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Synthesis and reactions of cyclopentadienyl complexes containing a palladium carbon σ-bond

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Abstract

Cyclopentadienyl complexes of the type $Pd(\eta^5\text{-}C_5H_5)(CH_2Z)(PPh_3)$ ($Z=COC_6H_5$ (**1**), $COCH_3$ (**2**), $COCH_2Cl$ (**3**), CN (**4**) and SCH_3 (**5**)) have been prepared and characterized. The chemical shift of the methylene protons bound to palladium are briefly discussed. The complexes **1**–**3** react with dry hydrogen chloride to give $Pd(\eta^5\text{-}C_5H_5)Cl(PPh_3)$ (**A**) as an intermediate and finally a dimeric complex $[PdCl_2(PPh_3)]_2$ (**B**). Complex **4** also reacts with dry hydrogen chloride to yield $[Pd(CH_2CN)Cl(PPh_3)]_n$ as an intermediate. Similar treatment of **5** produced a square planar complex $Pd\overline{(CH_2S}CH_3)Cl(PPh_3)$.

Introduction

Considerable attention has been recently focussed on the chemistry of cyclopentadienyl palladium complexes [1]. However complexes of the type $Pd(\eta^5\text{-}C_5H_5)(L)(PPh_3)$ (L = substituted methyl) have been less studied. Because these complexes contain two kinds of palladium carbon bonds it is also interesting to investigate their reaction with strong acids. Previously we briefly reported that the cyanomethyl complex $PdCl(CH_2CN)(PPh_3)_2$ prepared by the reaction of $ClCH_2CN$ with $Pd(PPh_3)_4$ reacts with TlC_5H_5 to give the complex $Pd(\eta^5\text{-}C_5H_5)(CH_2CN)(PPh_3)$ [2]. Recently we prepared square planar complexes of the type $PdCl(CH_2COY)(PPh_3)_2$ ($Y=C_6H_5$, CH_3, CH_2Cl) [3]. These complexes allowed us to prepare cyclopentadienyl palladium complexes with other substituted methyl derivatives. In this paper we report the synthesis and properties of cyclopentadienyl complexes containing a palladium carbon σ-bond. In addition the reactions of these complexes with dry hydrogen chloride or triphenylmethyl chloride have also been described.

Experimental

All the reactions were carried out under nitrogen at room temperature. Tetrahydrofuran was dried over sodium benzophenone ketyl and distilled before use. Benzene was degassed before use. TlC_5H_5 is available from Aldrich Chemical Co. and used as such. $PdCl(CH_2CN)(PPh_3)_2$ [4] and $PdCl(CH_2SCH_3)(PPh_3)$ [5] were prepared according to the literature methods. The complexes $PdCl(CH_2COY)(PPh_3)_2$ ($Y=C_6H_5$, CH_3, CH_2Cl) were obtained from the reaction of $ClCH_2COY$ with $Pd(PPh_3)_4$ [3]. High frequency spectra (4000–700 cm^{-1}) were taken on a JASCO-DS-402G spectrometer as mulls in Nujol and hexachlorobutadiene, whereas low frequency spectra (700–200 cm^{-1}) were recorded on a Hitachi-EPI-2L spectrometer as Nujol mulls. ^1H NMR spectra were recorded on a Jeol-C60H or a JNM-PMX-60Si spectrometer using TMS as an internal reference. Elemental analyses were determined by Wako Pure Chemical Industries, Ltd.

Preparation of $Pd(\eta^5\text{-}C_5H_5)(CH_2COC_6H_5)(PPh_3)$ (1)

To a suspension of $PdCl(CH_2COC_6H_5)(PPh_3)_2$ (2.2 g, 2.80 mmol) in benzene (150 ml) was added TlC_5H_5 (0.76 g, 2.82 mmol) with stirring and the mixture was further stirred for 3 h. After filtration the solvent was removed under reduced pressure to leave a violet solid which was recrystallized twice from dichloromethane/n-hexane to give violet crystals (0.45 g, 27%).

Preparation of $Pd(\eta^5\text{-}C_5H_5)(CH_2COCH_3)(PPh_3)$ (2)

To a suspension of $PdCl(CH_2COCH_3)(PPh_3)_2$ (3.2 g, 4.42 mmol) in benzene (250 ml) was added TlC_5H_5

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(2.1 g, 4.42 mmol) with stirring. The mixture was stirred for a further 2 h. After the solvent was removed under reduced pressure, the residue was extracted with diethyl ether and then dichloromethane. To the combined solution was added n-hexane and the resulting brown material was removed by filtration. The filtrate was concentrated under reduced pressure to leave a red–purple solid which was recrystallized from dichloromethane/diethyl ether (0.27 g, 14%).

Preparation of $Pd(\eta^5\text{-}C_5H_5)(CH_2COCH_2Cl)(PPh_3)$ *(3)*

To a suspension of $PdCl(CH_2COCH_2Cl)(PPh_3)_2$ (2.99 g, 3.94 mmol) in benzene (250 ml) was added TlC_5H_5 (2.04 g, 7.56 mmol) with stirring. The mixture was stirred for a further 2 h. After the solvent was removed under reduced pressure the residue was washed with diethyl ether and then extracted with dichloromethane. n-Hexane was added to the extract to precipitate brown materials. After filtration, the solvent was removed under reduced pressure to leave dark purple solids. Recrystallization from dichloromethane/petroleum ether (b.p. 40–60 °C) yielded violet needles (0.30 g, 14%).

Preparation of $Pd(\eta^5\text{-}C_5H_5)(CH_2CN)(PPh_3)$ *(4)*

To a suspension of $PdCl(CH_2CN)(PPh_3)_2$ (1.00 g, 1.42 mmol) in benzene (100 ml) was added TlC_5H_5 (0.40 g, 1.42 mmol) with stirring. The mixture was stirred overnight. After filtration the solvent was removed under reduced pressure and the residue was chromatographed on Florisil (1 × 10 cm column). Elution with diethyl ether gave a violet solution which was concentrated under reduced pressure to precipitate red–violet materials (0.138 g, 21%). The use of NaC_5H_5 also gave complex **4** in 17% yield.

Preparation of $Pd(\eta^5\text{-}C_5H_5)(CH_2SCH_3)(PPh_3)$ *(5)*

To a suspension of $\overline{PdCl(CH_2S}CH_3)(PPh_3)$ (1.00 g, 2.1 mmol) in benzene (100 ml) was added TlC_5H_5 (0.60 g, 2.3 mmol) with stirring. The mixture turned to deep red in a few minutes. After stirring overnight, the solution was filtered and the solvent was removed under reduced pressure to leave red–brown solids. It was recrystallized from diethyl ether/petroleum ether (b.p. 40–60 °C) to give red–brown crystals (0.34 g, 32%).

Reactions of the complexes 1–5 with hydrogen chloride or triphenylmethyl chloride

In a typical reaction, an NMR tube was charged with the complex (*c.* 0.02 g) dissolved in 0.6 ml of $CDCl_3$. Hydrogen chloride was bubbled through the solution. Subsequent characterization of the reaction intermediates was carried out by examination of the ^1H NMR spectrum of the reaction mixture. Reactions of the complexes with triphenylmethyl chloride in $CDCl_3$ was also monitored by the ^1H NMR spectrum of the mixture and the same intermediates were confirmed.

Reaction of 4 with triphenylmethyl chloride

Triphenylmethyl chloride (0.465 g, 1.67 mmol) was added to a suspension of **4** (0.79 g, 1.67 mmol) in a mixture of $CHCl_3$ (30 ml) and $(C_2H_5)_2O$ (50 ml). After stirring for 2 h, the solution changed colour from violet to yellow and a yellow compound **6** precipitated. It was filtered and washed with diethyl ether. Its IR spectrum was the same as that of the yellow compound precipitated by the reaction of **4** with hydrogen chloride. *Anal.* Found: C, 53.34; H, 3.87; N, 2.82. Calc. for $C_{40}H_{34}Cl_2N_2P_2Pd_2$: C, 54.05; H, 3.86; N, 3.15%.

Reaction of 6 with TlC_5H_5

To a suspension of **6** (0.10 g, 0.113 mmol) in benzene (50 ml) was added TlC_5H_5 (0.061 g, 0.113 mmol) with stirring. Subsequent workup gave **4** in 56% yield.

Results and discussion

Treatment of an organopalladium complex of the type $PdCl(CH_2Z)(PPh_3)_2$ with MC_5H_5 (M = Na, Tl) yields $Pd(\eta^5\text{-}C_5H_5)(CH_2Z)(PPh_3)$ in low yield (15–30%). This low yield might be due to the use of mononuclear complexes $PdCl(CH_2Z)(PPh_3)_2$ instead of $[PdCl(CH_2Z)(PPh_3)]_2$ which are not available at present. Physical properties and analytical results are summarized in Table 1. All of the complexes have a characteristic colour and are soluble in common organic solvents. They are moderately stable in the solid state and in solution. It is particularly interesting to note that complexes **1**–**3** in $CDCl_3$ did not show any ap-

TABLE 1. Physical properties and analytical data of cyclopentadienyl complexes of palladium

Complex	m.p.[b] (°C)	Analytical data (%)		Colour	Yield (%)
		C	H		
1	145–147	66.92 (67.34)[c]	5.33 (4.92)	violet	27
2	130–135	63.45 (63.62)	5.44 (5.13)	red–purple	14
3	125–127	59.05 (59.45)	4.87 (4.60)	violet	14
4[a]	128–130	63.10 (63.37)	4.92 (4.68)	red–violet	21
5	91–92	60.37 (60.67)	4.96 (5.09)	red	32

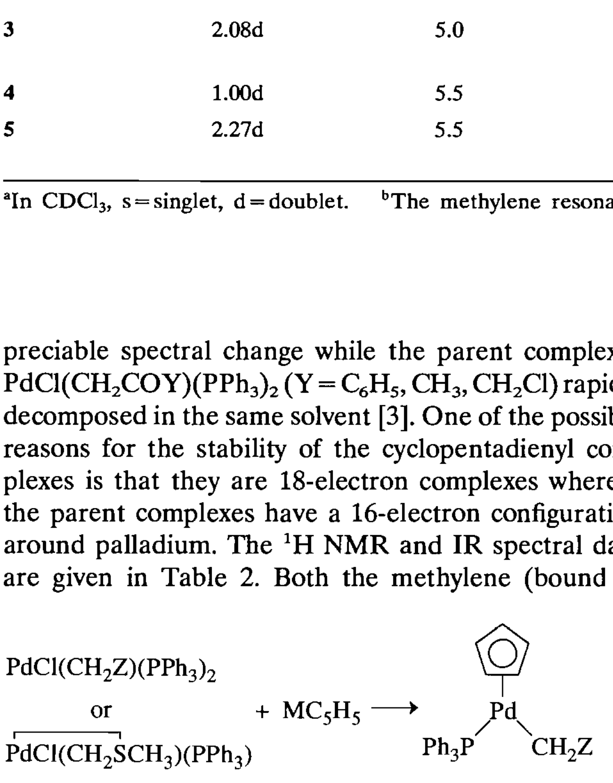
[a] N%: 3.01 (2.96). [b] With decomposition. [c] Calculated values in brackets.

TABLE 2. Selected spectroscopic data for the cyclopentadienyl complexes

Complex	^{1}H NMR[a]					IR (cm^{-1})
	Pd–CH_2		C_5H_5		Others δ (ppm)	
	δ (ppm)	J(PH) (Hz)	δ (ppm)	J(PH) (Hz)		
1	2.40d	5.0	5.23d	2.0		1625s[c] ν(CO)
2	2.0 ± 0.05[b]		5.50d	2.0	1.97s (CH_3)	1630s ν(CO)
3	2.08d	5.0	5.52d	2.0	3.93s (CH_2Cl)	1615s ν(CO)
4	1.00d	5.5	5.64d	2.0		2200s ν(CN)
5	2.27d	5.5	5.68d	3.0	1.95s (CH_3)	

[a] In $CDCl_3$, s = singlet, d = doublet. [b] The methylene resonance overlapped with the methyl resonance. [c] s = strong.

preciable spectral change while the parent complexes $PdCl(CH_2COY)(PPh_3)_2$ ($Y = C_6H_5, CH_3, CH_2Cl$) rapidly decomposed in the same solvent [3]. One of the possible reasons for the stability of the cyclopentadienyl complexes is that they are 18-electron complexes whereas the parent complexes have a 16-electron configuration around palladium. The ^{1}H NMR and IR spectral data are given in Table 2. Both the methylene (bound to Pd) and the cyclopentadienyl protons coupled with the phosphorus atom to give a doublet. But the J(PH) values of the methylene protons are larger than those of the cyclopentadienyl protons. The δ(Pd–CH_2) values of the cyclopentadienyl complexes are similar to those found for other cyclopentadienyl derivatives: 2.63 for $Mo(\eta^5\text{-}C_5H_5)(CH_2COC_6H_5)(CO)_3$ [6], 0.90 for $Fe(\eta^5\text{-}C_5H_5)(CH_2CN)(CO)_2$ [7], 2.46 for $W(\eta^5\text{-}C_5H_5)(CH_2SCH_3)(CO)_3$ [8]. Interestingly these values also resemble those of *trans*-$PdCl(CH_2Z)(PPh_3)_2$ but greatly differ from the corresponding *cis* isomers. For example the δ(Pd-CH_2) values of **3**, *trans*- and *cis*-$PdCl(CH_2COCH_2Cl)(PPh_3)_2$ are 2.08, 2.05 and 2.83 ppm, respectively [3]. The same is also true for **2** and $PdCl(CH_2COCH_3)(PPh_3)_2$ [3]. However since available data are limited it is difficult to ascertain whether this trend is general or not.



(1)

$Z = COC_6H_5$ (**1**), $COCH_3$ (**2**), $COCH_2Cl$ (**3**), CN (**4**), SCH_3 (**5**)

Reactions of complexes 1–3 with hydrogen chloride

Bubbling of hydrogen chloride through a $CDCl_3$ solution of **1** caused the spectral change shown in Fig. 1. Initially a new doublet (δ 5.54), a sharp singlet (δ 2.60) and two weak singlets (δ 3.00, 6.54) appeared (b) and were assigned to the cyclopentadienyl protons of $Pd(\eta^5\text{-}C_5H_5)Cl(PPh_3)$ (**A**) [9], methyl protons of acetophenone and cyclopentadiene [10], respectively. Further bubbling of hydrogen chloride increased the intensity of these resonances consuming the complex **1** (c). At this stage the colour of the solution was yellow-green indicating the formation of **A** (**A** is green in the solid state and in $CDCl_3$ solution). Finally the doublet due to **A** disappeared (d). Here the solution contained an orange crystalline solid which was identified as $Pd_2Cl_4(PPh_3)_2$ (**B**) on the basis of its far-IR spectrum [11]. However as it is clear from the Fig. 1, the methylene resonance due to one of possible intermediates $[Pd(CH_2COC_6H_5)Cl(PPh_3)]_2$ was not detected during the reaction. The reaction of **2** or **3** with HCl was performed in two ways. When HCl was bubbled through the $CDCl_3$ solution containing **2** or **3**, the formation of **A** was not observed although cyclopentadiene and acetone of chloroacetone were observed in the respective solutions. On the other hand the ^{1}H NMR spectra of these complexes dissolved in $CDCl_3$ saturated with HCl in advance showed clearly the formation of **A**. The failure to observe **A** in the former case is probably due to the difficulty in controlling the bubbling rate of HCl gas. This result indicates that the reaction of **2** or **3** with HCl also proceeds via **A**. Thus

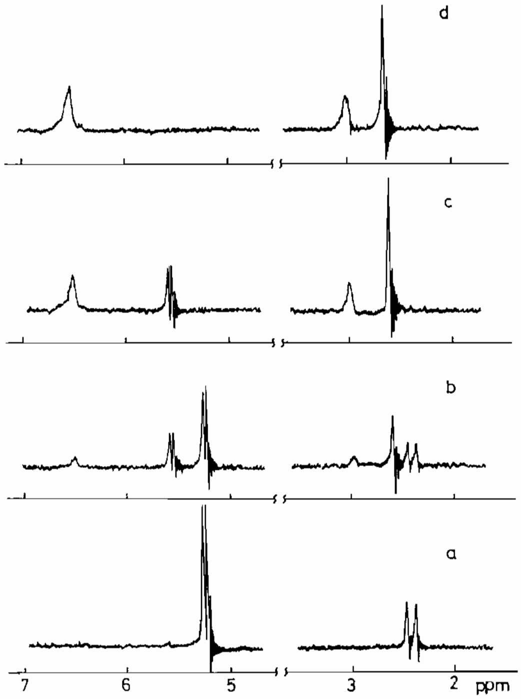


Fig. 1. ^1H NMR spectra taken at various times during the reaction of $Pd(\eta^5\text{-}C_5H_5)(CH_2COC_6H_5)(PPh_3)$ (0.02 g in 0.6 ml $CDCl_3$) with hydrogen chloride. The time for which HCl was bubbled through the solution is given in seconds: (a) 0, (b) 5, (c) 10 after spectrum (b) was taken, (d) 30 after spectrum (c) was taken.

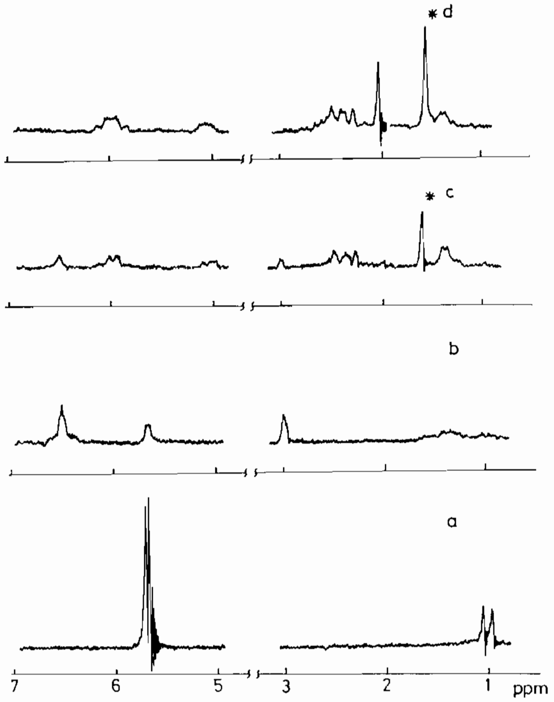
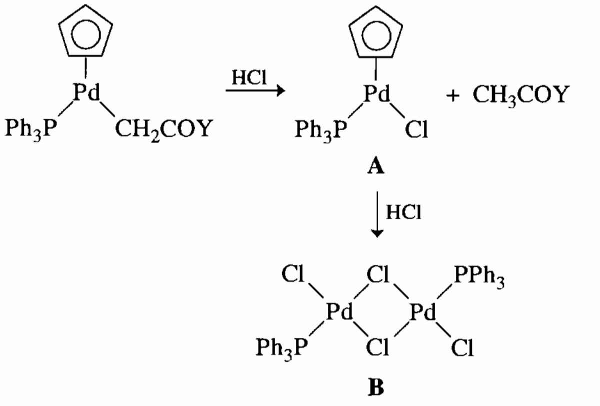


Fig. 2. ^1H NMR spectra taken at various times during the reaction of $Pd(\eta^5\text{-}C_5H_5)(CH_2CN)(PPh_3)$ (0.02 g in 0.6 ml $CDCl_3$) with hydrogen chloride. The time for which HCl was bubbled through the solution is given in minutes: (a) 0, (b) 2, (c) 2 after spectrum (b) was taken, (d) 5 after spectrum (c) was taken. $^*H_2O$.

the reaction pathway for these three complexes is summarized as follows:



(2)

Y = C_6H_5 (**1**), CH_3 (**2**), CH_2Cl (**3**)

The last step in eqn. (2) has been reported for the complex containing $P(O\text{-}o\text{-}Tol)_3$ instead of PPh_3 [12].

Reaction of complex 4 with hydrogen chloride

The intermediate of the reaction of **4** with hydrogen chloride is different from that of complexes **1**–**3**. As Fig. 2 shows the doublet due to the cyclopentadienyl protons of **4** disappeared by bubbling of hydrogen chloride. At the same time two resonances assigned to cyclopentadiene appeared (b), but the formation of **A** or CH_3CN was not detected. This result indicates that the first step in this case is elimination of cyclopentadiene from **4**. Further bubbling of hydrogen chloride decreased the intensity of cyclopentadiene and an ill-resolved doublet (δ 1.40) which we tentatively assigned to the cyanomethyl group in the palladium containing intermediate **6** (eqn. (3)) appeared together with three unidentified multiplets (δ *c.* 2.5, 5.0, 6.0) (c). In last spectrum (d), the resonance at δ 1.40 reduced in intensity and a new singlet assigned to acetonitrile appeared at δ 2.00 ppm. In order to isolate the intermediate **6** the solution which showed a ^1H NMR spectrum of (c) in Fig. 2 was concentrated to give a yellow residue. Unfortunately, owing to its insolubility in common organic solvents, the ^1H NMR spectrum for this compound was not available but its IR spectrum exhibits two bands assigned to $\nu(CN)$ at 2200 (weak) and 2245 (strong) cm^{-1} showing the existence of two kinds of cyanomethyl group, i.e. a monodentate (2200 cm^{-1}) and a bridging ligand (2245 cm^{-1}). Compound **6** obtained by the reaction of **4** with triphenylmethyl chloride also showed a similar IR spectrum (4000–700 cm^{-1}). Furthermore its far-IR spectrum showed three bands assigned to $\nu(Pd\text{–}Cl)$ (305(m), 280(bw), 260(bw)) and its elemental analysis suggested the composition $PdCl(CH_2CN)(PPh_3)$

(see 'Experimental'). Nakamura and co-workers also obtained the compound with the same composition by the reaction of $[Pd(CH_2CN)Cl(PPh_3)_2]$ with H_2O_2. Their compound showed two ν(CN) bands at 2250(s) and 2260(sh) cm^{-1} and two weak ν(Pd–Cl) bands at 315 and 280 cm^{-1}. They explained the product as a mixture of compounds which contain N-bonded CN-bridging structures [13]. Thus our compound is similar in composition and solubility to that reported by them but their IR spectra are somewhat different. The major component in these two compounds seems to be the same because they have a strong ν(CN) at 2245–2250 cm^{-1} and a weak ν(Pd–Cl) at 280 cm^{-1} but for further discussion the isolation of pure compounds is necessary. Compounds containing the cyanomethyl group as a bridging ligand have been isolated: *cis*-$[Pt(CH_2CN)(PPh_3)_2]_2(BF_4)_2$ [14] and $[Pd(CH_2CN)_2(PPh_3)]_2$ [15]. As expected, our compound **6** reacts with TlC_5H_5 to give **4** in a better yield (56%) than that found for the reaction of $PdCl(CH_2CN)(PPh_3)_2$ with TlC_5H_5. The reactions of **4** with HCl are summarized as follows:

$$\mathbf{4} \xrightarrow{HCl} \underset{\mathbf{6}}{[Pd(CH_2CN)Cl(PPh_3)]_n} \xrightarrow{HCl} \mathbf{B} + CH_3CN \qquad (3)$$

Reaction of complex 5 with hydrogen chloride

The ^1H NMR spectrum of the reaction mixture of complex **5** with HCl showed two doublets at δ 2.35d (J(PH) 5 Hz) and 2.70d (J(PH) 2 Hz) and two singlets at δ 3.0 and 6.5 ppm. The former two resonances were assigned to $\overline{PdCl(CH_2S}CH_3)(PPh_3)$ [5] and the latter to cyclopentadiene. Finally the reaction yielded the dimer $Pd_2Cl_4(PPh_3)_2$ as expected. However neither **A** nor $[PdCl(CH_2SCH_3)(PPh_3)]_2$, where the thiomethoxymethyl group behaves as a bridging ligand as found in a platinum analogue [16], was observed. The strong coordinating ability of the sulfur atom clearly plays an important role in the reaction as exemplified by the experimental fact that the recrystallization of $PdCl(CH_2SCH_3)(PPh_3)_2$ easily loses a molecule of PPh_3 forming a three-membered chelate ring containing $\overline{Pd–CH_2–S}CH_3$ [17].

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