Metallation of Aliphatic Carbon Atoms. Part 5.† Synthesis and Characterization of the Cyclopalladated Complexes of 2-(Trimethylsilyl)pyridine and Their Dynamic Behaviour observed by Proton Nuclear Magnetic Resonance Spectroscopy

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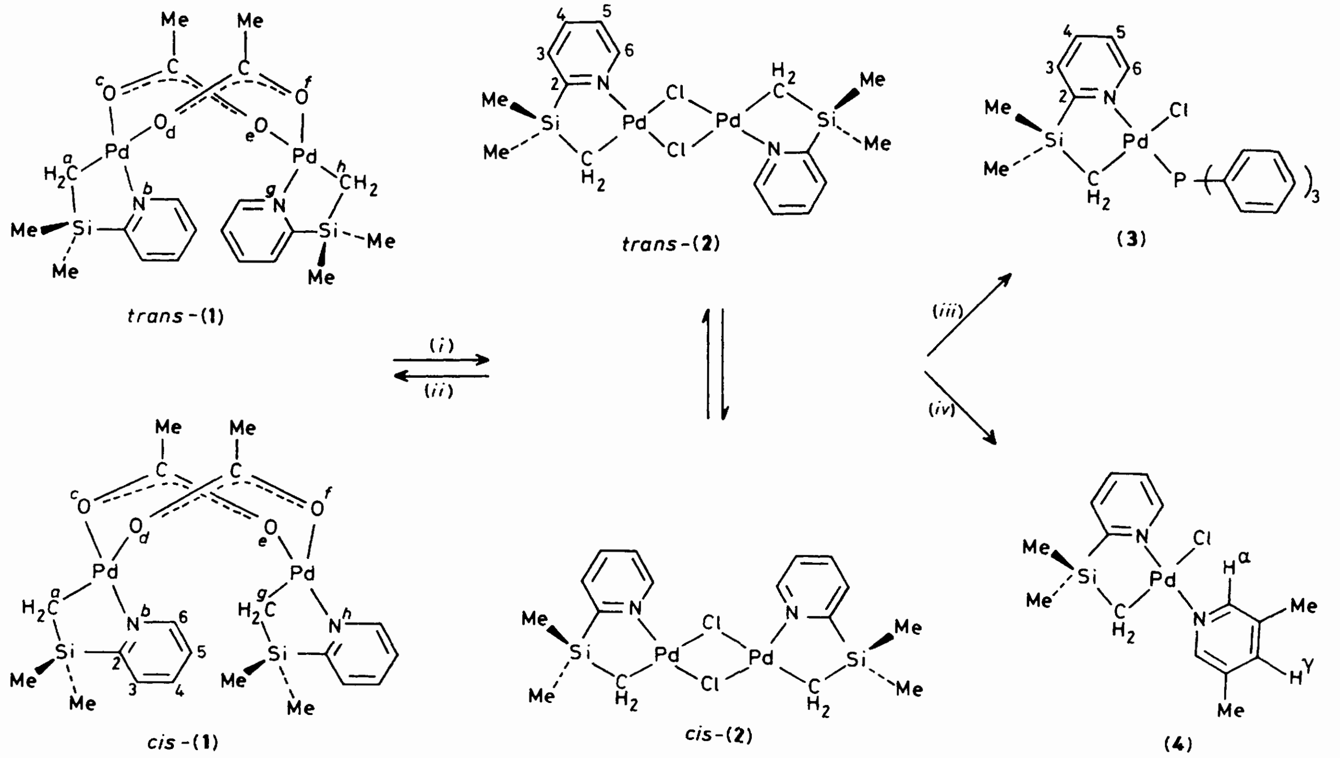
2-(Trimethylsilyl)pyridine reacts with palladium(II) acetate in benzene at 47 °C to give an acetato-bridged binuclear cyclopalladated complex $[\{\overline{Pd(CH_2SiMe_2C_5H_4N})(O_2CMe)\}_2]$ (**1**). Complex (**1**) is converted to a chloro-bridged analogue, $[\{\overline{Pd(CH_2SiMe_2C_5H_4N})Cl\}_2]$ (**2**), by metathetical reaction with $LiCl{\cdot}H_2O$. Each of complexes (**1**) and (**2**) is composed of *cis* and *trans* isomers, and shows dynamic behaviour in its ^1H n.m.r. spectrum. This phenomenon in (**1**) is ascribed to inversion of the acetato bridges, whereas that of (**2**) is associated with *cis–trans* isomerization. Complex (**2**) undergoes bridge-splitting reactions with triphenylphosphine and 3,5-dimethylpyridine to yield the corresponding mononuclear cyclopalladated complexes. All the cyclopalladated complexes are characterized by means of i.r. and n.m.r. spectroscopy.

Metallation of an aliphatic carbon atom is one of the current topics in organometallic chemistry in correlating the activation of C–H bonds by transition-metal compounds.[1,2] Recently, we reported the syntheses of six-membered cyclopalladated complexes of 2-neopentylpyridine through direct metallation of the aliphatic carbon atom using $Pd(O_2CMe)_2$.[3] Furthermore, it was found that *N,N*-dimethylneopentylamine reacted with $Pd(O_2CMe)_2$ to form a trinuclear cyclopalladated complex.[4]

In this study, we present the activation of the methyl group of the trimethylsilyl moiety of 2-(trimethylsilyl)pyridine using $Pd(O_2CMe)_2$, leading to the formation of a unique silicon-containing cyclopalladated complex.

Results and Discussion

2-(Trimethylsilyl)pyridine reacted with palladium(II) acetate at 47 °C in benzene to give a mixture of an acetato-bridged



Scheme. (*i*) $LiCl{\cdot}H_2O$; (*ii*) $Ag(O_2CMe)$; (*iii*) PPh_3; (*iv*) 3,5-dimethylpyridine

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† Part 4 is ref. 13.

binuclear cyclopalladated complex [{$Pd(CH_2SiMe_2C_5H_4N)(O_2CMe)$}$_2$] (**1**) and an addition complex, [$Pd(O_2CMe)_2(Me_3SiC_5H_4N)_2$]. Even after column chromatographic purification of the mixture, the addition complex could not be separated out completely. However, the addition complex and its chloro analogue could be removed when the mixture was treated with lithium chloride and subsequently purified by column chromatography. In this way a chloro-bridged, binuclear cyclopalladated complex [{$Pd(CH_2SiMe_2C_5H_4N)Cl$}$_2$] (**2**) was isolated.

The pure acetato-bridged complex (**1**) was obtained from complex (**2**) by reaction with silver acetate. The addition complex was not investigated further. It is noteworthy that the comparatively inert methyl group in 2-(trimethylsilyl)pyridine was cyclopalladated by palladium(II) acetate to afford (**1**), possessing unique silicon-containing chelates, Pd–C–Si–C–N. This is in contrast to the case of bis(benzonitrile)dichloropalladium(II) which gave only the addition complex, *trans*-dichlorobis[2-(trimethylsilyl)pyridine]palladium(II).[5] Direct activation of the methyl carbon of the trimethylsilyl group has recently been reported for [$H(\eta^5$-$C_5H_5)W(\mu$-σ:η^5-$C_5H_4)_2W(\eta^5$-$C_5H_5)(CH_2SiMe_3)$],[6] [{$Zr(\mu$-$CHSiMe_2NSiMe_3)[N(SiMe_3)_2]$}$_2$],[7] [$Rh${$CH(SiMe_2CHSiMe_3)_2PH$}(1—2:5—6-$\eta$-$C_8H_{12}$)],[8] [$Os${$(CH_2)_2SiMe_2$}$(PMe_3)_4$],[9] [$Mo_2(CH_2SiMe_3)_2${$\mu$-$(CH_2)_2SiMe_2$}$(PMe_3)_3$],[10] [$Ru${$(CH_2)_2SiMe_2$}$(PMe_3)_4$],[10] and [$Rh(CH_2SiMe_3)${$(CH_2)_2SiMe_2$}$(PMe_3)_3$].[10]

Complex (**2**) underwent typical bridge-splitting reactions with triphenylphosphine and 3,5-dimethylpyridine ($C_5H_3NMe_2$-3,5) to afford the corresponding mononuclear cyclopalladated complexes, [$Pd(CH_2SiMe_2C_5H_4N)Cl(PPh_3)$] (**3**) and [$Pd(CH_2SiMe_2C_5H_4N)Cl(NC_5H_3Me_2$-3,5)] (**4**), respectively. Yields, elemental analyses, molecular weights, and n.m.r. spectral data for complexes (**1**)—(**4**) are summarized in Tables 1 and 2. The i.r. spectra of complexes (**1**)—(**4**) resembled that of 2-(trimethylsilyl)pyridine, showing the presence of the [dimethyl(2-pyridyl)silyl]methyl group. The i.r. spectrum of (**1**) showed two strong absorption bands, due to the bridging acetato ligands, at 1 415 and 1 580 cm^{-1}.[11]

Complex (**1**) showed dynamic behaviour in its ^{1}H n.m.r. spectrum. The higher field region, from δ −0.1 to 1.25, changed with temperature, whereas pyridyl proton resonances, observed in the range δ 6.85—8.5, were largely unaltered. At −20 °C, complex (**1**) showed two sets of signals: one set consisted of three singlets at δ 0.07 (5.1 H, SiMe), 0.57 (5.1 H, SiMe), and 2.04 (5.1 H, $MeCO_2$);* the other consisted of four singlets at δ −0.08 (0.9 H, SiMe), 0.37 (0.9 H, SiMe), 2.02 (0.45 H, $MeCO_2$), and 2.08 (0.45 H, $MeCO_2$).* These data indicate that (**1**) is composed of two geometrical isomers in the population ratio of *ca.* 6:1. The major isomer, corresponding to the former set, has C_2 symmetry with (a-C^1,b-N)–(g-N,h-C^1) chelations (*trans* isomer), whereas the minor isomer, corresponding to the latter set, has C_s symmetry with (a-C^1,b-N)–(g-C^1,h-N) chelations (*cis* isomer), as shown in the Scheme. In addition, the spectrum exhibited one set of resonances of an AB-type quartet at δ 1.07 due to the methylene groups, formed by the cyclopalladation of one of the three methyl groups in 2-(trimethylsilyl)pyridine.†

The two stronger methyl proton signals at δ 0.07 and 0.57 broadened upon warming, coalesced near 40 °C, and became a broad singlet at δ 0.21 at 58 °C. The AB-type quartet also broadened near 40 °C and appeared as a broad singlet at δ 1.06 at 58 °C. The two weaker methyl proton signals at δ −0.08 and 0.37 broadened upon warming and overlapped with the stronger methyl proton signal at 58 °C. However, the acetato methyl proton signals remained virtually unchanged below 58 °C. Moreover, even at 58 °C, the H^6 proton of the pyridyl moiety appeared as two doublets at δ 8.34 (*cis*) and 8.59 (*trans*) corresponding to the *cis* and *trans* isomer ratio. Such a temperature dependence of the ^{1}H n.m.r. spectrum of (**1**) indicates that the inversion of the acetato bridge takes place rapidly on the n.m.r. time-scale above 40 °C and is quenched below −20 °C, and that *cis–trans* isomerization has not occurred below 58 °C.

Table 1. Yields, elemental analyses, and molecular weights

Complex	Yield (%)	M.p.^{a} (°C)	Found (calc.) (%) C	H	N	*M* Found (calc.)
(**1**)	60	140	38.0 (38.05)	4.8 (4.8)	4.4 (4.45)	b
(**2**)	37^c	135	33.25 (32.9)	4.2 (4.15)	4.5 (4.8)	588 (584.3)
(**3**)	56	166	56.45 (56.3)	5.0 (4.9)	2.95 (2.55)	b
(**4**)	61	156	45.05 (45.1)	5.3 (5.3)	6.85 (7.0)	388 (399.3)

^{a} With decomposition. ^{b} Not determined. ^{c} Based on palladium(II) acetate.

The rates of exchange of the two equally populated forms of complex (**1**) were measured by line-shape analysis of the methyl and methylene signals in the [dimethyl(2-pyridyl)silyl]methyl-*C*,*N* moiety of *trans*-(**1**). The Figure shows the experimental and simulated spectra together with the exchange rates k_{obs}. Activation parameters for the inversion of the acetato bridge calculated from Arrhenius and Eyring equations were: E_a = 66.1 kJ mol^{-1}, $\Delta G^\ddagger$ = 68.6 kJ mol^{-1}, $\Delta H^\ddagger$ = 63.6 kJ mol^{-1}, and $\Delta S^\ddagger$ = 7.0 J K^{-1} mol^{-1}. The comparatively small value of $\Delta S^\ddagger$ indicates that the transition state for the inversion does not involve bond breaking. This is consistent with the observation that *cis–trans* isomerization did not occur below 58 °C.

The ^{13}C-{^{1}H} n.m.r. spectrum of (**1**), measured at −20 °C in CD_2Cl_2, was consistent with the presence of the two isomers. Three acetato methyl carbon signals appeared at δ 23.5 (*cis*), 24.2 (*trans*), and 24.9 (*cis*), and two palladium-bonded methylene carbon signals were observed at δ 2.2 (*cis*) and 2.9 (*trans*). Reflecting the folded nature of the acetato-bridged dimer,[3,4,12] non-equivalent silicon-bonded methyl carbon signals of the *trans* isomer were observed at δ 0.70 and 0.92 with equal intensities. However, the signals corresponding to the *cis* isomer could not be detected.

The chloro-bridged complex (**2**) also showed a temperature-dependent ^{1}H n.m.r. spectrum. At −20 °C, palladium-bonded methylene protons resonated as two singlets at δ 1.42 (2.2 H) and 1.50 (1.8 H), and similarly H^6 of the pyridyl moiety appeared as two doublets at δ 8.78 (0.9 H) and 8.86 (1.1 H). These data indicate that (**2**) consists of two isomers, *cis* with (a-C^1,b-N)–(e-C^1,f-N) chelations and *trans* with (a-C^1,b-N)–(e-N,f-C^1) chelations in a population ratio of 45:55 (Scheme). The methylene proton singlets coalesced at 45 °C and changed to a broad singlet at δ 1.47 at 55 °C. In a similar way, the two doublets became a broad signal at *ca.* δ 8.9 at 55 °C. Similar dynamic behaviour to that in (**2**) has been observed for the halogeno-bridged binuclear cyclopalladated complex of 2-t-butylbenzothiazole, [{$Pd(CH_2CMe_2C_7H_4SN)X$}$_2$] (X = Cl or I), and was interpreted on the basis of the *cis–trans* isomerization.[13]

The ^{13}C-{^{1}H} n.m.r. spectrum of (**2**) was measured at 28 °C,

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* For the methylene and pyridyl protons, see Table 2.

† The AB quartet corresponded to the major isomer; the methylene signal corresponding to the minor isomer could not be distinguished due to overlap with the other signals.

Table 2. Proton and ^{13}C-{^{1}H} n.m.r. spectra of the complexes (py indicates pyridyl group)

	^{1}H N.m.r.			^{13}C N.m.r.	
Compound	δ(^{1}H)	*J*/Hz	Assignment	δ(^{13}C)	J_{CP}/Hz
cis-(**1**)[a]	−0.08 (s), 0.37 (s)		$SiMe_2$	*b*	
	b		$PdCH_2$	2.2 (s)	
	2.02 (s), 2.08 (s)		*Me*CO_2	23.5 (s), 24.9 (s)	
	6.85 (t)	$^{3}J_{HH}$ 6.5	py-5	129.8 (s)	
	7.23 (d)	$^{3}J_{HH}$ 6.5	py-3	123.9 (s)	
	7.54 (t)	$^{3}J_{HH}$ 6.5	py-4	135.3 (s)	
	8.20 (d)	$^{3}J_{HH}$ 6.5	py-6	150.8 (s)	
			py-2	178.5 (s)	
			Me*C*O_2	180.6 (s)	
trans-(**1**)[a]	0.07 (s), 0.57 (s)		$SiMe_2$	0.70 (s), 0.92 (s)	
	1.07 (q)	$^{2}J_{HH}$ 11.7 Δδ 0.34	$PdCH_2$	2.9 (s)	
	2.04 (s)		*Me*CO_2	24.2 (s)	
	7.15 (t)	$^{3}J_{HH}$ 6.6	py-5	129.8 (s)	
	7.33 (d)	$^{3}J_{HH}$ 6.6	py-3	124.3 (s)	
	7.62 (t)	$^{3}J_{HH}$ 6.6	py-4	135.3 (s)	
	8.49 (d)	$^{3}J_{HH}$ 6.6	py-6	152.0 (s)	
			py-2	178.5 (s)	
			Me*C*O_2	180.6 (s)	
(**2**)[a]	0.43 (s)		$SiMe_2$	0.70 (s)	
	1.42 (s),[c] 1.50 (s)		$PdCH_2$	10.1 (br)	
	7.18 (t),[c]	$^{3}J_{HH}$ 6.6	py-5	129.9 (s)	
	7.20 (t)	$^{3}J_{HH}$ 6.6			
	7.42 (d)	$^{3}J_{HH}$ 6.6	py-3	124.2 (s)	
	7.67 (t)	$^{3}J_{HH}$ 6.6	py-4	135.7 (s)	
	8.78 (d),[c] 8.86 (d)	$^{3}J_{HH}$ 6.6	py-6	152.1 (s)	
(**3**)	0.24 (s)		py-2	177.1 (s)	
	0.57 (d)	$^{3}J_{HH}$ 4.0	$SiMe_2$	0.12 (s)	
	b		$PdCH_2$	15.9 (d)	3.5
	b		py-5	129.1 (d)	2.0
	b		py-3	123.9 (d)	3.7
	9.65 (br)		py-4	135.9 (s)	
			py-6	152.5 (s)	
			py-2	174.3 (s)	
	7.45 (m)		Ph-*m*	128.1 (d)	9.8
			Ph-*p*	130.3 (d)	2.4
	7.75 (m)		Ph-*o*	134.6 (d)	11.0
			Ph-*i*	132.1 (d)	51.0
(**4**)[d]	0.44 (s)		$SiMe_2$		
	1.05 (s)		$PdCH_2$		
	1.31 (s)		*Me*$_2$py		
	7.20 (dt)	$^{3}J_{HH}$ 6.0, $^{4}J_{HH}$ 2.0	py-5		
	7.41 (d)	$^{3}J_{HH}$ 6.0	py-3		
	7.70 (dt)	$^{3}J_{HH}$ 6.0, $^{2}J_{HH}$ 6.0	py-4		
	9.45 (d)	$^{3}J_{HH}$ 6.0	py-6		
	7.35 (s)		Me_2py (H^{γ})/		
	8.44 (s)		Me_2py (H^{α})		

[a] At −20 °C. [b] Not distinguished. [c] Corresponding to minor isomer. [d] ^{13}C N.m.r. spectrum was not measured.

when isomerization occurs rapidly on the ^{1}H n.m.r. time-scale. Pyridyl and methyl carbon signals appeared as singlets as shown in Table 2. It is noted that the palladium-bonded methylene carbon signal was observed as a very broad peak at *ca.* δ 10.1.

The ^{1}H n.m.r. spectrum of (**3**) showed a doublet at δ 0.57 ($^{3}J_{HH}$ = 4 Hz) due to the palladium-bonded methylene protons. The comparatively high-field resonance of the methylene protons was probably associated with the donor ability of the PPh_3 ligand and the anisotropic effect of the phenyl rings of the ligand. In the ^{13}C-{^{1}H} n.m.r. spectrum of (**3**), the palladium-bonded methylene carbon resonated as a doublet at δ 15.9 ($^{2}J_{CP}$ = 3.5 Hz). This small coupling constant as well as that of the methylene protons indicates that the PPh_3 ligand is situated at *cis* to the methylene group. It is noted that C^3 and C^5 of the pyridyl group appeared as doublets at δ 123.9 ($^{4}J_{CP}$ = 3.7 Hz) and 129.1 ($^{4}J_{CP}$ = 2.0 Hz). By analogy with (**3**), (**4**) was also ascribed to the structure shown in the Scheme, where 3,5-dimethylpyridine was co-ordinated to palladium *cis* to the methylene group.

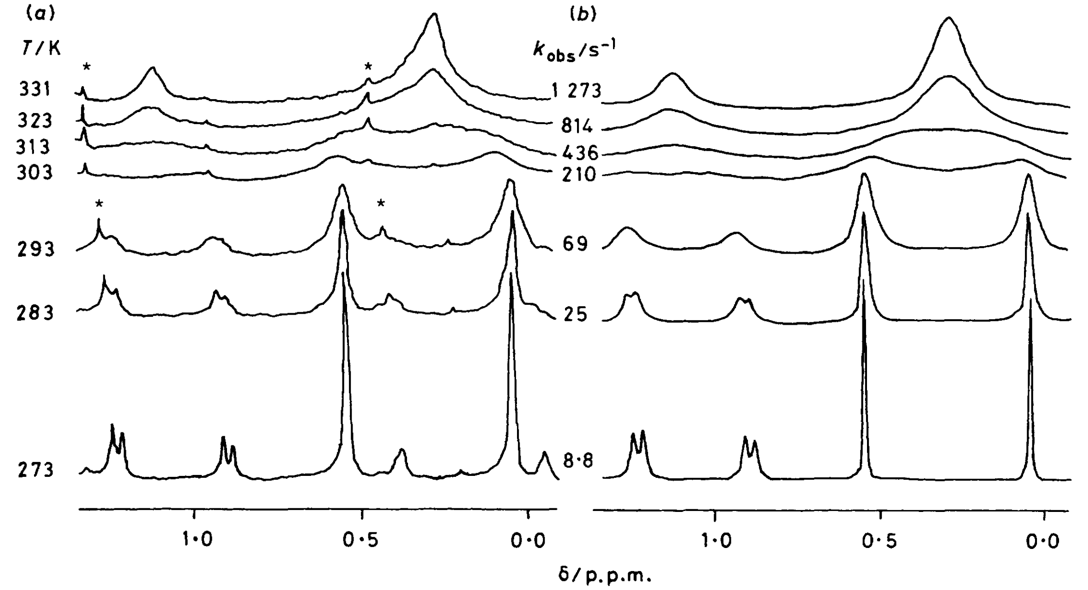

Figure. Methyl and methylene regions of the ^1H n.m.r. spectra of *trans*-(**1**). (*a*) Observed spectra. (*b*) Simulation curves. Asterisk denote impurities

Experimental

General.—^1H N.m.r. spectra were measured on JEOL JNM GX-400 and MH-100 spectrometers with $CDCl_3$ as solvent and internal reference (δ 7.26). $^{13}C-\{^1H\}$ N.m.r. spectra were measured on a JEOL FX-90Q spectrometer in CD_2Cl_2 as solvent and internal reference (δ 53.6). Assignment of the pyridyl group resonances was referred to data for 2-(trimethylsilyl)-pyridine.[14] Molecular weights were determined in benzene with a Corona model 114 molecular weight apparatus at 41.5 °C. Other general procedures were as described previously.[15] 2-(Trimethylsilyl)pyridine was prepared according to the literature method.[16]

Line-shape Analysis of trans-(**1**).—Experimental line shapes for the methyl and the methylene proton signals of the [dimethyl(2-pyridyl)silyl]methyl-*C*,*N* moiety were measured in the temperature range 273—331 K, and were matched against those calculated for different exchange rate constants k_{obs}, using the modified Bloch equation[17] and Binsch's[18] computer program QUABEX. The Arrhenius and Eyring equations were used to evaluate E_a, $\Delta H^‡$, and $\Delta S^‡$ from k_{obs}.

*Preparations.—Di-μ-chloro-bis{[dimethyl(2-pyridyl)silyl]-methyl-*C,N*}dipalladium*(II), (**2**). A benzene solution (20 cm^3) of palladium(II) acetate (4.4 mmol) and 2-(trimethylsilyl)pyridine (4.9 mmol) was heated at 47 °C with stirring for 8 h. After filtration, the filtrate was evacuated to dryness. An acetone solution (15 cm^3) of the residue and lithium chloride–water (1 : 1) (11.1 mmol) was stirred at room temperature for 14 h. Then the solvent was evaporated again from the reaction mixture. The ^1H n.m.r. spectrum of the residue in $CDCl_3$ exhibited signals due to *trans*-$[PdCl_2(Me_3SiC_5H_4N)_2]$ at δ 0.95 (s, $SiMe_3$), 7.3, [m,H^5(py)], 7.6 [m,$H^{3,4}$(py)], and 9.3 [m,H^6(py)],[5] besides those of (**2**). After extraction of the residue with benzene, the extract was chromatographed on a silica gel column. A yellow fraction, eluted by benzene, afforded $[\{\overline{Pd(CH_2SiMe_2C_5H_4N})Cl\}_2]$ (**2**).

*Di-μ-acetato-bis{[dimethyl(2-pyridyl)silyl]methyl-*C,N*}-dipalladium*(II), (**1**). An acetone solution (10 cm^3) of (**2**) (0.34 mmol) and silver acetate (0.72 mmol) was stirred at ambient temperature for 24 h. After the reaction mixture was filtered, the filtrate was concentrated and diluted with hexane to give $[\{\overline{Pd(CH_2SiMe_2C_5H_4N})(O_2CMe)\}_2]$ (**1**).

*Chloro{[dimethyl(2-pyridyl)silyl]methyl-*C,N*}(triphenyl-phosphine)palladium*(II), (**3**). A dichloromethane solution (10 cm^3) of (**2**) (0.26 mmol) and triphenylphosphine (0.55 mmol) was stirred at room temperature for 19 h. After filtration, the filtrate was concentrated under reduced pressure and diluted with hexane to give a pale yellow powder, $[\overline{Pd(CH_2SiMe_2C_5H_4N})Cl(PPh_3)]$ (**3**).

*Chloro(3,5-dimethylpyridine){[dimethyl(2-pyridyl)silyl]-methyl-*C,N*}palladium*(II), (**4**). Complex (**2**) reacted with 3,5-dimethylpyridine in dichloromethane at room temperature in a similar way to the preparation of (**3**), to give a yellow powder, $[\overline{Pd(CH_2SiMe_2C_5H_4N})Cl(NC_5H_3Me_2\text{-}3,5)]$ (**4**).

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Received 15*th June* 1987; *Paper* 7/1073