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TRANSITION METAL PROMOTED REACTIONS OF UNSATURATED HYDROCARBONS

III*. INSERTION OF 1,2-DIENES INTO ALLYLIC PALLADIUM BONDS

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SUMMARY

The insertions of allene, methylallene, 1,1-dimethylallene and 1,3-dimethylallene into the allylic palladium bonds of the complexes (π-All)Pd(X) (I): X= chloride, acetylacetonate, or hexafluoroacetylacetonate, to give new π-allylic products (II) [*e.g.* 2-C_3H_4–($CR^1R^2C{=}CR^3R^4$)Pd(X)] has been investigated. Reaction of (π-All)Pd(acac) complexes with liquid allene yields, as a side-product, bis(acetylacetonato)-2,2'-bi-π-allyldipalladium(II). Addition of 1,2-dienes to $CDCl_3$ solutions of complexes (I) promotes exchange on the NMR time scale of the allylic *syn*- and *anti*-protons via a σ-allylic intermediate. The rate of *syn–anti* proton exchange decreases in the order: All=2-chloroallyl > allyl > 2-methylallyl > 2-tert-butylallyl; 1,2-Diene=1,1-dimethylallene > 1,3-dimethylallene > methylallene > allene > tetramethylallene ≈ 1,3-di-t-butylallene; X=Hfacac ≫ Acac > Cl. The rate of formation of the insertion product (II) decreases in the order: All=2-chloroallyl > allyl > 2-methylallyl ≫ 2-tert-butylallyl; 1,2-Diene=1,3-dimethylallene > 1,1-dimethylallene > methylallene > allene ≫ tetramethylallene ≈ 1,3-di-t-butylallene; X=Hfacac > Acac ≈ Cl. To account for the stereochemical features of this reaction, and the unusual order of coordinative abilities and reactivities of the different 1,2-dienes, a mechanism is proposed in which the 1,2-diene preferentially coordinates to palladium via its less substituted olefinic function to generate a σ-allylic intermediate (σ-All) (1,2-diene)Pd(X). Direct carbon migration of the σ-bonded carbon of the σ-allyl to the central allenic carbon occurs to give the product (II). The relative reactivities of methyl substituted allenes may be rationalized in terms of a small degree of polarization of the π-1,2-diene–Pd bond in the transition state for the σ-allyl migration.

INTRODUCTION

The insertion of 1,2-dienes into various Pd–X bonds has been reported by

* For part II see ref. 1a; a preliminary account of part of this work has appeared[1b].

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several groups of workers. Insertion into the Pd–Cl bond has been shown[2–5] to occur in two ways, depending upon the 1,2-diene and the solvent. Shier has demonstrated that *trans*-$(PEt_3)_2PdCl(Ph)$ does not react with allene[6]. On addition of $AgBF_4$ however, AgCl is precipitated, and the ionic complex $[(\pi\text{-2-phenylallyl})Pd(PEt_3)_2]$-$BF_4$ derived from allene insertion into the phenyl–Pd bond is readily isolated[6].

This reaction serves to illustrate the importance of a vacant coordination site on the palladium being available to accommodate a molecule of allene prior to insertion, *i.e.* Cl^- must be stripped from the original complex in order for insertion to occur.

Clark *et al.*[7] have shown that the cationic platinum complex *trans*-$[PtMe(L)Q_2]^+PF_6^-$ ($Q = PMe_2Ph$, $AsMe_3$; L = acetone) reacts with allene below 0° to yield an analogous π-allene complex (L = allene). On warming, this rearranges via an intramolecular process to yield a π-2-methylallyl complex by allene insertion into the Pt–Me bond. Similar insertions of allene into Pt–H[8] and Rh–H[9] bonds have been reported.

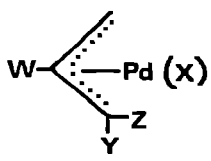
We here present the results of a study of the insertion of allene, and methyl-substituted allenes, into the allylic palladium bonds of (I) [X = Cl, Acac, Hfacac (hexafluoroacetylacetonate)] to give the new π-allylic complexes (II)–(IV).

During the course of this investigation the reaction of allene with complexes (I) [X = Cl] was reported[10–12] to yield complexes (II a, d) together with the chloro-bridged analogous of complexes (IIIe) and (IV b). These authors proposed a mechanism for allene insertion involving an intermediate containing a π-bonding-allyl and a π-allene ligand. Coordination of allene to palladium was envisualised as the rate-determining step for insertion. We have carried out a detailed study of 1,2-diene insertion into allylic–palladium bonds of (I) [X = Hfacac] using ^1H NMR spectroscopy. The results have shown the previous mechanistic proposals[10–12] to be incorrect. A mechanism, in which migration of a σ-allyl carbon to the central carbon of a coordinated allenic moiety, is the rate determining step, is proposed.

RESULTS AND DISCUSSION

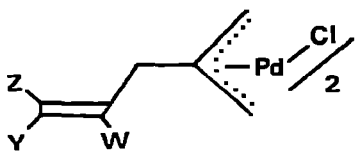
Isolation and characterisation of 1,2-*diene insertion products*

Reactions of complexes (I a, c, d) [X = Cl] with allene to give (IIa, c, d) were effected by sealed tube reactions at ambient temperatures using an excess of allene in benzene solution. The solid complex (I) [X = Cl] slowly went into solution over a period of one week. Longer reaction times could be used since the product (II) appeared reluctant to insert another molecule of allene. Complex (I b) (X = Cl], containing a π-2-methylallyl substituent also showed reluctance to insert a molecule of allene, and we were only able to isolate an inseparable mixture of (I b) and (II b). Longer reaction times led apparently to further insertion of allene into the allylic–palladium bond of (II b), in competition with insertion into (I b). A similar reaction procedure using complexes (Ia, c, d) [X = Acac] gave high yields of complexes (III a–d). Complex (I b) [X = Acac] showed a marked reluctance to insert allene and, parallelling the behaviour of its chloro analogue, only a mixture of (I b) and (III b) was obtained. Complex (III e) was isolated by allowing complex (I e) [X = Acac] to stand overnight in a saturated solution of allene in benzene. The sealed tube reactions of complexes (I a–d) [X = Acac] with excess allene also yielded trace ($\approx 1\%$) amounts



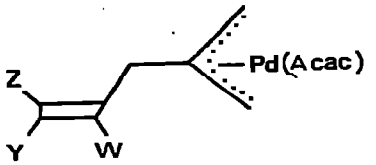
(I)

(a) W=Y=Z=H
(b) W=CH_3; Y=Z=H
(c) W=Z=H; Y=CH_3
(d) W=H; Y=Z=CH_3
(e) W=Z=H; Y=$COOCH_3$
(f) W=Cl; Y=Z=H
(g) W=^{t}Bu; Y=Z=H



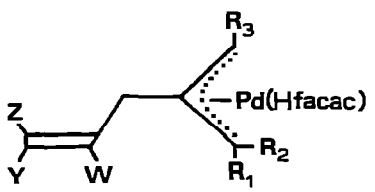
(II)

(a) W=Y=Z=H
(b) W=CH_3; Y=Z=H
(c) W=Z=H; Y=CH_3
(d) W=H; Y=Z=CH_3

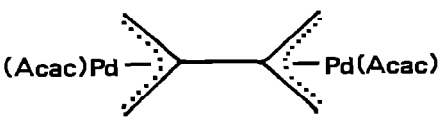


(III)

(a) W=Y=Z=H
(b) W=CH_3; Y=Z=H
(c) W=Z=H; Y=CH_3
(d) W=H; Y=Z=CH_3
(e) W=Z=H; Y=$COOCH_3$



(IV)



(V)

(a) W=Y=Z=H; R^1=R^2=R^3=H
(b) W=Cl; Y=Z=H; R^1=R^2=R^3=H
(c) W=Cl; Y=Z=H; R^1=CH_3; R^2=R^3=H
(d) W=Cl; Y=Z=H; R^1=R^2=CH_3; R^3=H
(e) W=Cl; Y=Z=H; R^1=R^3=CH_3; R^2=H
(f) W=Z=H; Y=$COOCH_3$; R^1=CH_3; R^2=R^3=H
(g) W=Z=H; Y=$COOCH_3$; R^1=R^3=CH_3; R^2=H

of an insoluble white complex, shown by unambiguous synthesis to be complex (V), containing a 2,2′-bi-π-allyl ligand[10]. The yield of complex (V) could be increased to ca. 40% by reaction of complexes (I a–d) [X=Acac] with neat liquid allene in a sealed tube. The major organic product of this side-reaction when using complex (I a) was shown by VPC analysis to be 1,5-hexadiene.

Reactions of complexes (I a, f) [X=hexafluoroacetylacetonate; Hfacac] with allene were found to proceed more rapidly than their chloro or Acac analogues, and yielded complexes (IV a) and (IV b) respectively. These reactions could be carried out on a 1/1 molar basis. Complexes (I e, f) also reacted readily with 1-methylallene, 1,1-dimethylallene or 1,3-dimethylallene to yield complexes (IV c–g). We have been unable to effect insertion of tetramethylallene or 1,3-di-tert-butylallene into the allylic–palladium bonds of complexes (I) [X=Cl, Acac, or Hfacac] and have also been unable to insert any of the 1,2-dienes into the 2-tert-butylallyl–palladium bond of complex (I g) [X=Hfacac], under the mild conditions described above. Reaction of complex (VI), containing a triphenylphosphine ligand, with allene in a sealed tube,

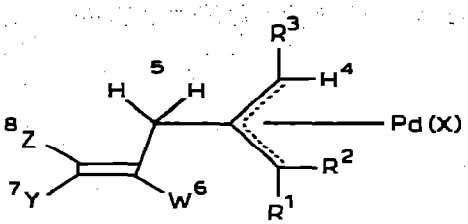
(*continued on p.* 414)

TABLE 1

^{1}H NMR DATA FOR COMPLEXES (II), (III) AND (IV) (60 MHz; $CDCl_3$, 34°)

Complex	*X*	*W*	*Y*	*Z*	R^1	R^2	R^3	*τ (multiplicity)[a]; J (Hz)*	
								H^1	H^2
(IIa)	Cl	H	H	H	H	H	H	6.13 (s)	7.09 (s)
(IIb)	Cl	CH_3	H	H	H	H	H	6.14 (s)	7.05 (s)
(IIc)	Cl	H	CH_3	H	H	H	H	6.15 (s)	7.10 (s)
(IId)	Cl	H	CH_3	CH_3	H	H	H	6.18 (s)	7.16 (s)
(IIIa)	Acac	H	H	H	H	H	H	6.37 (s)	7.24 (s)
(IIIc)	Acac	H	CH_3	H	H	H	H	6.35 (s)	7.24 (s)
(IIId)	Acac	H	CH_3	CH_3	H	H	H	6.37 (s)	7.28 (s)
(IIIe)	Acac	H	$COOCH_3$	H	H	H	H	6.37 (s)	7.18 (s)
(IVa)	Hfacac	H	H	H	H	H	H	≈6.10 (b)[c]	≈7.00 (b)[c]
(IVb)	Hfacac	Cl	H	H	H	H	H	5.94 (s)	6.90 (s)
(IVc)	Hfacac	Cl	H	H	CH_3	H	H	8.52 (d) $J_{1,2}$6.5	6.13 (q) $J_{1,2}$6.5
(IVc)[b]	Hfacac	Cl	H	H	CH_3	H	H	9.14 (d) $J_{1,2}$6.5	6.97 (q) $J_{1,2}$6.5
(IVd)	Hfacac	Cl	H	H	CH_3	CH_3	H	8.56 (s)	8.71 (s)
(IVe)	Hfacac	Cl	H	H	CH_3	H	CH_3	8.69 (d) $J_{1,2}$6.5	6.35 (q) $J_{1,2}$6.5
(IVe)[b]	Hfacac	Cl	H	H	CH_3	H	CH_3	9.10 (d) $J_{1,2}$6.5	7.10 (q) $J_{1,2}$6.5
(IVf)	Hfacac	H	$COOCH_3$	H	CH_3	H	H	8.73 (d) $J_{1,2}$6.5	≈6.2[d]
(IVf)[b]	Hfacac	H	$COOCH_3$	H	CH_3	H	H	9.27 (d) $J_{1,2}$6.5	7.08 (q) $J_{1,2}$6.5
(IVg)	Hfacac	H	$COOCH_3$	H	CH_3	H	CH_3	8.73 (d) $J_{1,2}$6.5	6.38 (q) $J_{1,2}$6.5
(IVg)[b]	Hfacac	H	$COOCH_3$	H	CH_3	H	CH_3	9.20 (d) $J_{1,2}$6.5	7.22 (q) $J_{1,2}$6.5

[a] Notation: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; b, broad. [b] In C_6D_6 solution. [c] The resonances of these protons are very broad due to an intermolecular site-exchange process. [d] Obscured by H^7 resonance.



H^3	H^4	H^5	H^6	H^7	H^8	X resonances
6.13 (s)	7.09 (s)	6.94 (dd) $J_{5,6}$6	4.01 (m)	4.86 (m)	4.73 (m)	
		$J_{5,8}$1				
6.14 (s)	7.05 (s)	6.98 (bs)	8.09 (t) $J_{6,5}$1	5.11 (bs)		
6.15 (s)	7.10 (s)	7.00 (bd) $J_{5,6}$6	≈4.40 (m)	8.30 (bd) $J_{7,8}$6	≈4.40 (m)	
6.18 (s)	7.16 (s)	7.00 (d) $J_{5,6}$8	4.71 (tq) $J_{5,6}$8 $J_{6,7}$1	8.26 (s) $J_{6,7}$1	8.30 (s)	
6.37 (s)	7.24 (s)	6.88 (bd) $J_{5,6}$6	4.10 (m)	4.97 (m)	4.75 (m)	CH, 4.65 (s); CH_3, 8.02 (s)
6.35 (s)	7.24 (s)	6.94 (bd) $J_{5,6}$4	≈4.40 (m)	8.30 (m)	≈4.40 (m)	CH 4.63 (s); CH_3, 8.05 (s)
6.37 (s)	7.28 (s)	6.93 (d) $J_{5,6}$8	4.71 (tq) $J_{5,6}$8 $J_{6,7}$1.5	8.27 (d) $J_{6,7}$1.5	8.33 (s)	CH, 4.63 (s); CH_3, 8.03 (s)
6.37 (s)	7.18 (s)	6.75 (dd) $J_{5,6}$7 $J_{5,8}$1.5	2.97 (dt) $J_{5,6}$7 $J_{6,8}$16	6.27 (s)	4.08 (dt) $J_{6,8}$16 $J_{5,8}$1.5	CH, 4.63 (s); CH_3, 8.03 (s)
≈6.10 (b)[c]	≈7.00 (b)[c]	6.90 (dd) $J_{5,6}$6 $J_{5,8}$1	4.30 (m)	5.00 (m)	4.75 (m)	CH, 4.05 (s)
5.94 (s)	6.90 (s)	6.58 (s)		4.60 (s)		CH, 4.03 (s)
6.08 (s)	7.15 (s)	6.54 (q) J_{gem}15		4.67 (s)		CH, 3.93 (s)
6.63 (s)	7.83 (s)	7.26 (q) J_{gem}15		5.03 (d) $J_{7,8}$1.5	5.27 (dt) $J_{7,8}$1.5 $J_{5,8}$1	CH, 3.80 (s)
6.11 (d) $J_{3,4}$2	6.66 (d) $J_{3,4}$2	6.51 (q) J_{gem}16		4.67 (d) $J_{7,8}$2	4.73 (dt) $J_{7,8}$ 2 $J_{5,8}$1	CH, 3.95 (s)
8.69 (d)	6.35 (q)	6.42 (bs)		4.69 (bs)		CH, 3.97 (s)
9.10 (d)	7.10 (q)	7.10 (bs)		5.01 (d) $J_{7,8}$1.5	5.26 (dt) $J_{7,8}$1.5 $J_{5,8}$1	CH, 3.79 (s)
≈6.2[d]	7.15 (s)	6.65 (td)[c] $J_{5,6}$7 $J_{5,8}$1.5	2.98 (dt) $J_{6,8}$16 $J_{5,6}$7	6.25 (s)	4.03 (dt) $J_{6,8}$15 $J_{5,8}$1.5	CH, 3.92 (s)
6.8 (s)	7.95 (s)	7.53 (ddd)[c] $J_{5,6}$7 $J_{5,8}$1.5	3.33 (dt) $J_{6,8}$16 $J_{5,6}$7	6.55 (s)	4.37 (dt) $J_{6,8}$16 $J_{5,8}$1.5	CH, 3.80 (s)
8.73 (d)	6.38 (q)	6.60 (dd) $J_{5,6}$6.5 $J_{5,8}$1.5	3.02 (dt) $J_{5,6}$6.5 $J_{6,8}$16	6.25 (s)	4.05 (dt) $J_{6,8}$16 $J_{5,8}$1.5	CH, 3.97 (s)
9.20 (d)	7.22 (d)	7.30 (dd) $J_{5,6}$7 $J_{5,8}$1.5	3.30 (dt) $J_{5,6}$6.5 $J_{6,8}$16	6.53 (s)	4.30 (dt) $J_{6,8}$16 $J_{5,8}$1.5	CH, 3.81 (s)

[c] Although the methylene protons in this complex are diastereotopic and give rise to anisochronous resonances, the outer lines of the expected AB system could not be distinguished. Hence J_{gem} could not be measured.

was extremely slow. However after a period of *one year* at room temperature, insertion was found to have occurred, yielding complex (VII).

Complexes (II)–(IV) and (VII) were characterised by ^{1}H NMR spectroscopy, mass spectrometry and elemental analysis. ^{1}H NMR data for complexes (II)–(IV) are presented in Table 1. Data for complex (II b) was obtained from a mixture of this complex and its π-allylic precursor (I b) [X=Cl]. An analysis of the ^{1}H NMR spectra of representative complexes fully illustrates the stereochemistry of the insertion reaction. The ^{1}H NMR spectra of complexes (II a–d), (III a–e) and (IV a, b) exhibit two singlet resonances for the allylic *syn*- and *anti*-protons, typical of a symmetrically bonded 2-substituted π-allylic moiety. The olefinic region of the spectra of all insertion products is only consistent with a structure in which the substituents W, Y and Z, originally present in the precursor complexes (I), occupy positions on the olefinic carbon atoms. Examination of the spectra of complexes (III e) or (IV f, g), derived from insertion of 1,2-dienes into the 1-*syn*-(methoxycarbonyl)allyl–palladium bond, demonstrates that the geometry of the olefin function in the products is *trans*-disubstituted, by virtue of the value of $J_{6,8}$(16 Hz)[13]. Thus the mode of 1,2-diene insertion into the allylic–palladium bond parallels the insertion of bicyclic olefins[1,14] in that the 1,2-diene inserts into the least substituted end of the allylic–palladium function and that the relative geometries of substituents W, Y and Z on the allylic group are retained in the products.

In the ^{1}H NMR spectra of complexes (IV c, d, f), derived from insertion of 1-methylallene, or 1,1-dimethylallene, the methylene protons ($-CH_2^5-$) [see Table 1] appear as a basic AB quartet pattern, typical of two geminal diastereotopic protons[13] directly attached to an asymmetric centre, as the allylic moiety in these complexes must be since it is unsymmetrically substituted. Complexes (IV e,g), derived from insertion of 1,3-dimethylallene do not show resonances due to diastereotopic methylene protons, and only one methyl resonance is observed. Thus the allylic palladium bond in complexes (IV e,g) must be symmetrical with respect to substituents *i.e.* the *syn, syn*- or *anti, anti*-isomer. Since no central allylic proton is present to couple to the terminal allylic protons in complexes (IV e, g), no unequivocal assignment of structure is possible. Since only one isomer is observed for each of (IV e, g) it is felt that the assignment of the terminal allylic methyl groups in these complexes to *syn*-positions is preferred[15].

In the ^{1}H NMR spectrum of pure complex (IV a) the resonances due to the *syn*- and *anti*-protons were partially collapsed at 34° indicating that *syn–anti* exchange was occurring via a $\pi \rightarrow \sigma \rightarrow \pi$ process. This process was shown to be concentration dependent by dilution studies. No analogous broadening of *syn*- and *anti*-proton resonances was observed in the spectra of complexes (IV b), (III a) or (II a) indicating that the exchange process observed in the spectrum of (IV a) was dependent upon the anionic ligand (X), and upon the nature of the olefinic function in the 2-alkenyl substituent. This phenomenon has been observed in related complexes derived from 1,3-diene insertion[16] into allylic–palladium bonds and is discussed in detail below.

Mass spectra of 1,2-diene insertion products

Mass spectral data for representative complexes of type (IV) are presented in Table 2. The behaviour of complexes (IV) under electron impact parallels closely

TABLE 2

MASS SPECTRAL DATA FOR COMPLEXES (IV)

Complex	*Ion (assignment) (m/e)*[a] [% *rel. abundance*][b]
(IVb)	P^+(428) [54]; AllPd(Hfacac)$^+$(388) [12][c]; P−Hfacac$^+$(221) [319]; P−Hfacac−HCl$^+$(185) [169]; AllPd(Hfacac)−Hfacac−HCl$^+$(145) [60]; Pd$^+$(106) [111]
(IVc)	P^+(442) [4]; AllPd(Hfacac)$^+$(388) [61]; P−Hfacac$^+$(235) [55]; P−Hfacac−HCl$^+$ (199) [114]; AllPd$^+$ (181) [237]: AllPd (Hfacac)−Hfacac−HCl$^+$(145) [134]: Pd$^+$ (106) [167]
(IVe)	P^+(456) [3]; AllPd(Hfacac)$^+$(388) [65]; P−Hfacac$^+$(249) [18]; P−Hfacac−HCl$^+$ (213) [37]; AllPd$^+$ (181) [270]: AllPd(Hfacac) −Hfacac−HCl$^+$(145) [137]; Pd$^+$ (106) [146]

[a] All *m/e* values quoted for ^{35}Cl, ^{106}Pd peak. [b] % abundance relative to $CF_3^+ = 100\%$. [c] All = allylic ligand regenerated by reversal of the original insertion.

the behaviour of the enyl products derived from bicyclic olefin insertion in (I) [X= Hfacac] in that reversal of the insertion process is a highly favoured mode of breakdown[1a].

^{1}H NMR rate studies of the insertion of 1,2-*dienes into allyl–palladium bonds*

The ^{1}H NMR studies were in most part confined to complexes (I) [X= Hfacac] since the fluorinated chelate ligand gave enhanced reactivity of complexes (I) towards insertion[1a]. It was thus possible to carry out the insertion reactions on a 1/1 molar basis in an NMR tube and to monitor the insertion rate. Addition of one molar equivalent of various 1,2-dienes to 0.82 *M* $CDCl_3$ solutions of complexes (I) [X=Cl, Acac, Hfacac] at 34° caused immediate collapse of the allylic *syn*- and *anti*-proton resonances, the resonances of the added 1,2-diene remaining unchanged from those in the absence of complexes (I)[17]. New signals in the NMR spectrum due to the insertion products were not observed until a later stage. The extent of *syn–anti* collapse in the spectra of complexes (I) under identical conditions of concentration (of complex and diene) and temperature, was found to depend upon (*i*) the substituents W, Y and Z on the allylic function of complexes (I), (*ii*) the substituents on the 1,2-diene, and (*iii*) the anionic ligand X. Keeping any two of these variables constant and varying the third, the following orders for the extent of *syn–anti* proton collapse were observed:

$$X = \text{Hfacac} > \text{Acac} \approx \text{Cl}$$

1,2-Diene = 1,1-dimethylallene > 1,3-dimethylallene > 1-methylallene > allene ≫ tetramethylallene ~ 1,3-di-tert-butylallene (see Fig. 1)

π-Allylic ligand = 2-chloroallyl > allyl > 2-methylallyl > 2-tert-butylallyl

The rates of formation of the 1,2-diene insertion products were monitored using ^{1}H NMR spectroscopy, by integrating the spectra at intervals of time. Using fixed conditions of concentration and temperature the rates of insertion of differently substituted 1,2-dienes into the 2-chloroallyl–palladium bond of complex (I f) [X= Hfacac] to yield complexes (IV b–e) were studied. The reactions were found to be first-order in each of complex (I f) concentration [*C*], and 1,2-diene concentration, according to the rate equation:

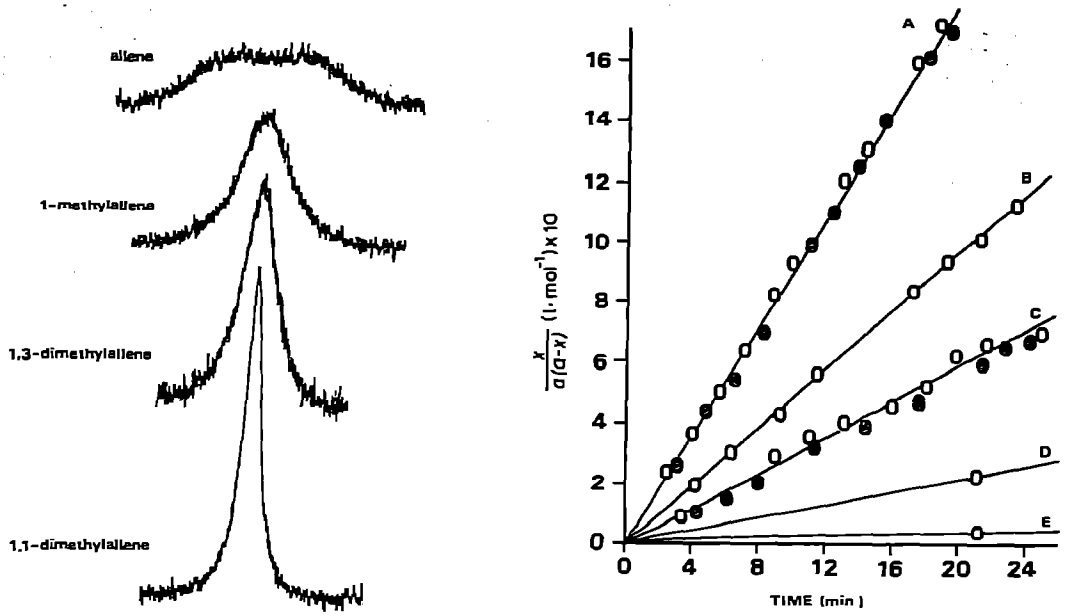


Fig. 1. ^{1}H NMR spectra (60 MHz; 34°); Extent of collapse of the *syn*- and *anti*-proton resonances of (π-2-Methylallyl)Pd(Hfacac) [0.82 *M* in $CDCl_3$] on addition of various 1,2-dienes (1 molar equivalent).

Fig. 2. Second order rate plots for the reaction of (π-2-Chloroallyl)Pd(Hfacac) [0.82 *M*] with various 1,2-dienes [0.82 *M*] to yield complexes (IV) [○ = $CDCl_3$ solution; ● = C_6D_6 solution: —A, 1,3-dimethylallene (34°); B, 1,1-dimethylallene (37°); C, 1,1-dimethylallene (34°); D, 1-methylallene (34°); E, allene (34°). [a = initial concentration of (π-2-Chloroallyl)Pd(Hfacac); X = concentration of product (IV) at time (*t*).]

TABLE 3

SECOND-ORDER RATE CONSTANTS (*k*) (34°) FOR INSERTION OF 1,2-DIENES INTO ALLYLIC–PALLADIUM BONDS[a]

Allylic function	*X*	*1,2-Diene*	k ($l \cdot mole^{-1} \cdot min$) × 10^5
2-Chloroallyl	Hfacac	1,3-Dimethylallene	9200[b]
2-Chloroallyl	Hfacac	1,1-Dimethylallene	3040[b]
2-Chloroallyl	Hfacac	1,1-Dimethylallene	4800[b,c]
2-Chloroallyl	Hfacac	1-Methylallene	1100[b]
2-Chloroallyl	Hfacac	Allene	165[b]
Allyl	Hfacac	1,1-Dimethylallene	≈ 20
2-Methylallyl	Hfacac	1,1-Dimethylallene	≈ 1
Allyl	Acac	Allene	≈ 1
1-Methylallyl	Acac	Allene	≈ 1
1,1-Dimethylallyl	Acac	Allene	≈ 10
1-Carbomethoxyallyl	Acac	Allene	≈ 50
Allyl	Cl	Allene	≈ 1

[a] No insertion of any of the 1,2-dienes into the 2-tert-butyallyl–palladium bond of complex (Ig) [X = Hfacac] was observed after 28 days. No insertion of either tetramethylallene or 1,3-di-tert-butylallene into the (2-chloroallyl)palladium bond of complex (If) [X = Hfacac] was observed after 28 days. [b] See Fig. 2. [c] Measured at 37°.

$$-dC/dt = k \cdot [C] \cdot [1,2\text{-Diene}]$$

Second order rate plots are shown in Fig. 2. Reactions of complex (I f) [X = Hfacac] with 1,1-dimethylallene and 1,3-dimethylallene were run under identical conditions in both $CDCl_3$ and C_6D_6 solution, and the rates were found to be invariant with solvent. By assuming the same rate law to hold for 1,2-diene insertion into other, differently substituted allylic ligands in complexes (I) [X = Cl, Acac, Hfacac], second-order rate constants for some of these reactions were calculated by only limited monitoring of the ^1H NMR spectra. The rate constants are assembled in Table 3.

The rates of 1,2-diene insertion were found to vary (*i*) with the substituents W, Y and Z on the allylic function of complexes (I), (*ii*) with the substituents on the 1,2-diene, and (*iii*) with the anionic ligand X, in the order:

X = Hfacac > Acac ≈ Cl

1,2-Diene = 1,3-dimethylallene > 1,1-dimethylallene > 1-methylallene > allene >>> tetramethylallene ≈ 1,3-di-tert-butylallene (no insertion observed)

π-Allylic ligand = 2-chloroallyl > allyl > 2-methylallyl ≫ 2-tert-butylallyl (no insertion observed)

(Terminal substituents) = 1-(methoxycarbonyl)allyl > 1,1-dimethylallyl > 1-methylallyl ≈ allyl

Effect of substituents on the allylic ligand on the rate of 1,2-*diene insertion*

The observation of *syn–anti* proton exchange in the NMR spectra of complexes (I) on addition of 1,2-dienes is only consistent with formation of a short-lived σ-allylic species (VIII) in solution, with rapid, reversible coordination of the 1,2-diene to palladium. As previously observed, the extent of *syn–anti* collapse reflects the ease of formation of this σ-allylic species and is dependent on the nature of the 2-substituent[17]. Since resonances in the ^1H NMR spectrum due to the insertion products do not appear until a later stage, this observation proves that coordination of the 1,2-diene to palladium cannot be the rate-determining step for product formation (*cf.* refs. 10–12).

The observed rate of insertion of a given 1,2-diene into a series of 2-substituted allylic–palladium bonds parallels the observed ease of formation of (VIII). Since the ease of formation of a species such as (VIII) is probably a good reflection of the relative concentration of this species in solution, this observation provides compelling evidence for the intermediacy of (VIII) in the insertion mechanism. For the series of terminally substituted π-allylic ligands (with the exception of 1-(methoxycarbonyl)-allyl for which no data is available) the ease of formation of a σ-allylic intermediate in complexes (π-All)PdOAc(PMe_2Ph) varies in the order[18]:

π-All = 1,1-dimethylallyl > 1-methylallyl ≈ allyl.

This parallels the observed rates of 1,2-diene insertion into these allylic–palladium bonds in complexes (I) [X = Acac] (see Table 3), again pointing to the intermediacy of a σ-allylic species in the insertion mechanism. It might be predicted that a σ-allylic intermediate (VIII) [W = Z = H; Y = $COOCH_3$] would have increased stability relative to other terminally methyl-substituted σ-allylic species since it contains an α,β-unsaturated ketone function.

The necessity for formation of a σ-allylic intermediate (VIII) in order for insertion of 1,2-dienes to occur also explains the observed reluctance of the insertion products (II), (III) and (IV) to insert a further mole of 1,2-diene, since these complexes all contain a bulky 2-alkyl substituent on the π-allylic ligand. Our results and others[18] have clearly demonstrated the reluctance of such allylic functions (*e.g.* 2-methylallyl, 2-tert-butylallyl) to form σ-allylic species, and consequently to insert 1,2-dienes.

Effect of substituents on the 1,2*-diene on the rate of insertion*

Introduction of methyl substituents on the 1,2-diene has two observable effects on its reaction with any given complex (II); it affects the extent of *syn–anti*-proton collapse induced by the 1,2-diene, and consequently must affect the coordinative ability of the olefinic functions in that 1,2-diene; and it affects the rate of insertion. With the notable exception of 1,3-dimethylallene, these two effects parallel one another.

The observed order of *syn–anti* proton collapse is only consistent with preferential coordination of either 1-methylallene, or 1,1-dimethylallene, via the least substituted olefinic function. If coordination of these two dienes occurred via the more substituted olefinic function, tetramethylallene would be expected to have the best coordinative ability of all the 1,2-dienes examined, instead of being one of the worst, as is observed. Evidence for preferential coordination of 1,1-dimethylallene via its least substituted olefinic function exists in *trans*-(1,1-dimethylallene)Pt(Py)-Cl_2[19] and (1,1-dimethylallene)$_2$Rh(Acac)[20].

Since the ease of formation of (VIII) is 1,1-dimethylallene > 1-methylallene > allene, there must be a mechanism operative whereby increasing methyl substitution on one of the two allenic double bonds in an unsymmetrically substituted 1,2-diene increases the coordinative ability of the *other* double bond towards palladium. ^{13}C NMR studies on the chemical shifts of 1,2-diene carbon atoms have shown that the two perpendicularly oriented double bonds are not independent of each other with respect to the electronic effects of substituents[21]. Crandall and Sojka[22] have used MO calculations and ^{13}C NMR studies to calculate the total π-electron density on the central allenic carbon in a series of methyl substituted 1,2-dienes. The total π-electron density, which must reflect the ability of the methyl substituents to inductively supply π-electron density to this carbon, decreases in the order:

tetramethylallene > 1,3-dimethylallene > 1,1-dimethylallene > 1-methylallene > allene

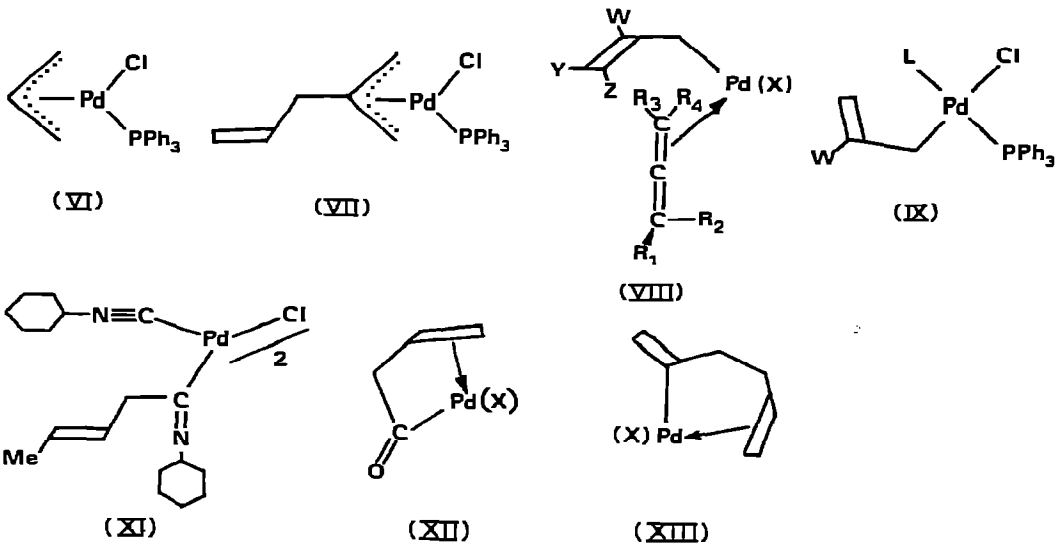
The solid state structures of several 1,2-diene complexes of Rh^{I}[20,23,24], Pt^{0}[25], and Pt^{II}[23], in which the 1,2-diene acts as a monodentate π-olefinic ligand, invariably show that the central allenic carbon is located closer to the metal than the terminal π-bonded allenic carbon. In square planar complexes of Pt^{II}[23] and Rh^{I}[20,23,24] the coordination plane intersects the C–C axis of the coordinated allenic olefin much closer to the central carbon than the terminal carbon. Thus an asymmetry exists in the 1,2-diene–transition metal bond, which may imply that the major contribution to the σ-donor component of the 1,2-diene–metal bond arises from the central allenic carbon atom.

The observation that tetramethylallene, and 1,3-di-tert-butylallene, have poorer coordinative abilities than the other 1,2-dienes must reflect a steric hindrance to coordination, which outweights the increased π-electron density at the central

allenic carbon. Similarly a steric effect in the case of 1,3-dimethylallene, which must coordinate via a methyl substituted olefinic function, must reduce its coordinative ability relative to the unsubstituted olefinic function of 1,1-dimethylallene, but notably does not make it a poorer coordinating ligand than 1-methylallene, the increased σ-donor power of 1,3-dimethylallene outweighting the steric effect in the latter comparison.

Effect of the trans-ligands on the rate of 1,2-*diene insertion*

The rate of insertion of a given 1,2-diene into a given allylic–palladium bond on varying the anionic ligand (X) in complexes (I) parallels the ease of formation of a σ-allylic species, and is fastest when X = Hfacac. If the 1,2-diene is considered as a nucleophile, as expected if the σ-donor component of the π-1,2-diene–palladium bond is of predominant importance, the presence of the fluorinated Hfacac ligand in complexes (I) would be expected to increase the electrophilicity of the palladium atom towards a given 1,2-diene relative to X = Acac or Cl, and hence stabilise an intermediate such as (VIII). The observation that chloro(triphenylphosphine)-π-allylpalladium (VI) is extremely reluctant to undergo insertion of allene to give (VII) can be rationalized in terms of the *trans* σ-bond weakening effect of the Ph_3P ligand.

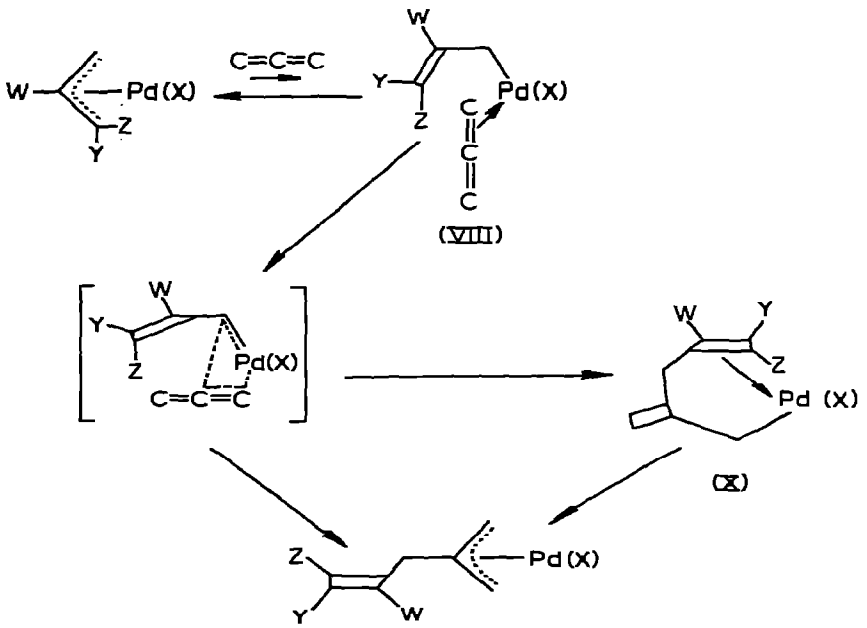


An S_N2 substitution by allene of the π-allyl ligand in (VI) would be expected to substitute the end of the allyl ligand situated *trans* to phosphorus to give a σ-allylic species (IX) [L = allene; W = H]. Such an intermediate would be expected to be destabilised by the strong electron donating power of the *trans*-phosphine *decreasing* the electrophilicity of the palladium towards the 1,2-diene. Clark *et al.*[26] recently reported that the electron-deficient acetylene, hexafluoro-2-butyne, inserts quite readily into the 2-methylallyl–palladium bond of chloro(dimethylphenylphosphine)-π-(2-methylallyl)palladium, presumably via an intermediate analogous to (IX) [$L = CF_3C{\equiv}CCF_3$; $W = CH_3$]. However no insertion of this acetylene into the π-2-methylallyl–palladium bonds of complexes (II b) [X = Cl, Hfacac] could be effected.

Hexafluoro-2-butyne is expected to have the opposite electronic requirements for bonding to a transition-metal than does allene (*i.e.* it is a weak σ-donor but a strong π-acceptor)[27] and as such a σ-allylic intermediate such as (IX) would be stabilised when $L = CF_3C{\equiv}CCF_3$.

The mechanism of 1,2-*diene insertion into the allyl–palladium bond*

The proposed mechanism for 1,2-diene insertion into allylic palladium bonds is shown in Scheme 1. Migration of the σ-allylic group to the central carbon atom of the coordinated allenic moiety is considered to be the rate determining step.



Scheme 1. Mechanism of insertion of 1,2-dienes into allylic–palladium bonds.

The available data do not allow any distinction to be made between a completely concerted rearrangement of (VIII) to give the product, or a two-step mechanism via the chelating enyl intermediate (X). This latter species contains an enyl ring system analogous to that obtained from the insertion of bicyclic olefins into allylic–palladium bonds, and is therefore a geometrically feasible entity. Previous studies have shown that carbon monoxide inserts into allyl-palladium chloride, the final product being the acyl halide and metallic palladium. Although the stereochemistry of this reaction is the same as that observed with allene, the reaction is second order in CO concentration[10]. Cyclohexyl isocyanide has been shown to react with complex (I c) [X = Cl], inserting into the least substituted end of the π-1-methylallyl–palladium bond to give complex (XI)[28]. However, insertion only occurs in the presence of two moles of isocyanide per mole of palladium.

These reactions are therefore different from 1,2-diene insertion in that they exhibit a second order dependency upon the inserting ligand. Examination of molecular models shows that a chelating intermediate such as (XII), analogous to (X),

is a highly strained species, and therefore a highly improbable intermediate in CO insertion reactions. The same is true for isocyanide insertions. Thus a second molecule of CO, or isocyanide, is presumably required in the rate-determining insertion step, to fill the vacant coordination site being vacated by the migrating allylic carbon.

The observation that the insertion of 1,2-dienes exhibits a first order dependency upon 1,2-diene concentration must therefore reflect the ability of this sytem to maintain a four-coordinate palladium atom throughout the rate-determining step. This may be achieved via the transition states shown in Figs. 3A and B. Figure 3A involves motion of the uncoordinated allenic double bond to fill the coordination site being vacated by the σ-allyl. This leads to a concerted insertion reaction. In Fig. 3B the σ-allyl olefin occupies the coordination site being vacated by the allylic σ-carbon resulting in a two-step mechanism. Conversion of (X) into the product could occur via intermolecular generation of a σ-allylic intermediate. The observed direction and relative rates of addition can be rationalised if the transition state leading to intermediate (X) (see Scheme 1) is considered to involve a small charge separation, as proposed for the insertion of bicyclic olefins[1a]. Two possible transition states are

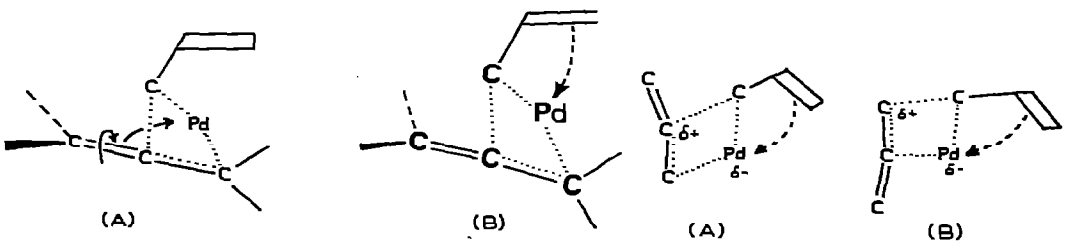


Fig. 3. Possible transition states for 1,2-diene insertion.

Fig. 4. Possible transition states for a 1,2-addition of Pd–C (A), and a 2,1 addition of Pd–C (B) to a 1,2-diene.

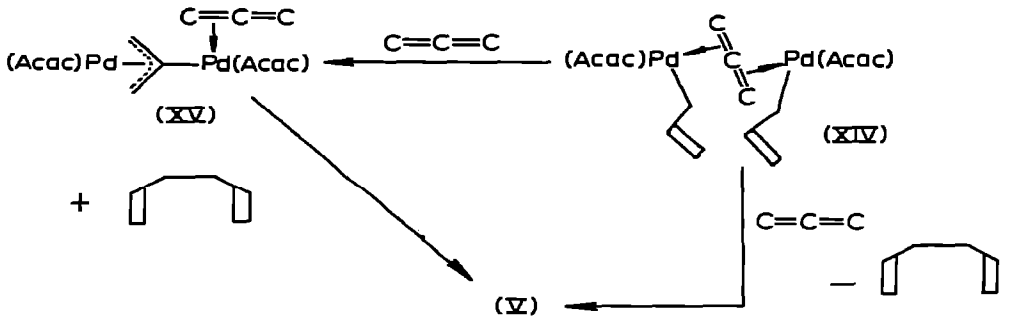
shown in Fig. 4. Transition state (B) would lead to a species (XIII), but does not apparently occur. Although the δ^+ charge in transition state (B) is generated on a pseudo-allylic terminal carbon it cannot be stabilized by allylic delocalisation since it is being generated in a p-orbital at right angles to (and not coplanar with) the remaining allenic olefin function. As such transition state (A) might be expected to be of lower energy since the δ^+ charge is generated at a secondary carbon centre rather than a primary carbon centre as in transition state (B). Transition state (A) also provides an explanation of why 1,3-dimethylallene, although generating a σ-allylic intermediate (VIII) less readily than 1,1-dimethylallene, in fact inserts more readily. Molecular orbital calculations[22] have shown that inductively the methyl groups in 1,3-dimethylallene generate more π-electron density at the central allenic carbon than do those on 1,1-dimethylallene, with a consequent greater stabilisation of transition state A (Fig. 4) in the former case.

There is no apparent way, as yet, of distinguishing between the concerted or two-step mechanism, although some evidence points to the two-step process by analogy to the mechanism of bicyclic olefin insertion[1a].

Formation of bis(acetylacetonato)-2,2'-bi-π-allyldipalladium(II)

Formation of complex (V) from the reaction of (π-Allyl)Pd(Acac) with high

concentrations of allene represents the first example of formation of the 2,2′-bi-π-allyl ligand from allene and a mononuclear transition metal complex. Formation of (bi-π-allyl) hexacarbonyldiiron occurs by reaction of allene with di- and trinuclear iron carbonyls[29,30]. A possible mechanism for the palladium reaction is presented in Scheme 2.



Scheme 2. Possible mechanism for formation of complex (V) from π-allyl Pd (Acac) and allene.

It should be emphasised that this mechanism is purely speculative, although it is based on known reactions and known types of complex *e.g.* a binuclear Rh^{I} complex (Acac)(CO)Rh(C_3H_4) Rh(CO)(Acac), containing a bridging allene ligand analogous to that in (XIV) has been isolated[20]. Similarly the proposed intermediate (XV) contains a bonded allene unit identical to that found in a binuclear iron complex[31,32].

The chemistry of 2,2′-bi-π-allyldipalladium(II) complexes is reported elsewhere[33].

CONCLUSION

Studies of the insertion of 1,2-dienes into allylic–palladium bonds show that the reaction proceeds via a σ-allylic intermediate and that rearrangement of this intermediate by an intramolecular process yields the observed products. A series of consecutive insertions of allene into allylic transition metal bonds would therefore yield the 1,2-polymer. Such insertions are presumably also of importance in the oligomerisations of allene.

EXPERIMENTAL

Starting materials

π-allylic palladium chloride[34], Acac[35], and Hfacac[16] complexes were prepared by previously reported methods. Allene, 1,1-dimethylallene, 1,3-dimethylallene, and tetramethylallene were commercial samples, used without further purification. 1,3-Di-tert-butylallene was prepared by the method of Borden and Corey[36]. We are grateful to Drs. J. C. Thompson and C. S. Liu for a sample of 1-methylallene.

Physical measurements

^{1}H NMR spectra were recorded on a Varian A56/60D spectrometer. Mass

spectra were recorded on a Bell and Howell Model 21–490 spectrometer at an ionisation energy of 70 eV. Melting points were recorded on a Kofler hot-stage and are corrected.

Monitoring of reaction rates

NMR tubes were precalibrated to a volume of 0.40 ml. Solutions of complexes (I) [0.82 *M*] were prepared by dissolving the appropriate weight of complex in this volume of $CDCl_3$. 1,2-Dienes were injected with a microsyringe, and the tube was quickly capped, shaken vigorously, and placed in the probe.

For reactions involving gaseous 1,2-dienes, (allene and 1-methylallene), a solution of the 1,2-diene in ethanol-free chloroform was prepared by bubbling the 1,2-diene through a sample of chloroform which had been passed down an alumina column. This solution was standardised by dissolving a known weight of an unreactive π-allylic palladium complex, *e.g.* $[(\pi\text{-2-tert-butylallyl})PdCl]_2$, in a known volume of solution in an NMR tube. Careful integration of the NMR spectrum allowed the molarity of the 1,2-diene in the solution to be calculated.

Reaction of allene with chloride-bridged π-allylic palladium complexes

Complex (*II a*). A solution of di-μ-chlorodi-π-allyl-dipalladium (II) (1.000 g) in benzene (5 ml) was placed in a thick-walled Pyrex Carius tube. Allene (5.0 g) was condensed into the tube at −78°. The tube was sealed, allowed to warm to room temperature, and shaken vigorously. A large amount of the starting complex was precipitated from solution. After standing for seven days at room temperature, all the starting complex had dissolved. The tube was opened and excess allene allowed to evaporate. Evaporation of the contents to dryness under reduced pressure, followed by recrystallisation of the residue from chloroform/petroleum ether (b.p. 30–60°), yielded the *product* as pale yellow prisms, (0.865 g; 71%), m.p. 105–115°. (Found: C, 31.75; H, 4.22. $C_{12}H_{18}Cl_2Pd_2$ calcd.: C, 32.32; H, 4.07%.)

Similarly prepared were: A ca. 1/1 mixture of complex (II b), and its π-2-methylallyl precursor (total yield 1.00 g), from di-μ-chlorobis(π-2- methylallyl) dipalladium(II) (1.000 g) and allene (5.0 g).

Complex (*II c*). Yellow prisms (1.510 g, 77%), m.p. 75–80°, from di-μ-chlorobis(π-*syn*-1-methylallyl)dipalladium(II) (1.631 g) and allene (5.0 g). Treatment of this complex with one molar equivalent of acetylacetonatothallium(I) yielded a complex having a ^1H NMR spectrum identical to that of complex (III c).

Complex (*II d*). Yellow prisms (1.510 g, 78%), m.p. 80–85°, from di-μ-chlorobis(π-1,1-dimethylallyl)dipalladium(II) (1.619 g) and allene (5.0 g). (Found: C, 38.40; H, 5.23. $C_{16}H_{26}Cl_2Pd_2$ calcd.: C, 38.27; H, 5.22%.)

Complex (*VII*). Pale yellow prisms (1.020 g; 92%), m.p. 140–145° dec., from chloro(π-allyl)(triphenylphosphine)palladium(II) (1.020 g) and allene (5.0 g), after standing for one year. (Found: C, 59.63; H, 5.27. $C_{24}H_{24}ClPPd$ calcd.: C, 59.40; H, 4.98%.)

Reaction of allene with acetylacetonato-π-allylic–palladium complexes

Complex (*III a*). A solution of acetylacetonato-π-allylpalladium(II) (1.000 g) in benzene (5 ml) was placed in a thick-walled Pyrex Carius tube. Allene (3.0 g) was condensed in at −78°, the tube was sealed, warmed to room temperature, and shaken

vigorously. After standing at room temperature for 2 h a cloudy white precipitate was observed. After standing for 10 days the tube was opened and excess allene allowed to evaporate. The contents were filtered, yielding bis(acetylacetonato)-2,2'-bi-π-allylpalladium(II) (0.038 g; 1.5%) as a white crystalline solid. VPC analysis [20' × 3/8" 15% SE30 (P.G.) Chrom. W column at 110°] of a sample of the filtrate showed the presence of allene (trace) and 1,5-hexadiene. Evaporation of the filtrate to dryness yielded the title compound as colourless needles (1.102 g, 95%), m.p. 45–50°, after recrystallisation from petroleum ether (b.p. 30–60°). (Found: C, 45.80; H, 5.64. $C_{11}H_{16}O_2Pd$ calcd.: C, 46.09; H, 5.62%.)

A similar procedure to the above *in the absence of solvent* yielded, after 19 days, bis(acetylacetonato)-2,2'-bi-π-allyldipalladium(II), (0.960; 38%), and the title compound (1.500 g; 51%).

Similarly prepared were:

Complex (*IIc*). Colourless prisms (2.010 g; 76%). m.p. 71–74° dec., together with bis(acetylacetonato)-2,2'-bi-π-allyldipalladium(II) (0.390 g; 17%) from the reaction of acetylacetonato-π-(*syn*-1-methylallyl)palladium(II) (2.292 g) with neat liquid allene (4.0 g). (Found: C, 48.53; H, 6.22. $C_{12}H_{18}O_2Pd$ calcd.: C, 47.95; H, 6.04%.)

Complex (*II d*). Colourless needle prisms (0.730 g, 62%), m.p. 55–65°, together with bis(acetylacetonato)-2,2'-bi-π-allyldipalladium(II) (0.130 g, 13%) from the reaction of acetylacetonato-π-(1,1-dimethylallyl)palladium(II) (1.027 g) with neat liquid allene (2.0 g).

Reaction of 1,2-*dienes with* π-*allylic Pd*(*Hfacac*) *complexes*

Complex (*I V a*). Allene was bubbled through a solution of 1,1,1,5,5,5-hexafluoropentane-2,4-dionato-π-allylpalladium(II) (0.116 g) in dichloromethane (1 ml) for 5 min, and the resultant solution was allowed to stand at room temperature for 15 h. Evaporation yielded the *product* as a pale yellow oil (0.120 g; 93%), identified by its ^{1}H NMR spectrum. Treatment of this complex with an equimolar amount of dry HCl in benzene gave a quantitative yield of complex (II a).

Similarly prepared were:

Complex (*IV b.*) A pale yellow oil (0.130 g; 92%) from the reaction of 1,1,1,5,5,-5-hexafluoropentane-2,4-dionato-π-(2-chloroallyl)palladium(II) (0.128 g) and allene. (Found: C, 30.58; H, 2.58. $C_{11}H_9ClF_6O_2Pd$ calcd.: C, 30.80; H, 2.11%.)

Complex (*IV c*). Yellow prisms (0.190 g, 92%), m.p. 75–80° from the reaction of 1,1,1,5,5,5-hexafluoropentane-2,4-dionato-π-2-chloroallylpalladium(II) (0.180 g) with 1-methylallene. (Found: C, 32.90; H, 2.74. Mol. wt. (osmometrically in C_6H_6), 435. $C_{12}H_{11}ClF_6O_2Pd$ calcd.: C, 32.53; H, 2.50%. Mol. wt. 443.

Complex (*III d*). A pale yellow oil (0.130 g; 86%), from the reaction of 1,1,1,-5,5,5-hexafluoropentane-2,4-dionato-π-(2-chloroallyl)palladium(II) (0.128 g) with 1,1-dimethylallene (33 μl). (Found: C, 34.92; H, 3.42. $C_{13}H_{13}ClF_6O_2Pd$ calcd.: C, 34.16; H, 2.87%.)

Complex (*IV e*). Yellow prisms (0.160 g; 89%), m.p. 95–99°, from the reaction of 1,1,1,5,5,5-hexafluoropentane-2,4-dionato-π-(2-chloroallyl)palladium(II) (0.153 g) and 1,3-dimethylallene (30 μl). (Found: C, 34.06; H, 2.84. Mol. wt. (osmometrically in C_6H_6), 488. $C_{13}H_{13}ClF_6O_2Pd$ calcd.: C, 34.16; H, 2.87%. Mol. wt. 457).

Complex (*IV f*). Pale yellow needles (0.150 g; 95%), m.p. 85–89°, from the

reaction of 1,1,1,5,5,5-hexafluoropentane-2,4-dionato-π-*syn*-[1-(methoxycarbonyl)-allyl]palladium(II) (0.143 g) with 1-methylallene. (Found: C, 36.26; H, 3.19. $C_{14}H_{14}F_6O_4Pd$ calcd.: C, 36.02; H, 3.02%.)

Complex (*IV g*). Pale yellow needles (0.150 g; 92%) m.p. 110–115°, from the reaction of 1,1,1,5,5,5-hexafluoropentane-2,4-dionato-π-[*syn*-1-(methoxycarbonyl)-allyl]palladium(II) (0.140 g) with 1,3-dimethylallene (33μl). (Identified by its NMR spectrum only).

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