Synthesis of the complexes [PdClR(cod)] (R = benzyl, ethyl; cod = 1,5-cyclooctadiene). β-Elimination from [PdClEt(cod)] to give the η^1,η^2, and η^3 isomers of $[Pd_2(\mu\text{-}Cl)_2(C_8H_{13})_2]$

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Abstract: Treatment of $[PdCl_2(cod)]$ with tetrabenzyltin gives the benzylpalladium complex $[PdCl(CH_2Ph)(cod)]$ (cod = 1,5-cyclooctadiene), **1a**, whose structure has been determined by X-ray crystallography. It adopts approximate square-planar geometry, with the double bonds perpendicular to the square plane. The corresponding ethylpalladium derivative **1b** has been prepared by a similar method, but it is considerably less stable. It decomposes by β-elimination to produce ethene and a transient hydride complex, which either undergoes migratory insertion to give $[Pd_2(\mu\text{-}Cl)_2(\eta^1,\eta^2\text{-}C_8H_{13})_2]$, **2a**, or dinuclear reductive elimination with a second molecule of **1b** to produce ethane, $[PdCl_2(cod)]$, free cyclooctadiene, and palladium metal. Complex **2a** has also been prepared by reaction of $[PdCl_2(cod)]$ with $NaBH_4$. At higher temperatures **2a** converts to an equilibrium mixture with its η^3-allyl isomer, **2b**. Reactions of $[PdCl_2(cod)]$ or K_2PdCl_4 in the presence of cyclooctadiene in aqueous solution to produce **2a** or **2b** have also been investigated.

Key words: palladium, diene complexes, allyl complexes, isomerization, β-elimination.

Résumé : Le traitement du $[PdCl_2(cod)]$ avec le tétrabenzylétain conduit au complexe benzylpalladium $[PdCl(CH_2Ph)(cod)]$ (cod = cycloocta-1,5-diène), **1a**, dont on a déterminé la structure par diffraction des rayons X. Il adopte une géométrie plan carré dans laquelle les doubles liaisons sont perpendiculaires au plan carré. On a préparé le dérivé éthylpalladium correspondant, **1b**, par une méthode semblable; il est toutefois beaucoup moins stable. Il se décompose par une élimination β pour former de l'éthène et un hydrure complexe transitoire qui peut donner lieu soit à une insertion migratoire conduisant au $[Pd_2(\mu\text{-}Cl)_2(\eta^1,\eta^2\text{-}C_8H_{13})_2]$, **2a**, soit à une élimination réductrice dinucléaire avec une deuxième molécule de **1b** qui fournit de l'éthane, du $[PdCl_2(cod)]$, du cyclooctadiène libre et du palladium métallique. On a aussi préparé le complexe **2a** par réaction du $[PdCl_2(cod)]$ avec le $NaBH_4$. À des températures plus élevées, le composé **2a** se transforme en un mélange à l'équilibre avec l'isomère η^3-allyle **2b**. On a aussi étudié les réactions du $[PdCl_2(cod)]$ ou du K_2PdCl_4 en solution aqueuse, en présence de cyclooctadiène, qui conduisent aux produits **2a** ou **2b**.

Mots clés : palladium, complexes diéniques, complexes allyliques, isomérisation, élimination β.

[Traduit par la rédaction]

Introduction

Since the first platinum complexes of the type [PtClR(cod)] (cod = 1,5-cyclooctadiene) were reported by Clark and Manzer (1), they have served as excellent precursors to a range of organoplatinum species, including bis(phosphine) (2) or diphosphine (3) compounds, or dppm-bridged A-frames (4).

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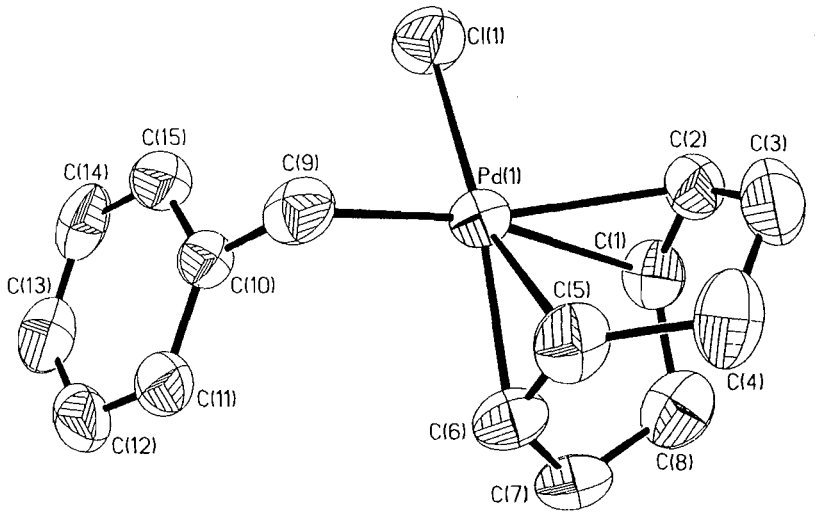
The corresponding palladium complexes have proved more elusive. The preparation of [PdClMe(cod)] was first reported in 1977, from the reaction of the dimethyl species with chlorinated solvents or with $[PdCl_2(cod)]$, but it was found to be unstable (5). More recently, a superior synthesis from $[PdCl_2(cod)]$ and tetramethyltin has been reported (6), and we have shown that [PdClMe(cod)] is a suitable precursor to a number of chloride-bridged methylpalladium complexes (7). The pentafluorophenyl complex $[PdCl(C_6F_5)(cod)]$ has been prepared and structurally characterized, and it has been shown to undergo rearrangements that involve migration of the aryl group on to the cyclooctadiene ring (8). In this paper, we report the preparation and structure of $[PdCl(CH_2Ph)(cod)]$, **1a**, and the difficult isolation and facile rearrangement of its ethyl analogue.

Results and discussion

The synthesis of $[PdCl(CH_2Ph)(cod)]$, **1a**, is similar to that of its methyl analogue (6, 7), except that a longer reaction time is required. Thus, refluxing a dichloromethane solution of

Fig. 1. Projection view of the molecular structure of [PdCl(CH_2Ph)(cod)], **1a**, showing the atom-labeling scheme.



[$PdCl_2$(cod)] with a slight excess of tetrabenzyltin for 7.5 h, followed by purification, gave the product as a yellow solid in good yield. Its ^{1}H and ^{13}C{^{1}H} NMR spectra exhibit the expected resonances. The ^{1}H NMR spectrum displays a singlet at 3.59 ppm due to the benzyl CH_2 hydrogens, and two multiplets at 4.87 and 5.89 ppm due to the coordinated alkene hydrogens *trans* to Cl and CH_2Ph, respectively, in addition to multiplets due to the cyclooctadiene CH_2 groups and the aromatic hydrogens. The significant difference between the two =CH chemical shifts is due to the difference in *trans* influence between the Cl and CH_2Ph groups, the benzyl group weakening the Pd–alkene interaction *trans* to itself and making it more like a free alkene. Consistently, the ^{13}C{^{1}H} NMR spectrum contains two signals due to the nonequivalent alkene moieties, two signals assigned to the aliphatic carbons of cyclooctadiene, a benzylic carbon resonance at 35.8 ppm, and four aromatic signals.

The crystal structure of **1a** belongs to the space group $P2_12_12_1$, and its molecular structure is shown in Fig. 1. Bond distances and angles are given in Table 1. The structure exhibits approximate square planar geometry about palladium, the metal center being coordinated by the two alkene groups of the diene, the benzyl CH_2 group and Cl. The double bonds lie approximately perpendicular to the square plane. The C—C distance for the alkene lying *trans* to the benzyl group is 1.334(10) Å, close to that expected for the free diene, whereas the other C—C bond is lengthened slightly (1.379(10) Å), indicating a stronger alkene–metal interaction *trans* to Cl. The Pd—C and Pd—Cl distances are 2.051(7) and 2.336(2) Å, respectively.

When compared with the few related organopalladium complexes that have been reported previously, namely, [PdClR(cod)] (R = C_6F_5 (8), CH_2SO_2Ph (9)) and the [PdCl{CH($SiMe_3$)PMe_2Ph}(cod)]$^+$ cation (10), the present complex displays the longest Pd—C(alkene) bonds *trans* to the organic fragment and the longest Pd—Cl distance. These features suggest that the benzyl group exhibits the greatest

Table 1. Bond lengths (Å) and angles (deg) for **1a**.

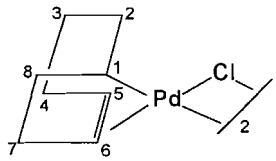
Pd(1)—C(9)	2.051(7)	Pd(1)—C(6)	2.155(7)
Pd(1)—C(5)	2.166(6)	Pd(1)—Cl(1)	2.336(2)
Pd(1)—C(2)	2.363(7)	Pd(1)—C(1)	2.420(7)
C(1)—C(2)	1.334(10)	C(1)—C(8)	1.499(10)
C(2)—C(3)	1.501(11)	C(3)—C(4)	1.507(11)
C(4)—C(5)	1.521(10)	C(5)—C(6)	1.379(10)
C(6)—C(7)	1.509(10)	C(7)—C(8)	1.528(10)
C(9)—C(10)	1.485(9)	C(10)—C(11)	1.382(9)
C(10)—C(15)	1.390(10)	C(11)—C(12)	1.387(9)
C(12)—C(13)	1.339(10)	C(13)—C(14)	1.360(11)
C(14)—C(15)	1.379(10)		
C(9)-Pd(1)-C(6)	91.0(3)	C(9)-Pd(1)-C(5)	93.4(3)
C(6)-Pd(1)-C(5)	37.2(3)	C(9)-Pd(1)-Cl(1)	89.1(2)
C(6)-Pd(1)-Cl(1)	165.9(2)	C(5)-Pd(1)-Cl(1)	156.8(2)
C(9)-Pd(1)-C(2)	162.6(3)	C(6)-Pd(1)-C(2)	93.9(3)
C(5)-Pd(1)-C(2)	80.6(3)	Cl(1)-Pd(1)-C(2)	90.2(2)
C(9)-Pd(1)-C(1)	164.4(3)	C(6)-Pd(1)-C(1)	79.2(3)
C(5)-Pd(1)-C(1)	86.2(3)	Cl(1)-Pd(1)-C(1)	97.4(2)
C(2)-Pd(1)-C(1)	32.4(2)	C(2)-C(1)-C(8)	124.8(8)
C(2)-C(1)-Pd(1)	71.5(4)	C(8)-C(1)-Pd(1)	107.4(5)
C(1)-C(2)-C(3)	126.8(8)	C(1)-C(2)-Pd(1)	76.2(4)
C(3)-C(2)-Pd(1)	102.1(5)	C(2)-C(3)-C(4)	115.6(7)
C(3)-C(4)-C(5)	115.5(7)	C(6)-C(5)-C(4)	124.8(8)
C(6)-C(5)-Pd(1)	71.0(4)	C(4)-C(5)-Pd(1)	111.8(5)
C(5)-C(6)-C(7)	127.0(8)	C(5)-C(6)-Pd(1)	71.8(4)
C(7)-C(6)-Pd(1)	109.1(5)	C(6)-C(7)-C(8)	115.3(7)
C(1)-C(8)-C(7)	113.4(7)	C(10)-C(9)-Pd(1)	112.1(4)
C(11)-C(10)-C(15)	116.8(7)	C(11)-C(10)-C(9)	122.4(7)
C(15)-C(10)-C(9)	120.8(7)	C(10)-C(11)-C(12)	121.5(7)
C(13)-C(12)-C(11)	119.8(8)	C(12)-C(13)-C(14)	120.9(8)
C(13)-C(14)-C(15)	119.9(8)	C(14)-C(15)-C(10)	121.1(7)

trans influence among these organic groups. Within the diene ligand a weaker Pd—C(alkene) interaction *trans* to the benzyl group may induce a stronger Pd—C(alkene) interaction *trans* to Cl which, in turn, results in weakening of the Pd—Cl bond.

Whereas [PdClMe(cod)] reacted with carbon monoxide to produce the corresponding acetyl complex (7), we found that treatment of the benzyl complex with CO (1 atm (101.3 kPa)) at ambient temperature resulted in rapid decomposition.

The reaction of $[PdCl_2(cod)]$ with tetraethyltin proved to be more complicated. When the reaction was performed at temperatures above 20°C extensive decomposition took place in addition to formation of dimeric species (vide infra), and long reaction times at ambient temperature also led to decomposition and the formation of palladium mirrors. On the other hand, at 0°C or below the reaction was extremely slow. Excess Et_4Sn also promoted decomposition. We have found that by use of a deficiency of Et_4Sn (ca. 0.6 mol-equiv. per Pd) and relatively short reaction times (ca. 4 h) at 20°C we can isolate [PdClEt(cod)], **1b**, in pure form, albeit in low yield. Since much of the $[PdCl_2(cod)]$ is recovered unchanged (and able to be used again), however, the yield of the ethylpalladium complex is 78% based on the amount of $[PdCl_2(cod)]$ actually consumed. Longer reaction times result in further reaction of [PdClEt(cod)] and lower isolated yields. The ^1H and $^{13}C\{^1H\}$ NMR spectra of [PdClEt(cod)] are unsurprising, resonances due to the ethyl group being observed in addition to the signals for coordinated cyclooctadiene.

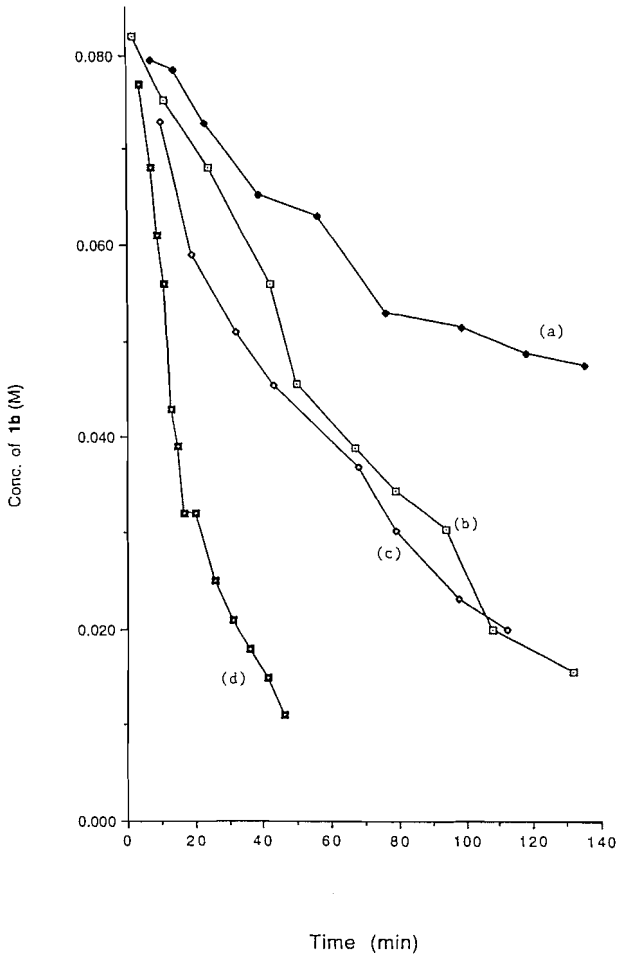
When a C_6D_6 solution of [PdClEt(cod)], **1b**, was allowed to stand at ambient temperature a precipitate formed, along with some palladium metal. Analysis of the remaining solution by ^1H NMR spectroscopy revealed the presence of the dimeric complex $[Pd_2(\mu\text{-}Cl)_2(\eta^1,\eta^2\text{-}C_8H_{13})_2]$, **2a**. Signals due to ethene (5.19 ppm) and ethane (0.80 ppm), as well as free 1,5-cyclooctadiene, were also observed. The precipitate was identified as $[PdCl_2(cod)]$, which is sparingly soluble in benzene, by its ^1H NMR spectrum in $CDCl_3$ solution. The structure of **2a** was determined from its ^1H and $^{13}C\{^1H\}$ NMR spectra (see Experimental), peak assignments being made from ^1H–^1H and ^{13}C–^1H correlation spectra. The ^1H NMR spectrum shows the expected two olefinic resonances, and the signal due to H1 appears as a multiplet at 3.90 ppm. The resonances for one hydrogen on each of the carbons adjacent to the site of metalation, i.e., C2 and C8, appear at an unusually low frequency (0.40 and 0.60 ppm, respectively), whereas the remaining hydrogens resonate between 1.1 and 2.1 ppm.



2a

The disappearance of [PdClEt(cod)], **1b**, in benzene solution may be accounted for by the sequence of reactions shown in Scheme 1. β-Hydride elimination from **1b** produces ethene and [PdClH(cod)] (although the latter has not been detected). The hydride complex may follow either of two competing pathways, namely, rearrangement and dimerization to give **2a**, or dinuclear reductive elimination with a molecule of **1b** to produce ethane, $[PdCl_2(cod)]$, cyclooctadiene, and palladium

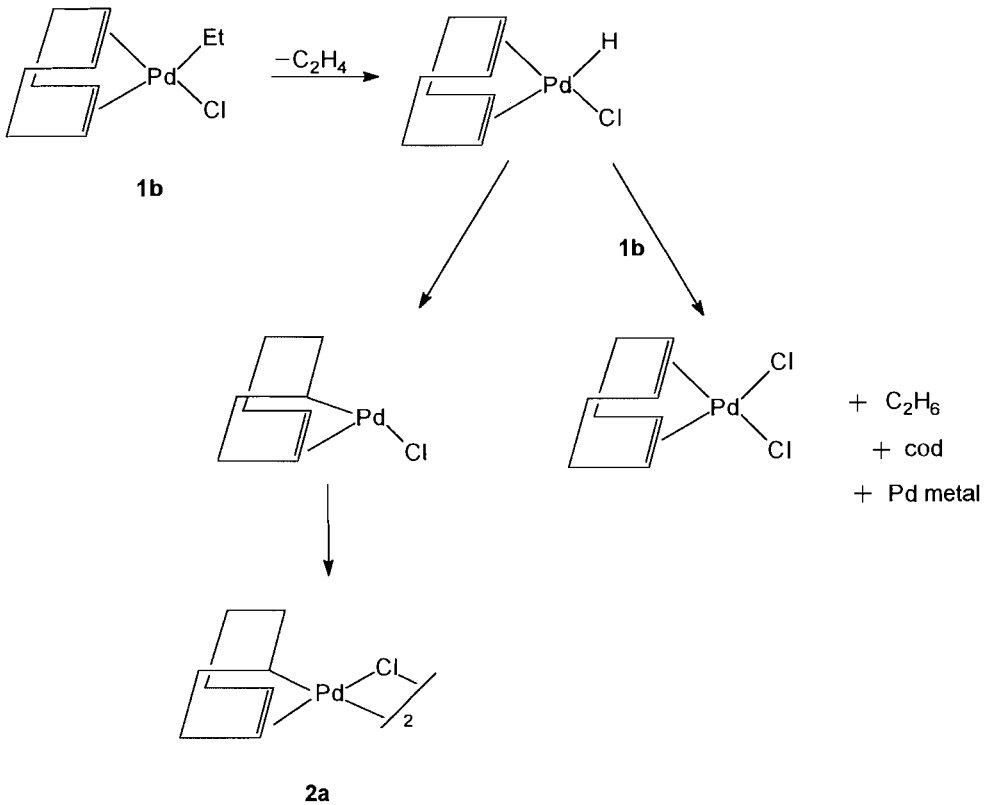
Fig. 2. Plot of the disappearance of **1b** with time (*a*) in dichloromethane, (*b*) in benzene, (*c*) in benzene in the presence of 0.1 mol-equiv. of Et_4Sn, (*d*) in benzene in the presence of 1.0 mol-equiv. of Et_4Sn.



metal. It might be anticipated that in the early stages of the reaction, when **1b** is present in relatively high concentration, reaction of [PdClH(cod)] with **1b** would be favored, but this is difficult to ascertain because $[PdCl_2(cod)]$ precipitates from solution.

When monitored in C_6D_6 solution, the disappearance of **1b** (which initially contained 10% **2a**) displayed a half-life of 70 min. The reaction occurred more slowly in CD_2Cl_2 solution (Fig. 2), with a half-life of 150 min. Reaction in dichloromethane also resulted in greater conversion to **2a** (ca. 60%). In contrast, when dissolved in CD_3CN **1b** reacted completely within 25 min to produce $[PdCl_2(cod)]$ and palladium metal, as well as free cyclooctadiene, ethene, and ethane, with no dimer being detected at all. Integration of the olefinic signals due to $[PdCl_2(cod)]$ and cyclooctadiene in the ^1H NMR spectrum indicated that they were formed in equal amounts. When 1 mol-equiv. of Et_4Sn was added to **1b** in C_6D_6 solution decomposition took place much more rapidly (Fig. 2) to give $[PdCl_2(cod)]$ and palladium metal, as well as C_2H_4 and C_2H_6, but **2a** was not formed. With 0.1 mol. equiv. of Et_4Sn the disappearance of **1b** was rapid initially (presumably until the

Scheme 1.



Et_4Sn was exhausted), then the rate of decomposition decreased to that of **1b** alone in benzene solution.

The origin of the observed rate difference in benzene and dichloromethane is uncertain. Acetonitrile may be a sufficiently good nucleophile for palladium to displace cyclooctadiene, and the resulting $[PdClEt(CD_3CN)_2]$ may decompose rapidly to give C_2H_4 and $[PdClH(CD_3CN)_2]$. Further reaction with **1b** would produce C_2H_6 and $[PdCl_2(cod)]$ and Pd metal, thereby accounting for the observed products. Rapid decomposition in the presence of Et_4Sn is consistent with our observations regarding the synthesis of **1b**. Excess Et_4Sn is likely to result in formation of $[PdEt_2(cod)]$, which would decompose by β-hydride elimination followed by reductive elimination of ethane. The dimethyl analogue was also reported to be unstable (5), although it would be susceptible only to Pd—C bond cleavage or reductive elimination. When the reaction of $[PdCl_2(cod)]$ with Et_4Sn was monitored by ^{119}Sn NMR, spectroscopy signals due to Et_4Sn and Et_3SnCl only were observed, indicating that only one ethyl group is transferred to palladium. Even with only 1 mol-equiv. of Et_4Sn, however, it is likely that some $[PdEt_2(cod)]$ is formed (leaving some $[PdCl_2(cod)]$ unreacted), which would decompose readily.

Complex **2a** underwent no further reaction in benzene or dichloromethane solution at ambient temperature, but when a C_6D_6 solution of **2a** was heated to 70°C rearrangement to its allyl isomer $[Pd_2(\mu\text{-}Cl)_2(\eta^3\text{-}C_8H_{13})_2]$, **2b**, occurred. The conversion was 60% complete after 5 h, but then the reaction appeared to reach equilibrium, and further heating caused decomposition. Complex **2b** was identified by its ^1H and $^{13}C\{^1H\}$ NMR spectra. It exhibits triplet and quartet resonances for the allyl functionality in its ^1H NMR spectrum, and the expected five resonances in its $^{13}C\{^1H\}$ NMR spectrum (see Experimental). That an equilibrium between **2a** and **2b** was indeed established was demonstrated by heating a toluene-d_8 solution of **2b** to 100°C for 30 min. Analysis of the solution revealed the presence of **2a** and **2b** in a 1:2 ratio, consistent with that found starting from **2a**.

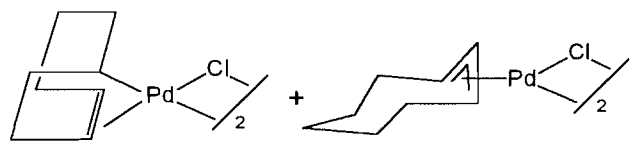
Espinet and co-workers have shown (8) that $[PdCl(C_6F_5)(cod)]$ undergoes a slow rearrangement in solution at ambient temperature to give a mixture of $[Pd_2(\mu\text{-}Cl)_2(\eta^1,\eta^2\text{-}C_8H_{12}\cdot C_6F_5)_2]$ and $[Pd_2(\mu\text{-}Cl)_2(\eta^3\text{-}C_8H_{12}\cdot C_6F_5)_2]$, the ratio of which was found to depend on the solvent employed. Interconversion of the two isomers was not detected at ambient temperature, and only 20% of $[Pd_2(\mu\text{-}Cl)_2(\eta^1,\eta^2\text{-}C_8H_{12}\cdot C_6F_5)_2]$ was converted to its η^3-allyl isomer after refluxing in chloroform for 80 h. They interpreted this to indicate that $[Pd_2(\mu\text{-}Cl)_2(\eta^1,\eta^2\text{-}C_8H_{12}\cdot C_6F_5)_2]$ is not an intermediate in the formation of the allyl complex, but that both are formed from a common intermediate $[Pd_2(\mu\text{-}Cl)_2(\eta^1\text{-}C_8H_{12}\cdot C_6F_5)_2]$, in which the remaining double bond is uncoordinated (8). In our work **2b** is not formed at 25°C so **2a** could be an intermediate in its formation, but a common intermediate of the type $[Pd_2(\mu\text{-}Cl)_2(\eta^1\text{-}C_8H_{13})_2]$ is also possible with coordination of the free double bond being much faster than rearrangement to the allyl form at ambient temperature. Equilibration of **2a** and **2b** occurs relatively easily at higher temper-

atures, suggesting that there is a lower activation barrier than in the pentafluorophenyl-substituted system. Espinet and coworkers pointed out the significance of slow isomerization of η^1,η^2- to η^3-allyl species and its relevance to organic synthesis via allylmetal complexes (11, 12). Related slow η^1,η^2- to η^3-allyl rearrangements have been observed previously (13, 14).

Although **2a** alone does not convert to **2b** at ambient temperature, we found that addition of free chloride ion (in the form of bis(triphenylphosphine)iminium chloride) to a CD_2Cl_2 solution of **2a** resulted in complete conversion to **2b** within 12 h. In contrast, addition of sodium acetate had no such effect. Addition of chloride to **2a** may result in bridge opening to form a species of the type $[PdCl_2(\eta^1,\eta^2\text{-}C_8H_{13})]^-$, in which rearrangement to the η^3 form occurs more readily. The rearrangement is likely to occur by a series of reversible β-eliminations, and this should be enhanced by the increased electron density on the palladium center in an anionic species. Since acetate is a weaker nucleophile for palladium, the addition of NaOAc resulted in no rate enhancement.

The formation of **2a** from [PtClEt(cod)], and its rearrangement to **2b**, prompted us to investigate alternative methods for the preparation of these dimeric complexes. It had been reported (15) that treatment of $PdCl_2$ with 2.3 equivalents of 1,5-cyclooctadiene in aqueous acetone for 20 h at ambient temperature produced **2a** in high yield. This was shown to occur by Wacker oxidation of one equivalent of cyclooctadiene to cycloocten-5-one, and addition of the HPdCl moiety thus formed to a second cyclooctadiene was proposed to account for the formation of **2a** (15). We have also obtained **2a** by this method. In addition, we found that **2a** can be prepared by treatment of $[PdCl_2(cod)]$ with 1.2 mol-equiv. of $NaBH_4$ in CH_2Cl_2–MeOH solution. When the reaction is carried out at ambient temperature extensive decomposition occurs, but if the reaction is performed at −60°C **2a** is formed cleanly and, although some decomposition to palladium metal occurs during the isolation procedure, the complex can be obtained in good yield. Complex **2b** has been prepared previously, by reaction of $[Pd(\eta^3\text{-}C_8H_{13})(cod)]ClO_4$ with excess LiCl (16). The corresponding bromide-bridged complex was also produced by passing CO through an ethanol solution of $PdCl_2$ and NaCl in the presence of excess 3-bromocyclooctene (17).

Since $[PdCl_2(cod)]$ is formed rapidly from cyclooctadiene and palladium(II) chloride or a tetrachloropalladate(II) salt, it seemed likely that it would be an intermediate in the formation of **2a** from $PdCl_2$ and 1,5-cyclooctadiene (15). Thus, we studied the reactions of $[PdCl_2(cod)]$ with free cyclooctadiene under a variety of conditions. When $[PdCl_2(cod)]$ alone was heated to 70°C for 5 min in water or in aqueous acetone a complex mixture of products was obtained, but when heated with 1 equivalent of cyclooctadiene in water conversion to **2a** occurred within 5 min, although considerable decomposition also took place. Decomposition was inhibited by addition of acetic acid. Thus, heating an aqueous acetic acid solution of $[PdCl_2(cod)]$ with free cyclooctadiene to 70°C for 5 min resulted in very little decomposition to palladium metal, and a mixture of **2a** and **2b** was obtained (eq. [1]). Heating to 100°C gave **2b** only. Whereas the presence of acetic acid appeared to stabilize the system (and promote allyl formation), reaction of $[PdCl_2(cod)]$ was inhibited by addition of hydrochloric acid. Heating a solution of the complex with 1 or 10 equivalents of cyclooctadiene in 6 M HCl resulted in quantitative recovery of $[PdCl_2(cod)]$. Similarly, heating an aqueous solution of $[PdCl_2(cod)]$ with free cyclooctadiene in the presence of 100 equivalents of sodium chloride produced no reaction.

[1] $[PdCl_2(cod)] + cod \xrightarrow[70°C,\ 5\ min]{H_2O/HOAc}$  **2a** + **2b**

Reactions involving K_2PdCl_4 gave similar results. When an aqueous solution of the salt containing 2 equivalents of cyclooctadiene was heated to 70°C for 5 min a mixture of $[PdCl_2(cod)]$ and **2a** was obtained, but considerable decomposition occurred. Addition of acetic acid again stabilized the system against decomposition. Prolonged heating to 70°C of an aqueous acetic acid solution of K_2PdCl_4 with cyclooctadiene produced a mixture of **2a** and **2b**, whereas heating of the mixture to 100°C gave the allyl complex **2b** as the sole product. Reaction of K_2PdCl_4 with cyclooctadiene was inhibited by excess HCl, only a small amount of $[PdCl_2(cod)]$ being formed after 35 min at 70°C, and neither of the dimeric complexes **2a** or **2b** was observed.

A number of points emerge from these studies. When $[PdCl_2(cod)]$ or K_2PdCl_4 was heated to 70°C in aqueous solution in the presence of excess cyclooctadiene a mixture of **2a** and **2b** was obtained within a few minutes. Thus, **2b** was formed much more rapidly than when **2a** was heated to the same temperature in benzene. At 100°C **2b** was formed as the exclusive product, suggesting that the equilibrium position between the two isomers considerably favors the η^3-allyl form at this temperature in aqueous solution. The role of acetic acid in preventing decomposition is unclear. On the other hand, the presence of excess HCl inhibited reaction of $[PdCl_2(cod)]$ to form **2a** and **2b**. If, as suggested by Stille and James (15), oxidation of cyclooctadiene proceeds by initial attack of water on the coordinated diene of $[PdCl_2(cod)]$ followed by loss of HCl, it would be expected that this process should be suppressed by the presence of HCl.

The observation that excess HCl also inhibits the formation of $[PdCl_2(cod)]$ from K_2PdCl_4 and cyclooctadiene is interesting. The reason for this may simply be that in the presence of a

Table 2. Crystal data and structure refinement for **1a**.

Emperical fomula	$C_{15}H_{19}ClPd$
Formula weight	341.15
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
Unit cell dimensions	a = 8.0378(12) Å, α = 90°
	b = 10.7825(10) Å, β = 90°
	c = 15.756(3) Å, γ = 90°
Volume, Z	1365.6(4) Å^3, 4
Density (calclulated)	1.659 Mg/m^3
Absorption coefficient	1.530 mm^{-1}
F(000)	688
Crystal size	0.4 × 0.1 × 0.06 mm
θ range for data collection	2.29°–27.50°
Limiting indices	$-10 \le h \le 10$, $-14 \le k \le 14$, $-20 \le l \le 20$
Reflections collected	6024
Independent reflections	3135 (R_{int} = 0.0915)
Absorption correction	Semi-empirical from ψ-scans
Max. and min. transmission	0.7957 and 0.7393
Refinement method	Full-matrix least squares on F^2
Data/restraints/parameters	3134/0/154
Goodness-of-fit on F^2	0.999
Final R indices [$I > 2\sigma(I)$]	$R1$ = 0.0518, $wR2$ = 0.0798
R indices (all data)	$R1$ = 0.0997, $wR2$ = 0.0918
Absolute structure parameter	−0.09(8)
Largest diff. peak and hole	0.583 and −0.498 e Å^{-3}

high concentration of free chloride, dissociation of Cl^- from $PdCl_4^{2-}$ is suppressed, thereby preventing coordination of the diene. This is significant in that reported procedures for the preparation of [$PdCl_2$(cod)] often involve the use of HCl. Whereas the initial report of the synthesis of the complex involved reaction of Na_2PdCl_4 with cyclooctadiene in methanol or acetone solution (18), more recent methods involve the use of a dilute solution of HCl in ethanol (19, 20). The concentration of HCl employed in these cases is considerably lower than that used here, but it should be pointed out that the presence of a high concentration of HCl could have a detrimental effect on the yield of [$PdCl_2$(cod)] prepared by this method.

Experimental

All reactions were carried out under an atmosphere of argon. Solvents were dried and distilled immediately prior to use. Tetraethyltin was obtained from Aldrich. Tetraphenyltin and tetrabenzyltin were prepared from $SnCl_4$ and the appropriate Grignard reagent. [$PdCl_2$(cod)] was prepared according to the method of Chatt et al. (18). NMR spectra were recorded on a Varian XL-300, Varian Unity plus 300, or Bruker ARX-500 spectrometer. ^{1}H and ^{13}C chemical shifts are relative to the residual solvent resonance. Microanalyses were performed by Atlantic Microlab, Inc, Norcross, Ga.

Preparation of [PdCl(CH_2Ph)(cod)], 1a

To a dichloromethane solution of [$PdCl_2$(cod)] (0.50 g, 1.8 mmol) was added $Sn(CH_2Ph)_4$ (1.2 g, 2.4 mmol). The yellow solution was refluxed for 7 h. The resulting black mixture was passed through a Hyflo Supercel column to remove palladium metal, then the solvent was evaporated. The residue was dissolved in a 80:20 mixture of CH_2Cl_2/hexane, and the solution was passed through a 14 × 1 cm silica column. The column was eluted with a total of 1 L of solvent, and the yellow fraction was collected. The solvents were evaporated, leaving the product as a yellow powder that was dried in vacuo (0.39 g, 66%). ^{1}H NMR ($CDCl_3$), δ(H): 2.39 m (CH_2), 3.59 s (CH_2Ph), 4.87 m, 5.89 m (=C*H*), 7.14 m, 7.43 m (C_6H_5). ^{13}C{^{1}H} NMR ($CDCl_3$); δ(C): 27.5, 30.9 (CH_2), 35.8 (CH_2Ph), 104.5, 123.7 (=*C*H), 125.7, 128.6, 129.5, 143.9 (C_6H_5). Anal. calcd for $C_{15}H_{19}ClPd$: C 52.81, H 5.61; found: C 52.81, H 5.66.

Preparation of [PdClEt(cod)], 1b

Tetraethyltin (0.307 mL, 1.55 mmol) was added by syringe to a CH_2Cl_2 (40 mL) solution of [$PdCl_2$(cod)] (0.772 g, 2.71 mmol). The system was protected from light, and stirred for 4 h at 20°C, then cooled in an ice bath. The solvent was evaporated at 0°C. The residue was washed with hexane to remove the tin compounds, then extracted with three 15 mL portions of benzene. The benzene extract was frozen in an ice bath, and the benzene was removed in vacuo, leaving the product as a yellow solid (0.156 g, 36% yield based on Et_4Sn used). ^{1}H NMR (CD_2Cl_2), δ(H): 1.26 t (CH_3), 1.57 m, 1.75 m (CH_2), 2.24 q (CH_2CH_3), 4.98 m, 5.72 m (=C*H*). ^{13}C{^{1}H} NMR (CD_2Cl_2), δ(C): 17.7 (CH_3), 27.3 (CH_2), 30.2 (CH_2CH_3), 30.7 (CH_2), 101.0, 123.6 (=*C*H). The benzene-insoluble material was identified as unreacted [$PdCl_2$(cod)] (0.567 g).

Table 3. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for **1a**. U(eq) is defined as one third of the trace of the orthogonalizede U_{ij} tensor.

Atom	x	y	z	U(eq)
Pd(1)	7713(1)	7935(1)	7052(1)	40(1)
Cl(1)	5972(3)	6341(2)	6582(1)	67(1)
C(1)	10114(9)	7409(7)	6198(5)	52(2)
C(2)	9016(9)	8000(8)	5708(4)	52(2)
C(3)	8985(11)	9361(9)	5510(5)	69(3)
C(4)	9378(11)	10212(7)	6241(5)	64(2)
C(5)	8740(10)	9790(6)	7103(6)	55(2)
C(6)	9605(9)	9040(7)	7658(5)	52(2)
C(7)	11280(9)	8445(8)	7511(5)	63(3)
C(8)	11602(9)	8001(8)	6604(5)	65(2)
C(9)	6106(8)	8248(6)	8040(5)	51(2)
C(10)	6327(8)	7336(6)	8737(4)	40(2)
C(11)	7306(10)	7577(6)	9439(4)	50(2)
C(12)	7454(10)	6728(8)	10096(5)	63(2)
C(13)	6669(10)	5635(8)	10047(6)	60(2)
C(14)	5702(11)	5351(7)	9366(5)	60(2)
C(15)	5529(10)	6193(8)	8713(5)	53(2)

Preparation of $[Pd_2(\mu\text{-}Cl)_2(\eta^1,\eta^2\text{-}C_8H_{13})_2]$, 2a

(a) From $[PdCl_2(cod)]$ and Et_4Sn

To a CH_2Cl_2 solution of $[PdCl_2(cod)]$ (0.30 g, 1.05 mmol) was added tetraethyltin (0.30 mL, 1.5 mmol) by syringe. The solution was stirred at ambient temperature for 15 h, during which time a mirror was deposited on the inside of the flask. The resulting solution was passed through a Hyflo Supercel column, and the solvent was evaporated. The yellow residue was washed with hexane, then extracted with benzene. The benzene solution was filtered to remove unreacted $[PdCl_2(cod)]$, then evaporated to dryness to leave the product as a yellow powder (0.12 g, 46%). ^1H NMR (C_6D_6), δ(H): 0.40 (m) H2; 0.60 (dd, 6.2 and 14.4 Hz) H8; 1.45 (dt, 10.8 and 4.4 Hz) H3, H3′; 1.55 (m) H7, H7′; 1.70 (m) H2′, H4; 1.92 (m) H4′; 2.13 (m) H8′; 3.90 (m) H1; 5.60 (m) H5; 5.88 (dt, 6.7 and 8.3 Hz) H6. $^{13}C\{^1H\}$ NMR (C_6D_6), δ(C): 26.3 (C7), 27.0 (C3), 28.7 (C4), 35.7 (C2), 40.2 (C8), 56.0 (C1), 100.7 (C5), 105.2 (C6). Anal. calcd. for $C_{16}H_{26}Cl_2Pd_2$: C 38.27, H 5.22; found: C 38.31, H 5.16.

(b) From $[PdCl_2(cod)]$ and $NaBH_4$

$[PdCl_2(cod)]$ (0.20 g, 0.70 mmol) was dissolved in CH_2Cl_2 (60 mL), and $NaBH_4$ (0.032 g, 0.85 mmol) was added. The mixture was cooled to −60°C and methanol (1 mL), previously cooled to −78°C, was added. After 24 h the solvents were removed in vacuo and the residue was extracted with CH_2Cl_2. After passing through a Hyflo Supercel column, the CH_2Cl_2 was evaporated to leave the product as a light yellow powder, which was washed with hexane and dried (0.134 g, 76%).

Preparation of $[Pd_2(\mu\text{-}Cl)_2(\eta^3\text{-}C_8H_{13})_2]$, 2b

K_2PdCl_4 (0.10 g, 0.31 mmol) was dissolved in a mixture of water (25 mL) and acetic acid (25 mL). The solution was heated to 100°C, then 1,5-cyclooctadiene (0.37 mL, 3.0 mmol) was introduced. The solution changed immediately from red to yellow, then to black. The mixture was maintained at this temperature for 20 min, then cooled in an ice bath, and extracted with CH_2Cl_2 (50 mL). The CH_2Cl_2 solution was washed with water (200 mL), then the solvent was evaporated to leave the product as a light yellow powder (0.043 g, 49%). ^1H NMR ($CDCl_3$), δ(H): 1.45 m, 6H (CH_2), 1.85 m, 2H (CH_2), 2.35 m, 2H (CH_2), 4.75 q, 2H (CH), 5.30 t, 1H (CH). δ(C): 23.2 (1C), 25.1 (2C), 31.1 (2C), 78.6 (2C), 105.0 (1C). Anal. calcd for $C_{16}H_{26}Cl_2Pd_2$: C 38.27, H 5.22; found: C 38.57, H 5.13.

Decomposition of 1b

The conversion of [PdClEt(cod)], **1b**, to $[Pd_2(\mu\text{-}Cl)_2(\eta^1,\eta^2\text{-}C_8H_{13})_2]$, **2a**, under various conditions was monitored by ^1H NMR spectroscopy using a Varian Unity plus 300 spectrometer. A 0.08 M solution of **1b**, containing about 10% **2a**, to which 0.01 M anisole was added as a standard, was prepared. A spectrum was recorded (using either a 1 s or 15 s delay between pulses) at ambient temperature approximately every 15 min. The olefinic signals due to the reactant and product were integrated relative to the anisole signal (3H) at 6.8 ppm.

X-ray structure determination

Light yellow colored rectangular plates were obtained by slow evaporation of a benzene/toluene (1:1) solution of $[PdCl(CH_2Ph)(cod)]$ at 0°C. A crystal of dimensions 0.4 × 0.1 × 0.06 mm was mounted on a glass fiber in random orientation and was coated with Superglue. Preliminary examination and data collection were performed using a Siemens P4RA automated single crystal X-ray diffractometer using monochromated Mo Kα radiation (λ = 0.71073 Å) at 22°C. Autoindexing of 10 centered reflections from the rotation photograph indicated an orthorhombic lattice. Equivalent reflections were checked to confirm the Laue symmetry and a fractional index search was conducted to confirm the cell lengths. Final cell constants and orientation matrix for data collection were calculated by least-squares refinement of the setting angles for 35 reflections ($12° < 2\theta < 25°$). Intensity data were collected using $\overline{\omega}$ scans with fixed scan speed. Friedel pairs were collected to confirm the absolute structure. Three representative reflections measured every 97 reflections showed 13.2% variation during data collection. Crystal data and intensity data collection parameters are listed in Table 2.

Data reduction was carried out using XSCANS and structure solution and refinement were carried out using the SHELXTL-PLUS (5.03) software (21). An absorption correction was applied to the data using equivalent reflections and $\overline{\psi}$ scan reflections. The structure was solved by the Patterson method and refined successfully in the space group $P2_12_12_1$. Full-matrix least-squares refinement was carried out by minimizing $\Sigma\omega(F_o^2 - F_c^2)^2$. The non-hydrogen atoms were refined using the appropriate riding model AFIX = m3. The final residual values were $R(F) = 5.18\%$ for 2042 observed reflections ($I > 2\sigma(I)$) and $wR(F^2) = 9.18\%$; $s = 1.0$ for all data. The absolute structure was confirmed by the Flack method ($x = -0.09(8)$). Structure refinement parameters are listed in Table 2. The atomic coordinates for the non-hydrogen atom are listed in Table 3. A projection view of the molecule, showing the atom labeling, is presented in Fig. 1 (non-hydrogen atoms are represented by 50% probability ellipsoids).

Complete listings of anisotropic displacements for the non-hydrogen atoms, and of positional and isotropic displacement

coefficients for the hydrogen atoms, have been submitted as supplementary material.[2]

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[2] Copies of material on deposit may be purchased from: The Depository of Unpublished Data, Document Delivery, CISTI, National Research Council Canada, Ottawa, Canada K1A 0S2. The table of hydrogen atom parameters has also been deposited with the Cambridge Crystallographic Data Centre, and can be obtained on request from The Director, Cambridge Crystallographic Data Centre, University Chemical Laboratory, 12 Union Road, Cambridge, CB2 1EZ, U.K.