent by Atwell and Bokermann [2], and was developed by Matsumoto and Nagai and their colleagues [3—6]. The latter group of workers showed that aryl bromides (and some chlorides) react with hexamethyldisilane in toluene or similar solvents in the presence of $[Pd(PPh_3)_4]$ to give aryltrimethylsilanes [3,4], thus providing an important new route to such compounds, especially those in which the aryl group bears a reactive substituent (e.g. NO_2) and so could not be attached to silicon by methods involving Grignard or organolithium reagents. They later extended the reaction to the use of allyl halides [5] and the methylchlorodisilanes $Me_nCl_{6-n}Si_2$ [6] as reagents and of $[PdCl_2(PPh_3)_2]$ as catalyst [6]. The method was further extended to the use of benzyl halides and $(Me_3Si)_2$ to give $XC_6H_4CH_2SiMe_3$ compounds [7], and of ArCOCl with $(Me_3Si)_2$ to give $ArCOSiMe_3$ [8]. Digermanes and distannanes have been shown to enter into similar reactions [7,9]. We now describe below a further study of the reactions between a range of organic halides and the disilanes $(Me_3Si)_2$ and $(Cl_3Si)_2$ in toluene in the presence of a variety of catalysts, especially those containing phosphine ligands denoted as follows:

L, PPh_3 L″, $P(C_6H_4OMe\text{-}p)_3$

L′, PMe_2Ph L‴, $P(C_6H_4CH_2SiMe_3\text{-}p)_3$

Results and discussion

The results obtained from the interaction of aryl, alkyl, allyl, benzyl and benzoyl halides with $(Me_3Si)_2$ or $(Cl_3Si)_2$ are shown in Tables 1—7; in all cases the yields of products were those indicated by GLC. Various aspects are considered below.

(a) Reactions of aryl halides. In reactions with $(Me_3Si)_2$, PhCl gave a much lower yield of $PhSiMe_3$ than PhBr, in agreement with the findings of Matsumoto et al. However, in contrast to the latter workers, who obtained no $PhSiMe_3$ from PhI (in a reaction in toluene in the presence of $[PdL_4]$ at 120°C) [3], we obtained this product in 29% yield from a reaction at 144°C catalysed by $[PdL_4]$ and in 51% yield from one catalysed by $[PdL_2I_2]$. In the reaction involving PhBr, $[PdL_2Br_2]$ was as good a catalyst as $[PdL_4]$, but $[PdL_2Cl_2]$ was somewhat less and $[PdL_2I_2]$ much less effective. The complex $[PdL_2(Ph)Br]$, which is readily formed from $[PdL_4]$ and PhBr, is also a quite effective catalyst.

In reactions of aryl bromides catalysed by $[PdL_4]$, the electron releasing substituents *p*-Me and *p*-OMe lowered the yield while the electron withdrawing *p*-NO_2 raised it, in keeping with earlier observations [3,4,7]. However, quite good yields of *p*-$MeOC_6H_4SiMe_3$ were obtained from *p*-$MeOC_6H_4Br$ when $[PdL_2Cl_2]$ or $[PdL'_2Cl_2]$ was used as catalyst, and $[PdL_2(C_6H_4OMe\text{-}p)Br]$ gave better results than $[PdL_4]$.

(b) Reactions of alkyl halides. (i) In the reactions of alkyl halides with $(Cl_3Si)_2$, good yields of $MeSiCl_3$ were obtained from MeBr and MeI in the presence of $[PdL_4]$. While $[PdL_2I_2]$ was very effective with MeI, all the $[PdL_2X_2]$ and $[PdL'_2X_2]$ complexes (X = Cl, Br, or I) were markedly less effective than

TABLE 1

REACTION OF ARYL HALIDES RX (10 mmol) WITH $Me_3SiSiMe_3$ (7 mmol) IN TOLUENE (5 cm^3) AT 144°C FOR 20 h IN PRESENCE OF SPECIFIED CATALYST (4×10^{-5} mol)

RX	Catalyst	Yield of $RSiMe_3$ (%) [a]
PhCl	PdL_4	15
	PdL_2Cl_2	10
	PdL_2Br_2	11
PhBr	PdL_4	89
	PdL_2Cl_2	74
	PdL_2Br_2	92
	PdL_2I_2	8
	$PdL_2(Ph)Br$	51
	NiL_2Br_2	1
PhI	PdL_4	29
	PdL_2I_2	51
p-MeO_6H_4Br	PdL_4	39
	PdL_2Cl_2	77
	PdL_2Br_2	48
	PdL_2I_2	10
	$PdL_2(R)Br$	56
	$PdL_2'Cl_2$	61
	$PdL_2'Br_2$	2
	$PdL_2'I_2$	6
p-MeC_6H_4Br	PdL_4	57
p-$O_2NC_6H_4Br$	PdL_4	98

[a] Yield based on amount of $Me_3SiSiMe_3$ taken.

PdL_4 with MeBr, but $[PdL''_2Br_2]$ gave the highest yield of all (92%). The complex $[PdL_2(SiCl_3)_2]$, which is formed from $[PdL_4]$ and $(Cl_3Si)_2$ (see below), is also active as a catalyst, as is $[NiL_4]$.

The most effective catalyst for the reaction of EtBr with $(Cl_3Si)_2$ was again $[PdL''_2Br_2]$, with which a 49% yield of $EtSiCl_3$ was obtained; several other catalysts, including the bridged species $[Pd_2L_2Br_4]$, gave yields in the 25—37% range. Yields of $EtSiCl_3$ in the neighbourhood of 40% were obtained from EtI by use of $[PdL_4]$ or $[PdL_2I_2]$. Only very small amounts of n-$PrSiCl_3$ were formed from n-PrBr with $[PdL_4]$ or $[PdL_2Br_2]$ as catalyst.

(ii) The reactions of $(Me_3Si)_2$ with alkyl halides gave much poorer yields, and only with MeBr were appreciable quantities of the expected product obtained; in particular, no Me_4Si was obtained from MeI. It is possible to rationalize some features of the results of the present and earlier studies in terms of the suggestion that the reactions fail if the ease of oxidative addition of the organic halide to the metal centre is very different from that of the disilane (cf. ref. 9), and it is possible that, while $(Cl_3Si)_2$ can compete effectively with MeI for the metal centre, $(Me_3Si)_2$, which is much less active in these oxidative additions, cannot.

(iii) A reaction between CF_3I and $(Me_3Si)_2$ in the presence of $[PdL_4]$ was carried out under the usual conditions (see Table 2). Examination of the product solution by GLC showed two peaks not attributable to the reactants (the very volatile CF_3CF_3 would not have been detected), and linked GLC-MS showed that these corresponded to compounds of molecular weights 142 and 200, which are those calculated for Me_3SiCF_3 and Me_3SiI. Another reaction was

TABLE 2

REACTIONS OF ALKYL HALIDES RX (10 mmol) AND $Me_3SiSiMe_3$ (7 mmol) IN TOLUENE (5 cm^3) FOR 20 h IN THE PRESENCE OF SPECIFIED CATALYST (4 × 10^{-5} mol)

RX	Temp. (°C)	Catalyst	Yield $RSiMe_3$ (%) [a]
MeBr	110	PdL_4	42
	110	PdL_2Br_2	31
MeI	110	PdL_4	0
	110	PdL_2I_2	0
EtBr	144	PdL_4	1
	144	PdL_2Br_2	2
EtI	110	PdL_4	0
	110	PdL_2I_2	0
n-$C_8H_{17}Br$	110	PdL_4	0
CF_3I	144	PdL_4	? [b]

[a] Yield based on amount of $Me_3SiSiMe_3$ taken. [b] See text.

carried out in the presence of [PdL_2Br_2], and the product mixture was roughly fractionated by trap-to-trap distillation. One fraction contained toluene and a second component, and its ^1H NMR spectrum showed only the toluene peaks along with an additional single peak at δ 0.43 ppm, and its ^{19}F NMR spectrum

TABLE 3

REACTIONS OF ALKYL HALIDES RX (10 mmol) AND $Cl_3SiSiCl_3$ (7 mmol) IN TOLUENE (5 cm^3) FOR 20 h IN THE PRESENCE OF SPECIFIED CATALYST (4 × 10^{-5} mol)

RX	Temp. (°C)	Catalyst	Yield $RSiCl_3$ (%) [a]
MeBr	110	PdL_4	78
	110	PdL_2Cl_2	19
	110	PdL_2Br_2	44
	110	PdL_2I_2	34
	110	PdL'_2Cl_2	11
	110	PdL'_2Br_2	13
	110	PdL'_2I_2	29
	110	PdL''_2Br_2	92
	110	$PdL_2(SiCl_3)_2$	39
	110	NiL_4	48
MeI	110	PdL_4	91
		PdL_2I_2	85
EtBr	110	PdL_4	25
	110	PdL_2Br_2	23
	144	PdL_4	37
	144	PdL_2Cl_2	27
	144	PdL_2Br_2	29
	144	PdL_2I_2	17
	144	PdL'_2Cl_2	15
	144	PdL'_2Br_2	37
	144	PdL'_2I_2	29
	144	PdL''_2Br_2	49
	144	$Pd_2L_2Br_4$	33
	144	NiL_4	25
EtI	110	PdL_4	45
	110	PdL_2I_2	38
n-PrBr	110	PdL_4	2
	110	PdL_2Br_2	1

[a] Yield based on amount of $Cl_3SiSiCl_3$ taken.

TABLE 4

REACTIONS OF ALLYL HALIDES $CH_2{=}CHCH_2X$ (10 mmol) WITH Y_3SiSiY_3 (7 mmol) IN TOLUENE (5 cm^3) IN THE PRESENCE OF THE SPECIFIED CATALYST (4 × 10^{-5} mol)

X	Y	Temp. (°C)	Time (h)	Catalyst	Yield of $RSiY_3$ [a]
Cl	Me	110	120	PdL_4	32
		110	20	PdL_2Br_2	43
Br	Me	110	20	PdL_4	65
		110	20	PdL_2Br_2	68
Br	Cl	110	20	PdL_4	49
		110	40	PdL_4	49
		75	88	PdL_4	63
	110	110	40	PtL_4	37
		25	190	PtL_4	45
		25	145	PtL'_4	46
		110	40	PtL'_4	46
		110	20	PtL'_2Cl_2	42

[a] Yield based on Y_3SiSiY_3 taken.

showed only a single peak, at 5 ppm (upfield from external $CFCl_3$). The IR spectrum of the vapour showed the presence of bands in the regions expected for CH_3—Si and CF_3 groups. It thus seems very probable that the previously elusive Me_3SiCF_3 had been obtained, but a larger scale reaction and isolation of this product is required for certainty.

(c) Reactions of allyl halides. In the reaction with $(Me_3Si)_2$, better yields were obtained from allyl bromide than from allyl chloride; in both cases $[PdL_2Br_2]$ gave slightly better results than $[PdL_4]$. Allyl bromide gave somewhat lower yields with $(Cl_3Si)_2$ than with $(Me_3Si)_2$ at 110° C in the presence of $[PdL_4]$, but a 63% yield of allyl-$SiCl_3$ was obtained from a reaction at 75° C for a longer period. Of special interest is that the platinum complexes $[PtL_4]$, $[PtL'_4]$ and $[PtL_2Cl_2]$, which are usually ineffective in this type of reaction, are comparable with the corresponding palladium species for the reaction between allyl bromide and $(Cl_3Si)_2$, and it is noteworthy that with $[PtL_4]$ or $[PtL'_4]$ as catalyst, the yields from reactions at 25° C (for longer periods) are similar to those from reactions at 110° C. An 89% yield of allyl$SiCl_3$ was reported by Atwell and Bokermann for the reaction between allyl chloride and $(Cl_3Si)_2$ with $[PtL'_2Cl_2]$ as catalyst at 100° C in the absence of a solvent [2].

(d) Reactions of benzyl halides. Poor yields of $XC_6H_4CH_2SiMe_3$ compounds were obtained from reactions of $XC_6H_4CH_2Br$ (X = H, *p*-Me, or *p*-OMe) or *p*-$NO_2C_6H_4CH_2Cl$ with $(Me_3Si)_2$ at 140° C with PdL_4 as catalyst; somewhat better, but still low, yields were previously obtained from similar reactions for longer times [7]. However, *p*-$O_2NC_6H_4CH_2SiMe_3$ was formed in almost 50% yield from *p*-$O_2NC_6H_4CH_2Cl$ in the presence of $[PdL''_4]$ or $[PdL'''_4]$ (confirming the previously reported superiority of these complexes over $[PdL_4]$ as catalysts for this reaction [7]). The yields are good enough to indicate that this approach could provide a useful preparative route to certain nitrobenzyltrialkylsilanes, as it does, for example, to *m*-nitrobenzyltrimethylstannane [9].

Of special interest is the formation of $PhSiMe_3$ in 5% yield along with $PhCH_2SiMe_3$ in 8% yield from the reaction between $PhCH_2Br$ and $(Me_3Si)_2$ in the presence of $[PdL_4]$. Possibly under the conditions used a $PhCH_2$—Pd complex is converted into a carbene complex containing the Ph—Pd ← CH_2 system.

TABLE 5

REACTIONS OF BENZYL HALIDES RX (10 mmol) WITH $Me_3SiSiMe_3$ (7 mmol) IN TOLUENE (5 cm^3) FOR 20 h IN THE PRESENCE OF THE SPECIFIED CATALYST (4×10^{-5} mol)

RX	Temp. (°C)	Catalyst	Yield of $RSiMe_3$ (%) [a]
$C_6H_4CH_2Br$	140	PdL_4	8 [b]
p-$MeC_6H_4CH_2Br$	140	PdL_4	3
p-$O_2NC_6H_4CH_2Br$	140	PdL_4	5
p-$O_2NC_6H_4CH_2Cl$	140	PdL_4	8
p-$O_2NC_6H_4CH_2Cl$	120	PdL''_4	48
p-$O_2NC_6H_4CH_2Cl$	100	PdL'''_4	46

[a] Yield based on $Me_3SiSiMe_3$ taken. [b] $PhSiMe_3$ was also formed in 5% yield.

The corresponding aryltrimethylsilanes were not detected from the reactions involving p-$MeOC_6H_4CH_2Br$ or p-$O_2NC_6H_4CH_2Cl$. Interaction of $PhCH_2Br$ with $(Cl_3Si)_2$ in the presence of $[NiL_4]$ gave $PhCH_2SiCl_3$ in 32% yield.

(e) Reactions of PhCOCl. The compound $PhCOSiMe_3$ was formed from PhCOCl and $(Me_3Si)_2$ at 140°C in the presence of a variety of catalysts, the maximum yield, 52%, being obtained by use of $[PdL_2I_2]$; some $PhSiMe_3$ was also formed. After we had completed this work, Yamamoto and his colleagues reported the isolation of $PhCOSiMe_3$ in 78% yield from the reaction catalysed by a 1 : 2 mixture of $[Pd(\eta^3\text{-allyl})Cl_2]$ and $P(OEt)_3$ at 110°C in the absence of a solvent; they also observed formation of $PhSiMe_3$ [8].

(f) Variation of the catalyst. Since $[PdL_4]$ must be rapidly converted into Pd^{II} species under the reaction conditions, no substantial difference would be expected between $[PdL_4]$ and $[PdL_2Br_2]$ as catalysts for the reactions between RBr and $(Me_3Si)_2$, and this is in accord with the results. The only reaction involving an alkyl or aryl bromide in which $[PdL_4]$ and $[PdL_2Br_2]$ were observed to have markedly different effects was that between MeBr and $(Cl_3Si)_2$, and the situation here will be complicated by the formation of $[PdL_2Cl_2]$ (which is evidently a much poorer catalyst in this case) and $[PdL_2(Br)(Cl)]$.

There are puzzling variations in the effectiveness of the $[PdL_2X_2]$ catalysts as

TABLE 6

REACTION OF PhCOCl (10 mmol) WITH $Me_3SiSiMe_3$ (7 mmol) IN TOLUENE (5 cm^3) AT 140°C FOR 20 h IN THE PRESENCE OF THE SPECIFIED CATALYST (4×10^{-5} mol)

Catalyst	Yield of $PhCOSiMe_3$ (%) [a]	Yield of $PhSiMe_3$ [a]
PdL_4	7	8
PdL_2Cl_2	9	8
PdL_2Br_2	26	8
PdL_2I_2	52	7
$PdL_2(COPh)Cl$	13	7
PdL'_2Cl_2	38	9
PdL'_2Br_2	11	4
PdL'_2I_2	1	2
$Pd_2L_2Br_2$	34	8
NiL_4	0	0

[a] Yield based on $Me_3SiSiMe_3$ taken.

TABLE 7

USE OF COMPLEXES OF METALS OTHER THAN Pd OR Pt AS CATALYSTS (4 × 10^{-5} mmol) FOR REACTIONS OF RX (10 mmol) WITH Y_3SiSiY_3 (7 mmol) IN TOLUENE (5 cm^3)

RX	Y	Catalyst	Temp. (°C)	Time (h)	Yield of $RSiMe_3$ (%)
PhBr	Me	NiL_2Br_2	144	20	1
PhBr	Me	$Ni(\pi\text{-}C_5H_5)_2$	80	70	0
PhBr	Cl	NiL_4	144	20	0
PhBr	Me	$Ir(CO)L_2Cl$	195	20	0
PgBr	Me	RhL_3Cl	80	21	0
$PhCH_2Br$	Cl	NiL_4	144	20	32
MeBr	Cl	NiL_4	110	20	48
EtBr	Cl	NiL_4	144	20	25
PhCOCl	Me	NiL_4	140	20	0

X is varied. Examples, for the reactions between $(Me_3Si)_2$ and aryl halides, are: (a) $[PdL_2I_2]$ is better than $[PdL_4]$ with PhBr; (b) $[PdL_2Cl_2]$ is much poorer than $[PdL_2Br_2]$ with PhBr, but much better than $[PdL_2Br_2]$ with p-$MeOC_6H_4Br$.

Variation of the phosphine ligands in $[Pd(PR_3)_4]$ and $[Pd(PR_3)_2X_2]$ catalysts can give rise to substantial changes in effectiveness, but again no general pattern can be discerned. It is possible that the relative effectiveness of various complexes is markedly affected by trace contaminants, and that different patterns will be found by different groups of workers. We should note, however, that the present work, using newly prepared samples of the complexes, confirmed the previous reported [7] superiority of $[Pd(PR_3)_4]$ with R = C_6H_4OMe-p over that with R = Ph for reactions involving substituted benzyl halides.

The platinum complexes $[PtL_4]$, $[PtL'_4]$ and $[PtL'_2Cl_2]$, which are not normally effective in this type of reaction, are quite effective for reaction of the very reactive allyl bromide with $(Cl_3Si)_2$. The nickel complex $[NiL_4]$ showed useful activity for the reactions of $PhCH_2Br$, MeBr, or EtBr, with $(Cl_3Si)_2$, but was ineffective for the reaction of PhBr or PhCOCl with $(Me_3Si)_2$. The complexes $[IrL_2(CO)Cl]$ and $[RhL_3Cl]$ were ineffective, under the conditions used, in the reaction between PhBr and $(Me_3Si)_2$.

Isolation or detection of possible intermediates

Attempts, some successful, were made to isolate or identify complexes which might be formed under the conditions used for the catalysed reactions. (a) An immediate reaction between $[PdL_4]$ and $(Cl_3Si)_2$ gave $[PdL_2(SiCl_3)_2]$, which was isolated as a very moisture-sensitive solid. The same product was obtained by treatment of $[PdL_4]$ with Cl_3SiH. (The corresponding reactions are known for the platinum complex $[PtL_4]$ [10,11].) However, no detectable reaction took place when $[PdL_4]$ and $(Me_3Si)_2$ were heated together at 120°C. (b) Since Me_3SiX is formed in the reactions between RX and $(Me_3Si)_2$, we examined the reaction of $[PdL_4]$ with Me_3SiCl, which was previously studied by Stille and Lau [12]. In contrast to the latter workers, we detected only a trace of $[PdL_2Cl_2]$ from a reaction under the conditions they used (25°C for 72 h in CH_2Cl_2), or with toluene as the solvent at room temperature. (When the toluene solution was heated to 90°C it became red. The IR spectrum indicated that little additional [PdL_2Cl_2] had been formed; probably decomposition to give a cluster complex had occurred.) However, when [PdL_4] was heated with $(Me_3Si)_2$ to 60°C in the absence of a solvent a quantitative yield of [PdL_2Cl_2] was obtained; in agreement with Stille and Lau, we found that $(Me_3Si)_2$ was also formed, along with $(Me_3Si)_2O$ presumably produced by accidental hydrolysis. The products [PdL_2Br_2], $(Me_3Si)_2$, and $(Me_3Si)_2O$ were obtained from the similar reaction, even at room temperature, between [PdL_4] and the more reactive Me_3SiBr in the absence of solvents. Only a small amount of [PdL_2Cl_2] was formed in the reaction of [PdL_4] with $SiCl_4$ at room temperature in the absence of solvent (possibly because of the low solubility of the complex), but a quantitative yield was obtained when the mixture was heated to 60°C.

Mechanism of the reactions

Numerous plausible catalytic cycles can be written involving oxidation additions of aryl halides and disilanes to Pd^{II} species (or initially to Pd^0 species where these are used as catalysts) and reductive eliminations of $RSiY_3$ and Y_3SiX (Y = Me or Cl) from Pd^{IV} species. (One possible analogous cycle involving the distannane $(Me_3Sn)_2$ was given in ref. 9.) In reactions involving $(Cl_3Si)_2$ catalysed by [PdL_4], the cycle might well be initiated by interaction of the latter with [PdL_4] to give [$PdL_2(SiCl_3)_2$], since we have seen that such a reaction occurs very readily. In the case of reactions involving $(Me_3Si)_2$, which appears not to react with [PdL_4] alone (though occurrence of a reversible reaction with the equilibrium lying well over towards the reactants cannot be ruled out), it seems more likely that reaction of the organic halide with the [PdL_4] is the initiating step. (The reactions of the [PdL_4] possibly involve initial dissociation, and it is known that the activity of this catalyst is suppressed by the presence of free L in the reactions involving distannanes [9].) Our results show that, as would be expected from the above suggestions, both [$PdL_2(R)(X)$] and [$PdL_2(SiCl_3)_2$] can act as catalysts.

Experimental

Preparations of complexes used as catalysts

The following were prepared by standard procedures: PdL_4 [13]; PdL''_4 [14], $Pd_2L_2X_2$ [15], $Pd_2L'_2X_2$ [15], PdL''_2X_2 [15], $Pd_2L_2Br_2$ [16], $PdL_2(Ph)Br$ [17], $PdL_2(C_6H_4OMe\text{-}p)Br$ [17], PtL_4 [18], $PtL_2(SiCl_3)_2$ [11], $Ni(\eta\text{-}C_5H_5)_2$ [19], NiL_2Br_2 [20], RhL_3Cl [21], $IrL_2(CO)Cl$ [22].

Reactions between organic halides and disilanes

The reactants, internal standard, and solvent were placed in a thick-walled glass ampoule, and the mixture was degassed three times by freeze-thaw cycles. The catalyst was added under nitrogen, and the tube was sealed under vacuum and placed inside a screw-capped metal container in a thermostatted oven. After an appropriate time the ampoule was cooled to room temperature and opened under nitrogen. The volatiles were evaporated off under reduced pressure, collected, and examined by GLC.

The products were identified by comparison of their retention times with those of authentic samples. For the GLC a Pye G.C.D. Chromatograph fitted with a dual flame ionization detector was used, and the column packing (1.6 m × 0.6 cm) was 5 wt-% OV101 on 100—120 mesh acid-washed Chromasorb G. The internal standard in each case was an appropriate saturated hydrocarbon C_nH_{2n+2} ($n = 9, 10, 12, 15$ or 18), and calibration curves were constructed relating the peak areas for authentic samples of products to those for the internal standards.

The yield reported in each case is the average value for at least three reactions; the individual values from triplicate runs agreed to within ±5%.

Reaction of CF_3I with $(Me_3Si)_2$

(a) A mixture of CF_3I (1.80 g, 9.2 mmol), $(Me_3Si)_2$ (1.00 g, 6.9 mmol), and toluene (5 cm^3) in a glass ampoule was degassed and $[PdL_4]$ (0.05 g, 4×10^{-5} mol) was added. The ampoule was sealed, kept at 100°C for 20 h, cooled, and opened, and the volatiles were taken off and collected, to leave red crystals, which were washed with Et_2O and shown to be essentially pure $[PdL_2I_2]$ by comparison with an authentic sample. The mixture of volatiles was examined by GLC, which showed the presence of two peaks not corresponding with reactants, and linked GLC-MS showed that these peaks were associated with parent ions of m/e 142 and 200, with strong $[M - 15]^+$ peaks at 127 and 185, respectively.

(b) (Experiment by Dr. H. Azizian) A mixture of $(Me_3Si)_2$ (0.59 g, 4 mmol), $[PdL_2Br_2]$ (0.037 g, 4.8×10^{-5} mol), and toluene (15 cm^3) was placed in an ampoule and degassed, and CF_3I (0.60 g, 3.5 mmol) was condensed in. The ampoule was sealed and kept at 100°C for 10 h, then cooled in liquid nitrogen and opened under vacuum; all the material which volatilized off at 20 mmHg at room temperature (ca. 21°C) was collected in a trap at —196°C, and then fractionated under vacuum into traps at —40, —80, and —196°C. The vapour of the fraction in the —40°C trap showed IR bands characteristic of CH_3 and CF_3 groups, and the ^1H NMR spectrum (in CCl_4) showed the presence of toluene and one other compound (ca. 20%) with δ 0.43 ppm, believed to be Me_3SiCF_3. The ^{19}F NMR spectrum showed a single resonance at 5 ppm upfield relative to external CF_3Cl.

The fraction in the —196°C trap showed strong CF_3 bands; it did not react with Hg, and was probably CF_3CF_3 rather than CF_3I.

Reaction of PdL_4 with silicon compounds

Schlenk tube techniques, with nitrogen atmospheres, were used for these reactions unless otherwise specified.

(a) A solution of $(Cl_3Si)_2$ (0.32 g, 1.16 mmol) in toluene (10 cm^3) was degassed and $[PdL_4]$ (0.43 g, 0.37 mmol) was added under nitrogen. The solution was stirred for 19 h, then the volatiles were evaporated off and the residue was washed with ether and shown to be $[PdL_2(SiCl_3)_2]$ (0.27 g, 82%). It was recrystallized from benzene/hexane; it showed the expected strong ν(SiCl) band at 540 cm^{-1} (Nujol mull), and gave a peak at m/e 507 in the mass spectrum (Found: C, 48.1; H, 3.4. Calcd. for $C_{36}H_{30}Cl_6PdSi_4$, C, 48.05; H, 3.4%).

The same complex was obtained by stirring Cl_3SiH (10.2 g, 0.07 mol) with $[PdL_4]$ (0.37 g, 0.32 mmol) for 2 h at room temperature. Evaporation of the residual Cl_3SiH and washing of the residue with Et_2O gave $[PdL_2(SiCl_3)_2]$, (0.26 g, 90%), identical with the previous sample.

(b) A degassed mixture of $(Me_3Si)_2$ (0.03 g), $[PdL_4]$ (0.19 g) and toluene (5 cm^3) was sealed under vacuum and kept at 120°C for 20 h. Removal of the volatiles left unchanged $[PdL_4]$ (0.18 g, 93%) (Found: C, 74.8; H, 5.2. Calcd. for $C_{72}H_{45}Pd$: C, 74.8; H, 5.2%).

(c) A mixture of Me_3SiCl (0.23 g), $[PdL_4]$ (0.50 g) and toluene (5 cm^3) was stirred at room temperature for 72 h. The volatiles were removed, and the residue was shown by IR and $^{31}P\text{-}\{^1H\}$ NMR spectroscopy to be $[PdL_4]$ containing a little *trans*-$[PdL_2Cl_2]$.

(d) A mixture of Me_3SiCl (0.17 g), $[PdL_4]$ (0.48 g), and CH_2Cl_2 (5 cm^3) was stirred under nitrogen at 25°C for 73 h. The volatiles were evaporated off, and shown by GLC to contain no detectable amount of $(Me_3Si)_2$. The residue was washed with Et_2O, and shown to be $[PdL_4]$ containing a trace of $[PdL_2Cl_2]$.

(e) A mixture of Me_3SiCl (1.49 g), $[PdL_4]$ (0.16 g), and toluene (5 cm^3) was kept at 90°C for 2 h. The volatiles were removed from the red solution and shown by GLC to contain no detectable amount of $(Me_3Si)_2$. The residue was not identified, but it was shown by IR and $^{31}P\text{-}\{^1H\}$ spectroscopy to contain only a trace of $[PdL_2Cl_2]$.

(f) A mixture of Me_3SiCl (0.49 g) and $[PdL_4]$ (0.07 g) was heated at 60°C for 4 h. The volatiles were collected, and shown by GLC to contain both $(Me_3Si)_2$ and $(Me_3Si)_2O$. The residue was washed with Et_2O, and shown to be $[PdL_2Cl_2]$ (0.03 g, 80%) by comparison with an authentic sample (Found: C, 61.7; H, 4.3. Calcd. for $C_{36}H_{30}Cl_2Pd$: C, 61.6; H, 4.3%).

(g) A mixture of $SiCl_4$ (3.22 g) and $[PdL_4]$ (0.25 g) was stirred at 60°C for 14 h. Evaporation of the volatiles left a residue, which was washed with Et_2O and shown to be essentially pure $[PdL_2Cl_2]$ (0.12 g, 89%) (Found: C, 61.6; H, 4.3%).

A similar procedure, but at room temperature for 40 h gave $[PdL_4]$ containing only a trace of $[PdL_2Cl_2]$.

(h) A mixture of Me_3SiBr (0.47 g) and $[PdL_4]$ (0.16 g) was stirred at 25°C for 21 h. The volatiles were collected and shown to contain $(Me_3Si)_2$ and $(Me_3Si)_2O$. The residue was washed with ether, and shown to be essentially pure $[PdL_2Br_2]$ (0.09 g, 82%) (Found: C, 54.6; H, 3.8. Calcd. for $C_{36}H_{30}Br_2Pd$: C, 54.7; H, 3.8%).

Preparation of $[PdL_2(COPh)Cl]$

A mixture of PhCOCl (0.12 g, 1 mmol) and $[PdL_4]$ (0.30 g, 0.3 mmol) was stirred under nitrogen in a Schlenk tube for 13 h at 21°C. The residual PhCOCl was evaporated off, and the residue was washed with Et_2O and dried to give $[PdL_2(COPh)Cl]$ (0.19 g, 95%); IR (Nujol mull ν(C = 0) 1630s, ν(Pd—Cl) 260 cm^{-1} (Found: C, 66.9; H, 4.50. Calcd. for $C_{42}H_{35}Cl_2OPd$: C, 67.0; H, 4.6%).

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