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ALLYLPALLADIUM(II) COMPLEXES DERIVED FROM 1,2,6-HEPTATRIENE AND 1,2,8-NONATRIENE

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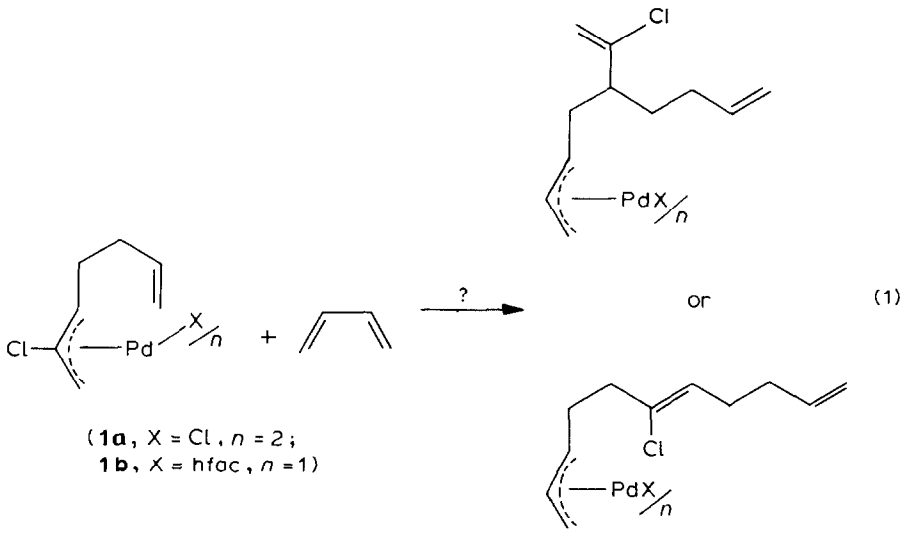
Summary

The reaction of 1,2,6-heptatriene with $PdCl_2(PhCN)_2$ gives a mixture of di-μ-chlorodi[1-(but-3-en-1-yl)-2-chloroallyl]di-palladium(II) and di-μ-chloro-di(η^3-2-methylene-3-chlorocyclohexyl)dipalladium(II) which could not be separated by conventional techniques. The structures of these compounds are ascertained from a study of the ^1H and ^{13}C NMR spectra and chemical properties of the mixture. A mechanism is proposed to account for the formation of the cyclic η^3-2-methylene-3-chlorocyclohexyl ligand. A corresponding reaction of 1,2,8-nonatriene with $PdCl_2(PhCN)_2$ gives di-μ-chlorodi[1-(hex-5-en-1-yl)-2-chloroallyl]dipalladium(II) as the sole product.

Introduction

The insertion reaction of 1,3-dienes into η^3-allylic palladium bonds has been the subject of numerous investigations and the mechanism of reaction has been discussed in terms of electrocyclic carbon–carbon bond formation [1]. It was further proposed that the mode of diene addition to the η^3-allylic function in subsequent steps leading to 1,2 or 1,4, polymerisation, could be subject to anchimeric control by the substituent side chain olefinic function [2,3]. To obtain further evidence for this effect, it was intended to study the 'insertion reactions' of the complex di-μ-chloro-di[-1-(but-3-en-1-yl)-2-chloroallyl]-dipalladium(II) (**1**), with 1,3-dienes (i.e. reaction 1). Previous studies have shown 2-chloroallyl palladium systems to be the most reactive with respect to olefin and diene insertion reactions [1,4,5] and consequently the η^3-allylic product(s) obtained from 'insertion' of a 1,3-diene into **1** should be less reactive with respect to subsequent diene insertions. This would facilitate a detailed study of reaction 1.

A good synthetic route to 2-chloro allylic complexes of palladium(II) is the reaction of 1,2-dienes with $PdCl_2(PhCN)_2$ [6,7]. This paper describes the reaction of $PdCl_2(PhCN)_2$ with 1,2,6-heptatriene (chosen in the hope of synthesising **1**) and with 1,2,8-nonatriene.



(**1a**, X = Cl, $n = 2$;
1b, X = hfac, $n = 1$)

Results and discussion

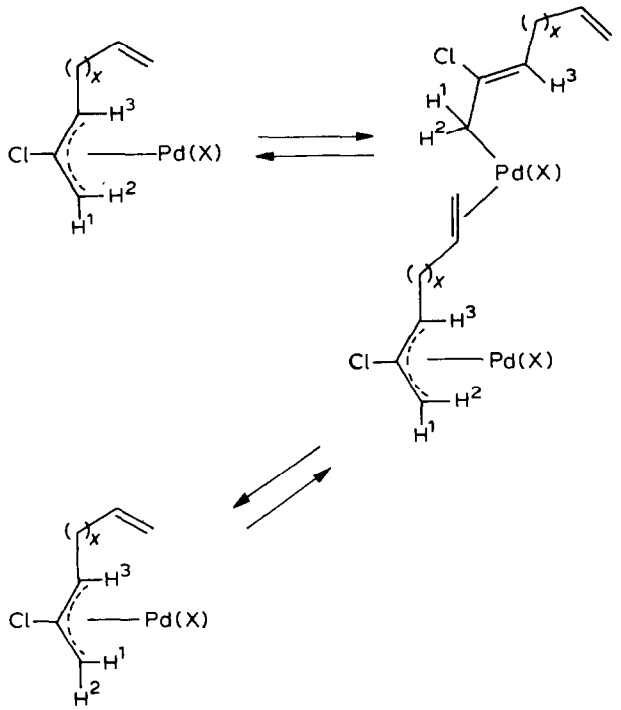
The reactions of $PdCl_2(PhCN)_2$ with 1,2,8-nonatriene in benzene gave the expected complex di-μ-chloro-di[1-hex-5-en-1-yl)-2-chloroallyl]dipalladium(II) (**2a**) as the only product. The structure **2a** was confirmed by elemental analysis and by analysis of the ^1H and ^{13}C NMR spectra of **2a** and its hexafluoroacetylacetonate derivative **2b**. (See Tables 1 and 2). Assignment of the spectra is based on analogy with those previously reported for 1-(but-3-en-1-yl)allylpalladium(II) derivatives [1,2]. The room temperature 60 MHz ^1H NMR spectrum of **2a** contained a broad singlet whilst that of **2b** exhibited a sharp singlet of relative intensity 2 assignable to the *syn* and *anti* protons H^1 and H^2. On cooling to $-70°C$ two distinct resonances for H^1 and H^2 are observed. Close to the coalescence temperature the line shape is particularly sensitive to changes in concentration indicative of an intermolecular exchange mechanism. The mechanism outlined in Scheme 1 is consistent with the experimental observations and has been previously observed in structurally related

TABLE 1

^1H NMR DATA [a] (δ, ppm downfield relative to internal standard TMS) FOR COMPLEXES **1** AND **2** IN $CDCl_3$, 34°C (60 MHz) (See Scheme 1 for numbering of protons b, broad; s, singlet; t, triplet)

Complex	X	$H^1 + H^2$ [b]	H^3	CH_2	X
1a	Cl	ca. 3.65(bs)	3.97(t) $J(H^3-CH_2)$ 6.5	– [c]	
1b	hfac	3.67(s)	4.01(t) $J(H^3-CH_2)$ 6.5	– [c]	6.07(s)
2a	Cl	ca. 3.6(bs)	3.94(t) $J(H^3-CH_2)$ 6.0	2.4–1.1	
2b	hfac	3.7(s)	3.96(t) $J(H^3-CH_2)$ 6.0	2.4–1.1	6.07(s)

[a] Vinylic protons excluded. [b] Resonances collapsed at 34°C due to rapid intermolecular exchange process (see text). [c] Further complicated due to presence of isomeric complex. (Coupling constants in Hz).



SCHEME 1. Mechanism of *syn-anti* exchange in complexes **1** ($x = 2$) and **2** ($x = 4$).

systems [1]. Addition of two molar equivalents of a tertiary phosphine (PPh_3 or $PMePh_2$) to **2a** resulted in the formation of $PdCl_2(PR_3)_2$ with liberation of 1,2,8-nonatriene (identified by its characteristic ^1H NMR) consistent with previous studies of 2-chloroallylpalladium chloride [6].

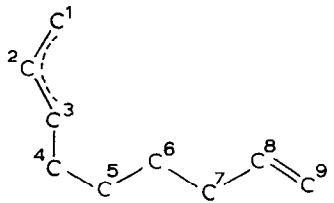
In contrast to the above studies the analogous reaction of $PdCl_2(PhCN)_2$ with 1,2,6-heptatriene yielded a mixture of two structurally isomeric complexes (of empirical formula $C_{14}H_{10}Cl_4Pd_2$ based on elemental analysis of the mixture) of which the complex di-μ-chloro-di[1-(but-3-en-1-yl)-2-chloroallyl]dipalladium(II) (**1a**) was one component (reaction 2). The ratio of **1a** to the isomeric product **3a** was

$$PdCl_2(PhCN)_2 + H_2C{=}C{=}CHCH_2CH_2CH{=}CH_2 \longrightarrow \underset{\textbf{(3a)}}{\text{Cl, H, Pd—Cl}_2} + \underset{\textbf{(1a)}}{\text{Cl—Pd—Cl}_2} \qquad (2)$$

found to be dependent on the reaction temperature. Reaction at 20°C in toluene afforded a ca. 1/1 mixture, whereas ratios of 1/1.3 and 1/2.6 (**1a**/isomeric product) were obtained from reactions at −40 and −78°C respectively. Separation of these

TABLE 2

^{13}C CHEMICAL SHIFT DATA FOR COMPLEXES **1a** AND **2a** RECORDED IN $CDCl_3$ AND C_6D_6 AT 34°C (Shifts quoted in ppm downfield from a TMS internal standard s, singlet; d, doublet; t, triplet)



Complex	Solvent	C^1	C^2	C^3	C^4	C^5	C^6	C^7	C^8	C^9
1a	$CDCl_3$	59.8	122.4	82.1	31.9 [c]	–	–	29.5 [c]	136.6	115.4
1a	C_6D_6	59.8	121.9	81.6	32.1 [c]	–	–	29.8 [c]	137.0	115.5
		^1J(C–H) [a,b]		J(C–H) [a,b]	^1J(C–H) [a,b]			^1J(C–H) [a,b]	^1J(C–H) [a,b]	
		164(t)	(s)	158(d)	130(t)			128(t)	154(d)	[e]
2a	$CDCl_3$	59.3	122.3	82.9	33.4 [c]	29.9 [c]	28.6 [c]	27.3 [c]	138.3	114.5
		^1J(C–H) [a,b]		^1J(C–H) [a,b]	^1J(C–H) [a,b]	^1J(C–H) [a,b]	^1J(C–H) [a,b]	^1J(C–H) [a,b]	^1J(C–H) [a,b]	^1J(C–H) [a,b]
		164(t)	(s)	158(d)	128(t)	130(t)	128(t)	128(t) [d]	154(d)	154(t)

[a] Coupling constants quoted in Hz to nearest integral value. [b] Multiplicities in parentheses. [c] Indicates assignments may be interchanged. [d] Approximate values due to mutual overlap. [e] Undetermined value.

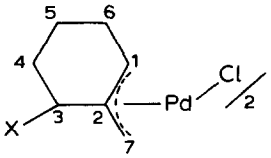
products using conventional techniques failed. The structural identification of **1a** is based on ^1H and ^{13}C NMR spectra of the product mixtures. Differences in relative intensities with changes in reaction temperatures together with comparison with the spectral features of **2a,b** and structural analogs [1] facilitated the assignment of resonances to complex **1a** and **1b** (the isomeric mixture was converted to a mixture of hfac derivatives by treatment with Tlhfac). The data are given in Tables 1 and 2. Again an intermolecular exchange of H^1 and H^2 of the type outlined in Scheme 1 was observed. Furthermore, addition of excess PPh_3 to the mixture of **1a** + isomeric product in $CDCl_3$ gave a complex ^1H NMR spectrum in which the resonances of 1,2,6-heptatriene (derived from the reaction of PR_3 with **1a**) were readily identified.

After assignment of resonances to **1a** there remain seven ^{13}C NMR resonances assignable to the isomeric product **3a**. These are given in Table 3 together with $J(^{13}C-^1H)$ data. The data are consistent with the isomeric product containing a $C_7H_{10}Cl$ unit composed of four 'CH_2', two 'CH' and one quaternary C group and are consistent with the η^3-2-methylene-3-chlorocyclohexyl structure **3a**. (For comparison Table 3 contains the ^{13}C NMR data for (η^3-2-methylene-3-methylcyclohexylpalladium chloride dimer [9].) The central and unsubstituted terminal allylic carbon atoms C^2 and C^7 were assigned to the singlet resonance at 121.2 ppm and the triplet resonance centred at 57.2 ppm respectively, typical of carbon nuclei in these environments.

The expected triplet splitting for the resonance assigned to carbon nucleus C^7 in the ^1H-coupled spectrum, clearly differentiated it from the neighbouring upfield resonance at 55.1 ppm which showed only a doublet splitting. This doublet resonance, was therefore assigned to the chloro-substituted tertiary ring carbon on the basis of its multiplicity and chemical shift value, which is in the expected region for this type of carbon nucleus [8]. It was not possible, however, on the basis of ^{13}C NMR data alone to determine which of the four non-allylic ring carbons bore the chlorine substituent, and confirmation of substitution at the 3-position adjacent to

TABLE 3

^{13}C NMR SPECTRAL PARAMETERS FOR (η^3-2-METHYLENE-3-METHYLCYCLOHEXYL)PALLADIUM CHLORIDE [9] AND COMPLEX **3a** RECORDED IN $CDCl_3$ AND C_6D_6 AT 34°C (Shifts quoted in ppm downfield from internal standard TMS)



Solvent	X	C^1	C^2	C^3	C^4	C^5	C^6	C^7
$CDCl_3$	Me [a]	71.71	121.76	20.99	29.3 [c]	26.81 [c]	16.01 [c]	57.27
$CDCl_3$	Cl	82.1	121.4	55.0	32.2 [c]	25.0 [c]	18.1 [c]	57.7
C_6D_6	Cl	81.6	121.2	55.1	32.4 [c]	25.0 [c]	18.2 [c]	57.2
		^1J(C–H) [b]		^1J(C–H) [b]			^1J(C–H) [b]	^1J(C–H) [b]
		158 (d)	(s)	164(d)	[d]	[d]	133(t)	162(t)

[a] Taken from ref. 9. [b] Multiplicities in parentheses; J in Hz: s, singlet; d, doublet; t, triplet. [c] Indicates values may be interchanged. [d] Undetermined values due to crowding.

the central allylic carbon atom relied on the 220 MHz ^{1}H NMR analysis of the resonance assigned to the proton on this carbon atom (see below). The ^{13}C NMR resonances of the remaining three methylene ring carbons occur at 32.4, 25.0, and 18.2 ppm, but no specific assignments for these signals are given. The assignment of the remaining resonance at 81.6 ppm (which overlaps with the signal for C^3 in complex **1a**), to the allylic ring carbon C^1 is supported by the doublet splitting and carbon–hydrogen coupling constant of 158 Hz exhibited by this resonance in the ^{1}H-coupled spectrum. The $\delta(^{13}C)$ chemical shift values in deuterochloroform for the unsubstituted analogous complex di-μ-chloro-di-[η^3-2-methylene-cyclohexyl]dipalladium(II), together with the 3-Me and 5-Me substituted derivatives have been reported [9]. Carbon atom C^1 of the unsubstituted complex was found to resonate at 65.5 ppm, while for the 3-Me and 5-Me derivatives this resonance experienced a small downfield shift of the order of 3 ppm. It is of interest to note that the introduction of a chloro substituent at the 3-position of the ring resulted in a substantial downfield shift of ~ 13 ppm, in the signal for this carbon atom [9]. Remote substituent effects of this order of magnitude while not unknown in ^{13}C NMR spectroscopy do not often occur, and the contributing factors to this deshielding are not clear. To further ascertain the structure proposed for complex **3a** several differential chemical tests were performed on samples of the mixture of isomeric complexes. Each of these tests was designed on the basis of expected differential chemical behaviour with the aim of obtaining evidence for the gross structural features of complex **3a** and are listed below.

(a) Attempted sublimation of (η^3-2-chloroallyl)Pd hfacac has been reported to result in disproportionation of this complex to form bis(hexafluoroacetylacetonate)palladium(II) and palladium chloride with loss of free allene [10]. Similarly, pyrolysis of the hexafluoroacetylacetonate derivatives (**1b** + **2b**) under a non-static vacuum successfully degraded the 2-Cl-allylic complex **1b** (i.e. reaction 3). Addition

$$\mathbf{1b} + \mathbf{3b} \xrightarrow[\text{vacuo}]{\text{heat}} Pd(hfac)_2 + PdCl_2 + \mathbf{3b} + \text{1,2,6-heptatriene} \quad (3)$$

of pentene to a a deuterochloroform solution of the residue (after removal of $Pd(hfac)_2$ and $PdCl_2$) caused further collapse of the two broad resonances at δ 3.87 and 2.78 ppm. These resonances are also present in the spectrum of the mixture of isomers but show a greater degree of collapse due to the presence of the terminal olefin in the non-cyclic isomer **1b**. These signals were, therefore, assigned to a pair of *syn/anti* allylic hydrogen atoms in the hfac complex **3b**. Collapse of each signal to a sharp singlet on double irradiation of the other signal showed that these protons were coupled to each other with a geminal coupling constant of 1 Hz. The lack of any further coupling to these protons confirms the 2-alkyl-substituted structure proposed for the η^3-allylic unit in **3**.

(b) Refluxing a benzene solution of the complex $[PdCl(C_3H_4Cl)(PPh_3)]$ leads to the expulsion of allene, and precipitation of the insoluble chloro-bridged dimer $[PdCl_2(PPh_3)]_2$ [6]. Similarly, treatment of the mixture of dimeric chloride-bridged isomers (**1a** + **3a**) with triphenylphosphine in a 1/2 ratio followed by open reflux to allow removal of the free 1,2,6-heptatriene, afforded, on precipitation of $[PdCl_2(PPh_3)]_2$ and work-up, off-white crystals of the mononuclear triphenyl-phosphine adduct **4**. Microanalytical and ^{1}H NMR data are consistent with the structure shown. The ^{1}H NMR spectrum of **4** in $CDCl_3$ as well as the peak assignments are

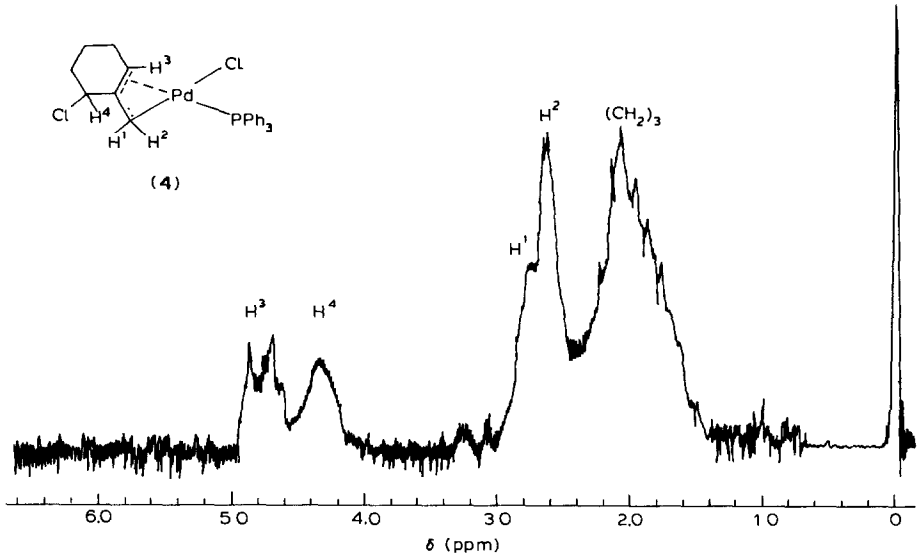


Fig. 1. ^{1}H NMR spectrum and peak assignments for complex **4** (60 MHz; $CDCl_3$; 34°C).

shown in Fig. 1. Individual proton assignments were made on the same basis as previous studies [11]. Protons H^1 and H^2 appear in the spectrum at δ 2.75 and 2.63 ppm respectively, as a pair of broad overlapping resonances. Proton H^3 resonated as a very broad doublet at δ 4.77 ppm coupled to the *trans* phosphorous ligand. The magnitude of this coupling constant was observed to be ~ 9 Hz, which is the expected value for coupling between an *anti* proton and a *trans* phosphine ligand. The proton H^4 on the chloro-substituted tertiary ring carbon appeared as a broad signal in the spectrum, with a chemical shift of δ 4.37 ppm, in good agreement with protons in this environment. The broad envelope in the δ 2.4–1.5 region was

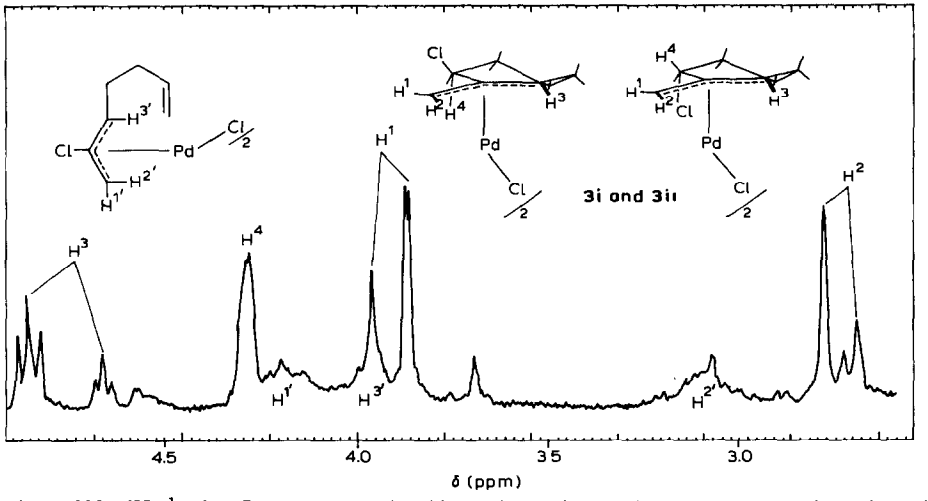


Fig. 2. 220 MHz ^{1}H NMR spectrum of the chloride-bridged isomeric mixture of complexes **1a** and **3a** recorded in $CDCl_3$ at 20°C (ring methylene proton resonances not shown).

assigned to the remaining six methylene protons on the ring carbons.

The complementary chemical ^{13}C and ^{1}H NMR data presented so far has established the basic structure of the carbon skeleton of the cyclic isomer **3**. The 220 MHz ^{1}H NMR spectrum of the isomeric mixture (**1a** + **3a**) (Fig. 2) confirms that the chlorine atom is attached to carbon atom C^3 and provides assignments of the allylic and methine proton resonances for the cyclic complex **3a**. The 220 MHz ^{1}H NMR spectrum (Fig. 2) shows two major sets of resonances in a 2.5/1 ratio for each of the allylic protons H^1, H^2 and H^3 of complex **3a** consistent with two isostructural forms **3i** and **3ii**. The multiplicity of the H^3 resonances confirms coupling to a neighbouring 'CH_2'. The corresponding resonances for proton H^4 on the chloro-substituted tertiary ring carbon were shown by integration to occur as a single broad resonance at $\sim \delta$ 4.29 ppm as a result of mutual overlap of the individual resonance. Due to the almost identical chemical shifts for proton H^4 in the two cyclic species **3i**, **3ii** resolution of neither resonance could be achieved, disallowing any stereochemical or positional assignments on the basis of individual peak multiplicities. However, by analogy to cyclohexene, the pseudo-cyclohexene ring of **3** is expected to adopt the more energetically favourable half-chair conformation [12]. Assuming the proton spin–spin coupling constants between equatorial-axial and diequatorial protons to be 2–3 Hz, and between diaxial protons to be 8–10 Hz, the respective predicted values for the total coupling for the 'CHCl' proton resonance is as follows: 3-Cl_{eq} 10–13 Hz; 3-Cl_{ax} 4–6 Hz; 4-Cl_{eq} 20–26 Hz; 4-Cl_{ax} 8–12 Hz (see Table 3 for numbering of carbon atoms). The value of the half-height peak-width for the resonance attributed to two H^4 protons was 10 Hz, consistent with the presence of both the 3-chloro-substituted equatorial and axial conformers. The two major sets of resonances in the spectrum are, therefore, assigned to the quasi-equatorially and quasi-axially 3-chloro-substituted conformers **3i** and **3ii** and chemical shift data for each conformer are tabulated in Table 4. Assignment of each conformer to a particular set of resonances could not be made unambiguously. Whilst it might be expected that the equatorial conformer (**3i**) may exist in greater abundance solely on steric grounds, a consideration of dipolar interactions (C–Cl with C–Pd) could well be more important thereby favouring **3ii** as the major species. Support for the latter conclusion comes from a structural study of 2-(3'-chloro-propen-2-yl)allylpalladium chloride dimer which shows the 3'-Cl substituent to be closely associated, in an axial position, with the Pd atom [13].

Chemical shift values for the allylic protons H^1 and H^2 on the unsubstituted end

TABLE 4

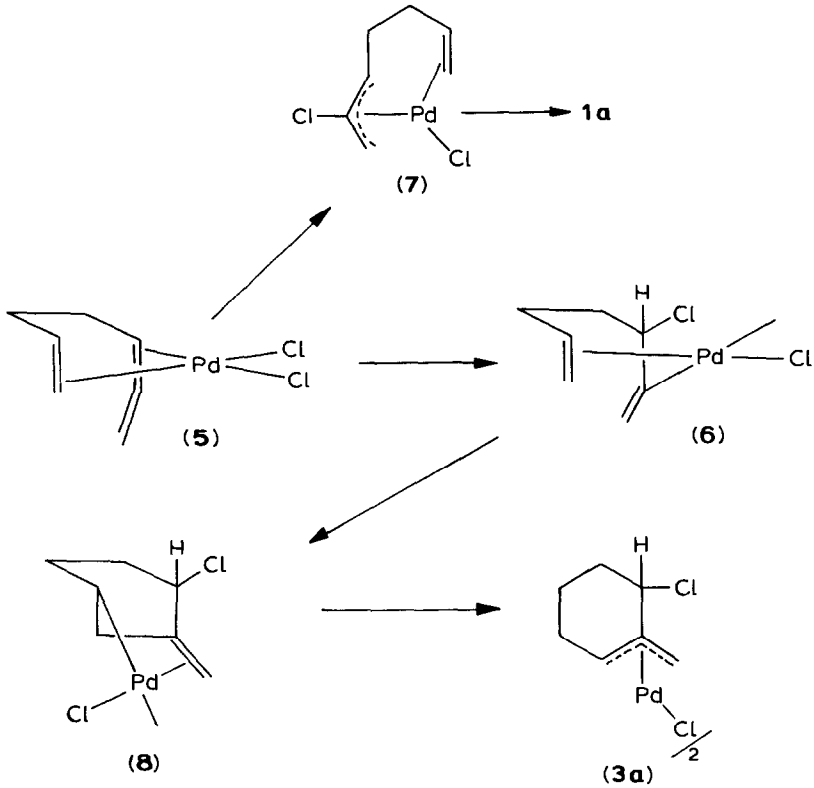
^{1}H NMR CHEMICAL SHIFTS (δ ppm downfield relative to TMS) FOR THE ALLYLIC PROTONS AND METHINE RING PROTON OF THE TWO CONFORMERS OF COMPLEX **3** IN $CDCl_3$ AT 20°C (220 MHz) (See Fig. 2 for proton numbering scheme; b, very broad; u, unresolved; s, singlet; d, doublet)

Conformer	H^1	H^2	$H^{4\,a}$	$H^{3\,b}$
A	3.87(d) $J(1-2)$ 1.5 Hz	2.78(ud)	~ 4.29(bs)	4.85(dd)
B	3.96 [c](s)	2.68(s)	~ 4.29(bs)	4.66(dd)

[a] Approximate value due to mutual overlap of the two resonances. [b] J values all of the order of 5–6 Hz. [c] Overlaps with resonance for proton H^3 in complex **1a**.

of the allylic function, and the methine proton H^4 of the conformers **3i** and **3ii** are all within the usual range generally observed for these types of proton nuclei. The low field values of δ 4.85 and 4.66 ppm found for the *anti*-protons H^3 on the substituted allylic carbon atoms were noticeably to lower field than previously assigned protons in similar environments [9,14]. For the unsubstituted complex di-μ-chloro-di-[η^3-2-methylenecyclohexyl]dipalladium(II) a value of δ 4.14 was reported for this proton, which was shifted to δ 4.43 ppm for the 3-methyl-substituted analogue.

The proposed mechanism of cyclisation leading to the formation of complex **3a** is outlined in Scheme 2. The formation of the intermediate **5**, in which the 1,2,6-

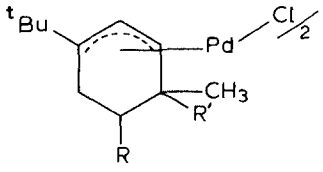


SCHEME 2. Proposed mechanism for the formation of **1a** and **3a**.

heptatriene molecule acts as a bidentate pseudo 1,5-diene ligand, has ample precedence from the complexes of 1,5-hexadiene and 1,5-cyclooctadiene with palladium(II) [15]. Insertion of the coordinated allenic double bond into a Pd–Cl bond in which the chlorine migrates to carbon atom C^3 would give rise to the 1,5-dienyl complex **6**. The alternative route involving chlorine migration to the central carbon atom C^2 would be expected to result in formation of the 2-chloroallylic complex **7** which would readily rearrange to **1a** [1]. Insertion of the coordinated olefin into the Pd–C σ-vinyl bond of **6** leads to the proposed intermediate **8**. Several reactions of this type are known and have been found to occur under mild conditions [16,17]. A rapid

1,2-hydrogen and palladium shift (via β-H transfer) then follows to give the product **3a**.

The molecular transformations outlined in Scheme 2 provide a plausible explanation for the formation of **3a** from 1,2,6-heptatriene. A similar series of steps has been used to rationalise the formation of η^3-allylic palladium complexes in the non-oxidative coupling reaction of mono-olefins and acetylenes [16] (the Pd–vinyl bond in this case is derived from the initial insertion of the acetylene into a Pd–Cl bond). Some similarities are also apparent between the mechanism outlined in Scheme 2 and the previously proposed mechanism for the formation of **9** from the reaction of



(9)

2-t-butyl-1,3-butadiene with η^3-allyl palladium chlorides [17]. The overall reaction sequence for formation of **3a** can therefore be classed as a non-oxidative cyclisation reaction.

The absence of a cyclic product from the reaction of 1,2,8-nonatriene with dichlorobis(benzonitrile)palladium(II) is seen as a consequence of the inability of the 1,2,8-nonatriene molecule to act as an effective chelating bidentate ligand.

Experimental section

^{1}H NMR spectra were run on Varian Associates Model T-60, or HR-220 spectrometers. ^{13}C NMR spectra were run on a Varian Associates Model CFT-20 spectrometer operating in the pulsed Fourier Transform mode.

Dichlorobis(benzonitrile)palladium(II) was prepared by the method of Kharasch [18]. 1,1,1,5,5,5-Hexafluoropentan-2,4-dionatothallium(I) was prepared by the literature method [19]. 1,2,8-Nonatriene was prepared by the one step olefin-to-allene conversion starting from 1,7-octadiene. The preparation of 1,2,6-heptatriene was carried out in two stages with intermediate isolation of 1,1-dibromo-2-(3-butenyl)cyclopropane [20,21]. 1,7-Octadiene, 1,5-hexadiene, dimethylphenylphosphine and triphenylphosphine were commercial samples used without further purification.

*Complexes **1**: di-μ-chloro-di-[1-(but-3-en-1-yl)-2-chloroallyl]dipalladium(II) and **3a**: di-μ-chloro-di-(η^3-2-methylene-3-chlorocyclohexyl)dipalladium(II)*

1,2,6-Heptatriene (1.06 ml, 0.0083 mol) was added dropwise at room temperature to a solution of dichlorobis(benzonitrile)palladium(II) (3.2 g, 0.0083 mol) in benzene (90 ml) and the resultant clear yellow solution stirred 15 min. Solvent was removed in vacuo and the residue columned on Florisil eluting with pentane then benzene. Reduction of volume of the benzene eluate followed by addition of pentane induced crystallisation yielding the products in an equimolar ratio as a yellow solid (1.125 g, 50%).

Found: C, 31.04; H, 3.83; Cl, 25.93. $C_{14}H_{20}Cl_4Pd_2$ calcd.: C, 30.95; H, 3.69; Cl, 26.16%.

Complex ***2a****: di-μ-chloro-di[1-(hex-5-en-1-yl)-2-chloroallyldipalladium(II)*, was prepared as above and isolated as a yellow solid on recrystallisation from hexane (30%), m.p. 116°C.

Found: C, 36.09; H, 4.79; Cl, 23.57. $C_{18}H_{28}Cl_4Pd_2$ calcd.: C, 36.07; H, 4.68; Cl, 23.71%.

Hexafluoroacetylacetonate derivatives

Complexes ***1b****: 1,1,1,5,5,5-hexafluoropentan-2,4-dionato-[1-(but-3-en-1-yl)-2-chloroallyl]palladium(II) and* ***3b****: 1,1,1,5,5,5-hexafluoropentan-2,4-dionato-[-2-methylene-3-chlorocyclohexyl]palladium(II)*

A 1/1 solution mixture of **1a** and **3a** (0.772 g) in dichloromethane (25 ml) was treated with 1,1,1,5,5,5-hexafluoropentan-2,4-dionato-thallium(I) (1.17 g) and stirred (3 h). The precipitated thallous chloride was filtered off and the filtrate passed through a short Florisil column eluting with dichloromethane. Evaporation of the eluate to dryness and pumping under high vacuum yielded the products as a yellow oil (1.04 g, 82%). The products were identified by ^{1}H NMR spectroscopy and mass spectral analysis which showed a parent ion at *m/e* 442 (based on the ^{106}Pd isotope).

Complex ***2b****: 1,1,1,5,5,5-hexafluoropentan-2,4-dionato-[1-(hex-5-en-1-yl)-2-chloroallyl]palladium(II)*, was similarly prepared and isolated as cream needles identified by ^{1}H NMR spectroscopy and mass spectral analysis which showed a parent ion at *m/e* 470 (based on the ^{106}Pd isotope).

Complex ***4****.* A 1/1 mixture of di-μ-chloro-di[1-(but-3-en-1-yl)-2-chloroallyl]dipalladium(II) and di-μ-chloro-di-[η^3-2-methylene-3-chlorocyclohexyl]dipalladium(II) (0.149 g) in hot benzene (4 ml), was treated with triphenylphosphine (0.146 g) in hot benzene (1 ml). The resultant solution was open refluxed for 3 h, and solvent replenished to allow removal of liberated 1,2,6-heptatriene from the system. Evaporation of the solvent under reduced pressure and recrystallisation of the residue from absolute ethanol yielded off-white crystals of *(η^3-2-methylene-3-chlorocyclohexyl)-chloro-(triphenylphosphine)palladium(II)* (0.074 g, 25%), m.p. 76.5–77.5°C.

Found: C, 55.43; H, 5.32; Cl, 12.41. $C_{25}H_{25}Cl_2PPd \cdot EtOH$ calcd.: C, 55.93; H, 5.39; Cl, 12.23%. (EtOH of solvation confirmed by ^{1}H NMR).

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