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THE REACTION OF *endo*-ALKOXYTETRAPHENYLCYCLOBUTENYLPALLADIUM COMPLEXES WITH ALKENES, 1,2-DIENES AND 1,3-DIENES

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Summary

The complexes $[(endo\text{-}C_4Ph_4OMe)PdX]_n$ (X = Cl, n = 2; X = acac, hfac, n = 1) (Ia—Ic), readily react with unsaturated hydrocarbons in chloroform at room temperature. "Alkene insertion" occurs via hydride shifts to form η^3-allylic palladium(II) derivatives. The X-ray structure of the product derived from the reaction of isobutene with Ic indicates that "olefin insertion" has occurred either with disrotatory ring-opening of the cyclobutenyl moiety or with a conrotatory ring-opening followed by a subsequent isomerization of the initially formed insertion product. Arguments in favour of the latter alternative are presented. 1,2-Dienes give either 2-substituted allyl complexes (allene, 1,3-dimethylallene, tetramethylallene) or oligomers (1,1-dimethylallene). 1,3-Dienes (excluding isoprene) form η^3-allylic products via an insertion process which is stereochemically different to that observed for simple η^3-allylic palladium(II) compounds in that carbon—carbon bond formation occurs at the least substituted end of the 1,3-diene. In addition to "insertion" into the least substituted double bond, isoprene shows a minor product arising from insertion into the more substituted olefinic function.

Introduction

The "insertion" of unsaturated hydrocarbons into allyl—palladium bonds has been investigated by a number of researchers, with great interest focussing on the mechanisms and stereochemistry of these reactions [1—3]. 1,2- and 1,3-dienes have been shown to react giving allylic palladium products, while insertion of strained olefins yields "enyl" type complexes [2]. Simple unstrained

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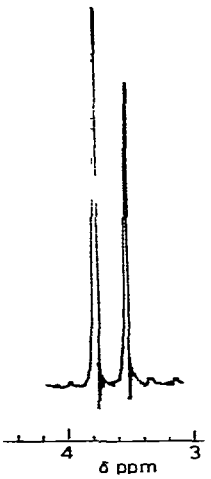
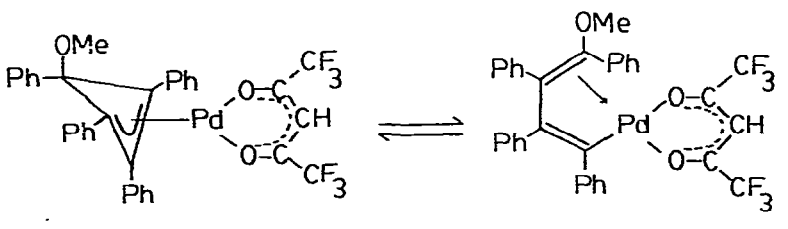
alkenes do not normally undergo insertion but generate unstable (alkene)-(η^1-allyl)palladium(II) species [2]. An important observation in the 1,3-diene insertions is that carbon—carbon bond formation occurs at the more substituted end of the diene, and in order to account for this, an electrocyclisation process has been proposed [3]. ^{1}H NMR studies of the reaction mixtures indicate that in all cases a dynamic η^1-allyl species formed by substrate complexation at the least substituted C=C double bond, is the reactive intermediate.

We [4] and others [5] have recently reported that the allylic cyclobutenyl complexes [(*endo*-C_4Ph_4OR)PdX] (R = Me, Et; X = acac, hfac) and [(*endo*-C_4Tol_4Ph)PdX] (X = Cl, acac) either exist in a η^3-cyclobutenyl $\rightleftharpoons$ η^1-dienyl equilibrium in solution [4], or may readily be converted to a ring-opened butadienyl form by reaction with appropriate donor ligands [4,5]. Thus, the ^{1}H NMR spectra of [(*endo*-C_4Ph_4OMe)Pdhfac] (Ic) exhibits two types of methoxy resonances (Fig. 1) which may be assigned to the ring-opened and ring-closed species IIc and Ic. By analogy to η^3-allylic palladium complexes, a σ-butadienyl species should be reactive towards unsaturated substrates, providing a vacant coordination site is available. The cyclobutenyl complexes above have been reported to react with acetylenes in protic [6] or aprotic [7] solvents leading





(I c) (II c)

Fig. 1. The methoxy region of the ^{1}H NMR spectrum of [(*endo*-C_4Ph_4OMe)Pdhfac] showing the Ic $\rightleftharpoons$ IIc equilibrium mixture ($CDCl_3$, 34°C, 60 MHz).

to novel acetylene trimer and tetramer compounds, e.g.:

$$[(endo\text{-}C_4Ph_4OR)Pdhfac] + RC{\equiv}CR \xrightarrow{R'OH} Pd_2(\eta^5\text{-}C_5Ph_3R_2)_2(\mu\text{-}RC{\equiv}CR)$$

$$[(endo\text{-}C_4Tol_4Ph)PdCl]_2 + MeC{\equiv}CMe \xrightarrow{CHCl_3} Pd(\eta^3\text{-}C_6Me_2PhTol_4)Cl$$

We now report that complexes $[(endo\text{-}C_4Ph_4OMe)PdX]_n$ (X = Cl, n = 2; X = acac, hfac, n = 1) (Ia—Ic) also readily react with alkenes, 1,2-dienes and 1,3-dienes in aprotic solvents at room temperature [8]. The reactivity and mode of insertion of Ia—Ic are in some cases significantly different from their simple allylic palladium counterparts.

Results and discussion

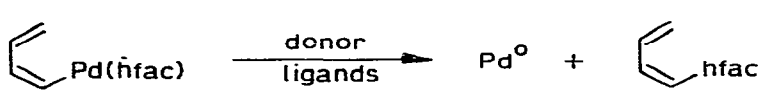
Reaction of Ia—Ic with olefins. A chloroform solution of the appropriate palladium complex (Ia—Ic) was treated with one equivalent of the olefin neat, or in the case of gaseous olefins, as an aliquot of standardized $CDCl_3$ solution, and product formation monitored by ^1H NMR spectroscopy. Where X = hfac, the two methoxy resonances characteristic of the equilibrium mixture of ring-opened dienyl ⇌ ring-closed cyclobutenyl (i.e., IIc ⇌ Ic) rapidly disappeared at about the same rate and were replaced by a single new OMe peak at higher field. Evaporation of the solvent and purification by column chromatography gave the products as a deep yellow glass (X = acac or hfac) or solid (X = Cl). Some decomposition during reaction was noted for the hfac and acac compounds *, the exact amount depending upon reaction conditions and the nature of the olefin. Reactivity of the starting $[(endo\text{-}C_4Ph_4OMe)PdX]_n$ complexes were X = hfac > acac >> Cl. A similar order has been noted with allylpalladium insertions [3].

For reasons of reactivity, solubility and volatility the hfac derivatives were examined in the greatest detail. Product characterization was performed by elemental analysis, osmometry and mass spectra (β-diketonates) in addition to ^1H and in some cases ^{13}C NMR spectra. These are all consistent with the formulation of the products as η^3-allylpalladium(II) complexes IIIa—IIIq, where insertion into the butadienyl moiety has occurred at a terminal olefinic double bond via a hydride shift (Tables 1—3). These reactions would therefore represent a further example of the insertion of olefins into vinyl—palladium bonds which are known to occur with hydride shifts [10,11].

Thus, for example, the products IIIa derived from the reaction of [(*endo*-C_4Ph_4OMe)Pdhfac] with ethylene has the ^1H NMR shown in Fig. 2a. The peak at δ 3.18 ppm (s, 3p) is assignable to the methoxy protons while the doublet at δ 1.03 ppm (d, 3p, J 6 Hz) and quartet at δ 4.68 ppm (q, 1p, J 6 Hz) are

(Continued on p. 392)

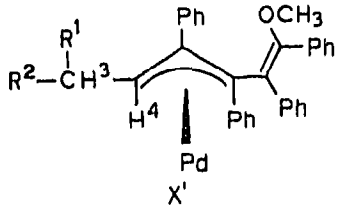
* A possible decomposition pathway is the olefin promoted reductive coupling of the butadienyl and β-diketonate functions, i.e.:



(cf. CO induced coupling of η^3-allylic palladium(II) β-diketonates [19]).

TABLE 1

^{1}H NMR DATA FOR OLEFIN INSERTION PRODUCTS IIIa–IIIq (ppm, 34°C, 60 MHz, $CDCl_3$) (chemical shifts in ppm)



(III)

IIIa, IIIl, IIIp: $R^1 = R^2 = H$
IIIb, IIIm: $R^1 = H$, $R^2 = Me$
IIIc, IIIn: $R^1 = R^2 = Me$
IIId, IIIo: $R^1 = H$, $R^2 = C_6H_5$
IIIe, IIIf, IIIg: $R^1 = H$, $R^2 = p\text{-}XC_6H_5$
IIIh: $R^1 = H$, $R^2 =$ t-Bu
IIIi, IIIq: $R^1 = H$, $R^2 = Et$
IIIj: $R^1 = Me$, $R^2 =$ i-Pr
IIIk: $R^1 = Me$, $R^2 = C_6H_5$

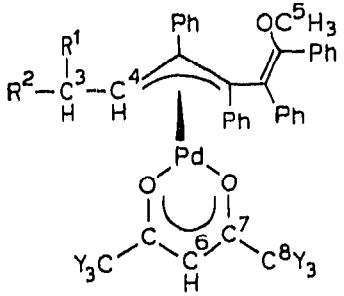
Complex	Olefin	X	R^1	R^2	H^3	H^4	OMe	X
IIIa	Ethylene	hfac	1.03(d)	1.03(d)	1.03(d)	4.68(q)	3.18(s)	CH, 5.96
IIIb	Propene	hfac	1.32(m)	0.74(t)	1.32(m)	4.38(t)	3.02(s)	CH, 5.89
IIIc	Isobutene	hfac	1.20(d)	0.44(d-br) [a]	1.90(br)	4.20(d)	3.06(s-br)	CH, 5.98
IIId	Styrene	hfac	2.82(d)	Ph, 6.8–7.8	2.82(d)	4.68(t)	2.95(s)	CH, 6.06
IIIe	*p*-Nitrostyrene	hfac	2.80(d)	Ph, 6.8–7.8	2.80(d)	4.42(t)	2.90(s)	CH, 6.02
IIIf	*p*-Methoxystyrene	hfac	2.70	Ph, 6.8–7.7; OMe, 3.62	2.70(d)	4.60(t)	2.90(s)	CH, 6.02

IIIg	*p*-Chlorostyrene	hfac	2.72	Ph, 6.8—7.8	2.72(d)	4.43(t)	2.87(s)	CH, 6.00
IIIh	3,3'-Dimethyl-1-butene	hfac	1.34(d)	0.60(s)	1.34(d)	4.42(t)	2.95(s-br)	CH, 5.97
IIIi	*cis*- or *trans*-But-2-ene, 1-butene	hfac	CH_2—CH_2, 1.0—1.6(m, br); CH_3, 0.65(t)		1.0—1.6(br)	4.43(t)	3.05(s)	5.95(s)
IIIj	Tetramethylethylene, 2,3-dimethyl-1-butene	hfac	0.45(d-br) [a]	CH, ca. 1.8(m); CH_3, 0.79; 1.10(d)	ca. 1.8(m)	4.43(d)	3.12(s-br)	5.87(s)
IIIk	α-Methylstyrene	hfac	1.45(d)	Ph, 6.6—7.8	ca. 3.0(br)	4.60(d)	2.80(s)	6.07(s)
IIIl	Ethylene	acac	1.15(d)	1.15(d)	1.15(d)	4.53(q)	3.30(s)	CH, 5.15; CH_3, 1.83, 1.94
IIIm	Propene	acac	ca. 1.4(m)	0.93(t)	ca. 1.4	4.30 (d of d)	3.27(s)	CH, 5.13; CH_3, 1.60, 1.93
IIIn	Isobutene	acac	1.27(d)	0.57(d-br)	ca. 1.9	4.00(d)	3.23(s)	CH, 5.07; CH_3, 1.60, 1.93
IIIo	Styrene	acac	ca. 2.95	Ph, 6.8—7.6	ca. 2.95	4.54	3.00(s)	CH, 5.22, CH_3, 1.68, 2.02
IIIp	Ethylene	Cl	1.10(d), 1.07(d)	1.10(d) 1.07(d)	1.10, 1.07(d)	4.65, 4.73(d)	3.20, 3.33(s)	
IIIq	1-Butene	Cl	CH_2—CH_2, 0.8—1.8(m, br); CH_3, 0.3—0.7(d)		0.8—1.8(br)	4.27, 4.38(q)	3.12, 3.17(s)	

[a] Sharp double t at +55°C; s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad.

TABLE 2

$^{13}C\{^1H\}$ NMR DATA FOR acac, hfac COMPLEXES OF OLEFIN INSERTION PRODUCTS III (chemical shifts in ppm, coupling constants in Hz)



Complex	Olefin	Y	C^1	C^2	C^3	C^4	C^5	C^6	C^7	C^8
IIIa	Ethylene	F	--	—	14.6	72.0	56.5	56.5 J(CF) 164	175.6 J(CF) 269	122.7 J(CF) 33
IIIc	Isobutene	F	28.7	20.8	20.8	84.6	56.2	89.1 J(CF) 164	176.4 J(CF) 269	118.4 J(CF) 34
IIIg	Styrene	F	—	—	34.6	75.8	56.0	89.4 J(CF) 164	175.4 J(CF) 267	117.6 J(CF) 33
IIIi	1-Butene	F	13.4 21.2	—	30.8	77.3	56.2	89.3 J(CF) 164	175.5 J(CF) 268	117.4 J(CF) 33
IIIk	α-Methylstyrene	F	21.5	—	39.9	82.0	55.7	89.3 J(CF) 164	175.5 J(CF) 268	117.4 J(CF) 33
IIIl	Ethylene	H	—	—	14.0	67.6	56.7	99.3		28.2 27.9
IIIm	Propene	H	12.9	—	22.2	74.4	56.6	99.2		28.1 27.8

TABLE 3

ANALYTICAL DATA FOR OLEFIN INSERTION PRODUCTS III

Complex	X	Physical appearance	M.p. (°C)	Analysis (Found (calcd.) (%)			Molecular weight [c] (Found (calcd.))	Mass spectral data, major organic fragments, ion (assignment *m/e*)
				C	H	Cl		
IIIa	hfac	Yellow glass	73—75	61.63 (60.99) [b]	4.23 (4.07) [b]			P^+ = $[(C_2H_4)(C_4Ph_4OCH_3)]^+$ (415) $[(C_2H_4)(C_4Ph_4OCH_2)]^+$ (414)
IIIb	hfac	Yellow glass	69—72	61.63 (61.43) [b]	4.64 (4.25) [b]		723 (742)	P^+ = $[(C_3H_6)(C_4Ph_4OCH_3)]^+$ (429) $[(C_3H_6)(C_4Ph_4OCH_2)]^+$ (428)
IIIc	hfac	Orange prisms [a]	105—107	60.34 (60.28)	4.25 (4.26)			P^+ = $[(C_4H_8)(C_4Ph_4OCH_3)]^+$ (443) $[(C_4H_8)(C_4Ph_4OCH_2)]^+$ (442)
IIId	hfac	Yellow glass	67—70	62.72 (62.66)	4.16 (4.01)		735 (804)	P^+ = $[(C_8H_8)(C_4Ph_4OCH_3)]^+$ (491) $[(C_8H_8)(C_4Ph_4OCH_2)]^+$ (490)
IIIh	hfac	Yellow glass	72—76	62.90 (62.67) [b]	5.06 (4.77) [b]			P^+ = $[(C_6H_{12})(C_4Ph_4OCH_3)]^+$ (471) $[(C_6H_{12})(C_4Ph_4OCH_2)]^+$ (470)
IIIi	hfac	Yellow glass	65—67	59.92 (60.29)	4.53 (4.26)		831 (756)	P^+ = $[(C_4H_8)(C_4Ph_4OCH_3)]^+$ (443) $[(C_4H_8)(C_4Ph_4OCH_2)]^+$ (442)
IIIj	hfac	Yellow glass	58—64	61.62 (61.19)	4.83 (4.62)			
IIIk	hfac	Yellow glass	68—71	63.17 (63.05)	4.31 (4.18)			
IIIl	acac	Yellow glass	77—79	69.01 (69.62)	5.10 (5.52)			P^+ = $[(C_2H_4)(C_4Ph_4OCH_3)]^+$ (415) $[(C_2H_4)(C_4Ph_4OCH_2)]^+$ (414)
IIIm	acac	Yellow glass	70—73	69.70 (68.98)	5.36 (5.71)			P^+ = $[(C_3H_6)(C_4Ph_4OCH_3)]^+$ (429) $[(C_3H_6)(C_4Ph_4OCH_2)]^+$ (428)
IIIn	acac	Yellow glass	79—83	70.69 (70.31)	5.51 (5.90)			
IIIp	Cl	Yellow prisms	134—140	66.35 (66.80)	5.04 (4.88)	5.84 (6.36)	1071 (1058)	
IIIq	Cl	Yellow prisms	128—131	67.48 (67.70)	5.45 (5.34)	5.89 (6.06)		

[a] From n-pentane. [b] Contains $\frac{1}{2}$ C_6H_6 solvent of crystallization (identified by ^1H NMR). [b] In C_6H_6.

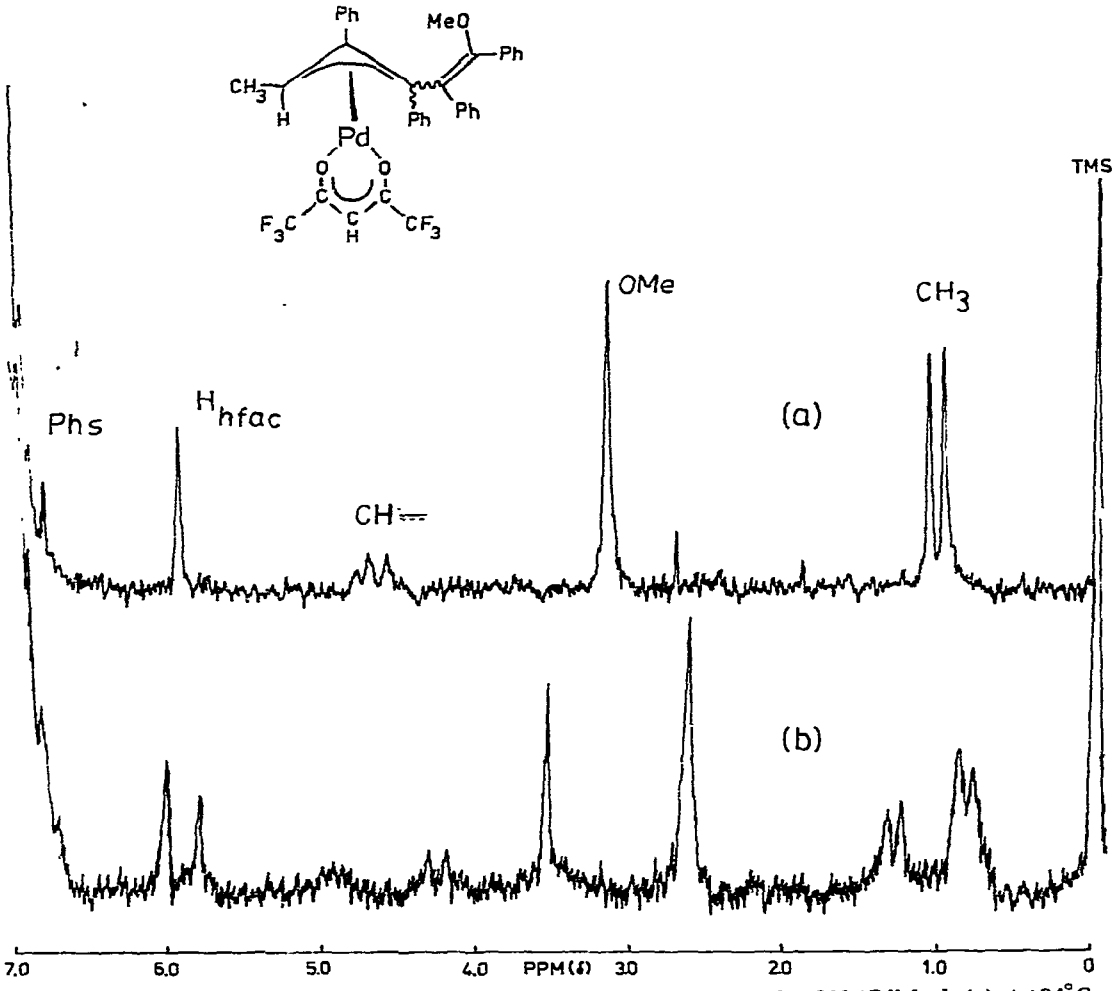
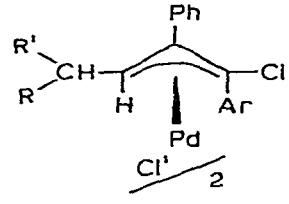


Fig. 2. ^{1}H NMR spectrum of IIIa, ethylene insertion product of [(*endo*-C_4Ph_4OMe)Pdhfac], (a) at +34°C (b) at −40°C ($CDCl_3$, 60 MHz).

clearly assignable to a CH_3CH⋯ moiety. Furthermore, the ^{13}C NMR spectrum contains a resonance at δ 71.99 ppm (d) typical of an allylic carbon bound to palladium(II) [12]. Assignment of the 1-alkyl allylic substituents in the *syn* position was made on the basis of chemical shift arguments. Proton chemical shift values of IIIa, IIIc, IIIh are similar to those reported by Staicu et al. for the similar complexes IV [13]. For the simple unstrained olefin reactions, ele-

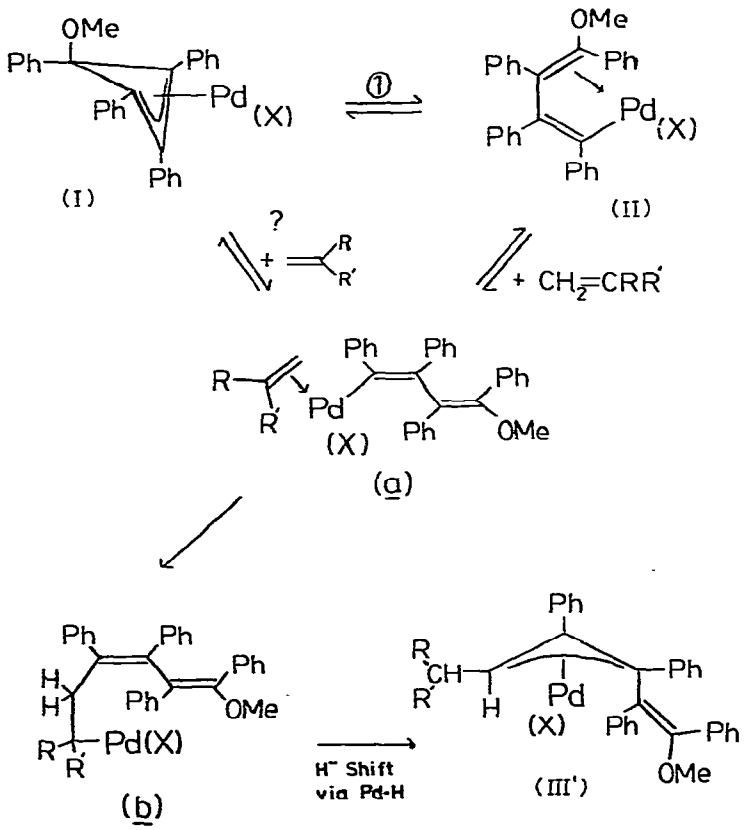


(IV)

mental analyses and mass spectra of the hfac and acac derivatives showed that only a single molecule of alkene had inserted.

The NMR data, although supporting the allylic structures for products IIIa—IIIq, does not fully confirm them (in particular, resonances associated with the butadienyl chain carbons could not be located in the ^{13}C NMR spectra, and must lie in the aromatic region). Furthermore, we initially assumed that the products would have the stereochemistry as shown (complex III′, Scheme 1). This stereochemistry is expected if insertion of the olefin occurs with normal conrotatory ring-opening of the cyclobutenyl complex (vide infra). As shown in Scheme 1, coordination of the olefin to the ring-opened species II generates the intermediate (π-olefin)(η^1-butadienyl)palladium complex a, which then undergoes insertion followed by palladium hydride rearrangement giving III′ (it is probable that this latter rearrangement proceeds via a palladium hydride-triene intermediate [10]). It is unclear as to whether or not olefin coordination to I may take place. While the ^1H NMR spectra of Ib, Ic show the presence of

SCHEME 1. Olefin insertion mechanism. The structure of III′ is that expected for olefin insertion following conrotatory ring-opening of I. The actual structure of the products IIIa—IIIq is that of III′ with the positions of the terminal methoxy and phenyl groups interchanged (see Fig. 3).



both ring-opened and ring-closed species I and II, only one species corresponding to Ia, the ring-closed complex, is observed for X = Cl. Since olefin insertion is observed on reaction with $[(endo\text{-}C_4Ph_4OMe)PdCl]_2$, either equilibrium 1 lies far to the left, or direct reaction of olefin with the ring-closed form Ia is occurring.

In order to confirm the η^3-allylic structure suggested on the basis of spectral assignments, crystals of the isobutene insertion product, IIIc, were grown by slow evaporation of an n-pentane solution, and submitted for X-ray analysis. The structure as determined by Ng and Nyburg [14] is illustrated in Fig. 3. This showed that while the allylic nature of the insertion product was essentially correct and that olefin insertion with an accompanying hydride shift had occurred, the stereochemistry of the vinylic substituent CPh=CPhOMe at the end of the butadienyl chain was unexpectedly *cis*. The phenyl groups of the PhC=CPhOMe moiety should be mutually *trans* if the olefin insertion had occurred as in Scheme 1, i.e., a conrotatory ring-opening of the cyclobutenyl function followed by olefin insertion and hydride migration. In order to explain the observed stereochemistry, the reaction pathway must involve either an olefin-promoted disrotatory ring-opening of the cyclobutenyl ligand prior to insertion, or a conrotatory opening with subsequent isomerization of the PhC=CPhOMe function after insertion of the olefin. We favour the latter for the following reasons: (i) X-ray crystal structures of the PMe_2Ph derivatives $[(endo\text{-}C_4Ph_4OEt)Pd(PMe_2Ph)acac]$ [4,15] and $[(endo\text{-}C_4Tol_4Ph)Pd(PMe_2Ph)acac]$ [5,16] have confirmed that conrotatory ring-opening of the cyclobutenyl moiety has taken place; (ii) Maitlis and co-workers recently isolated both the conrotatory and apparent disrotatory ring-opened butadienyl forms of $[Pd(C_4Tol_4Ph)(S_2CN\text{-}i\text{-}Pr_2)]$ (Va, Vb) and their PMe_2Ph derivatives [5,16]. It was shown, however, that the "disrotatory" product Vb had formed via isomerization of the normal conrotatory form, Va, after ring-opening had

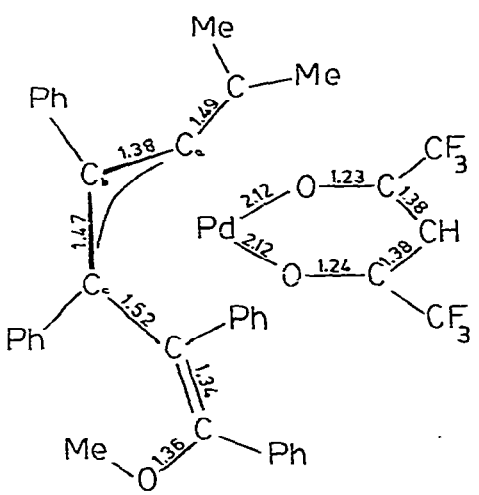


Fig. 3. The molecular structure of IIIc as determined by X-ray crystallography [14]. Bond lengths shown in Å. Pd equidistant from allylic carbons, thus Pd—C_a = 2.11(1) Å, Pd—C_b = 2.11(1) Å, Pd—C_c = 2.15(1) Å. An unusual feature is the dihedral angle between the plane of the allylic function ($C_aC_bC_c$) and the (Pdhfac) unit, which is 71.3°.

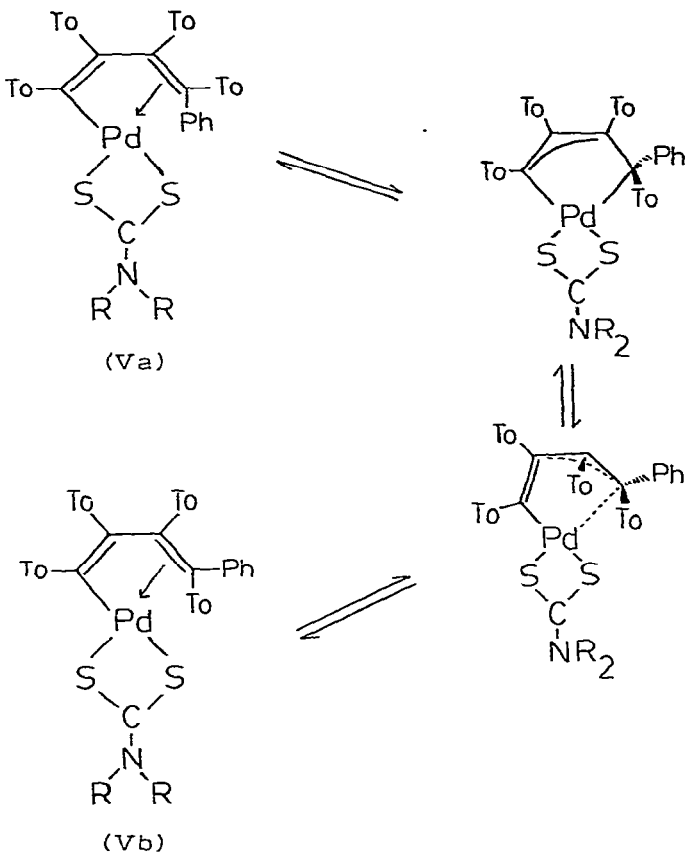
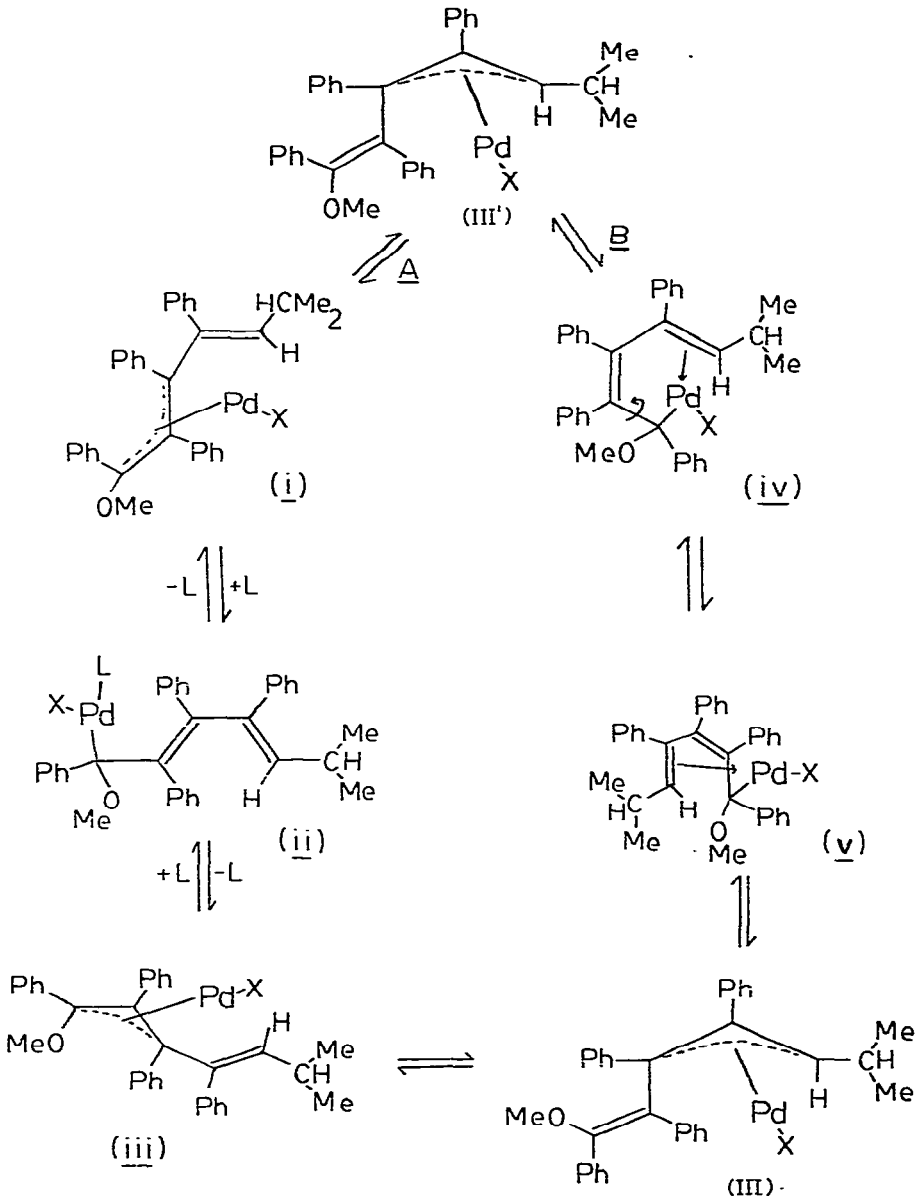


Fig. 4.

occurred, presumably through a metallocyclopentenyl intermediate (Fig. 4). The reaction mixtures contained Va and Vb in a 2/3 ratio and separate resonances for each isomer were observed in the ^{1}H NMR.

Examination of the ^{1}H and ^{13}C NMR spectra of our olefin insertion products IIIa—IIIq showed that in all cases only one species was present (excluding *syn-anti* isomers, vide infra). In view of the observed conrotatory ring-opening of the phosphine derivatives and since isomerization of a conrotatory to disrotatory type before insertion should have lead to a mixture of products, we conclude that an isomerization occurs after carbon—carbon bond formation. Two plausible mechanisms for isomerization may be visualised as shown in Scheme 2. In Path A, formation of the alternate η^3-allyl, (i), followed by coordination of L generates a η^1-allyl, (ii), which may undergo carbon—carbon bond rotation and reform the η^3-allyl, (iii). The result of the *syn-anti* isomerism of the methoxy and phenyl groups is the *cis* disposition of the phenyl groups as the η^3-allyl may "slip" down the chain to give the observed product III. Alternately, in Path B, the generation of a pentadienyl intermediate, (iv), followed by C—C bond rotation and η^3-allyl complexation could also account for the formation of III.

SCHEME 2. Mechanisms proposed for the isomerisation of anticipated olefin insertion product III' to observed complex III.



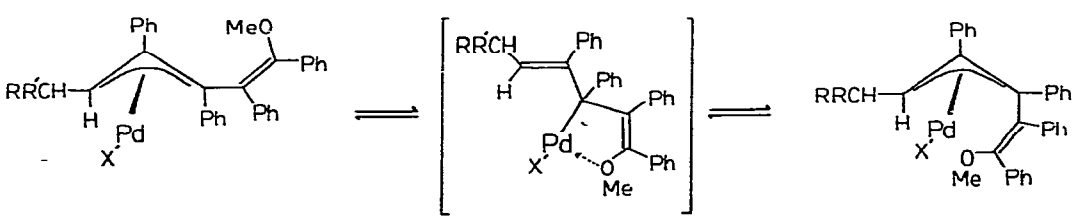
The addition of isomeric 2-butenes to Ic would be expected to yield, via a hydride shift, a 1-ethyl, 1-methyl allylic complex. However, both *cis*- and *trans*-but-2-ene gave products whose spectra (^{1}H and ^{13}C) were identical to the 1-butene insertion complex IIIi. Moreover, the reaction of tetramethylethylene, an alkene with no olefinic hydrogens, with Ic proceeded very slowly (ca. 2 weeks in a sealed tube) to give the product identical to that obtained on reaction of Ic with 2,3-dimethyl-1-butene. Battiste et al. have noted a similar effect

on $(PhCN)_2PdCl_2$ catalyzed coupling of olefins with diphenylacetylene [17]. They reported that reaction of either *cis*-2-butene or 1-butene with tolan gave only the terminal olefinic product. The ^1H NMR of mixtures of *cis*- or *trans*-2-butene with Ic showed only the resonances associated with the starting olefin (1-butene resonances not observed), which dropped in intensity as product formation occurred. Furthermore, the reaction rates of *cis*- and *trans*-2-butene and 1-butene were approximately the same with Ic, implying that olefin isomerization is not rate-determining in these insertion reactions.

The reaction of complexes Ia—Ic with the strained olefins norbornene or 2,5-norbornadiene resulted in the formation of polymeric materials due to multiple insertions of the olefin, as indicated by ^1H NMR spectroscopy. Further characterization was not attempted. These results may be contrasted with the reaction of simple η^3-allylic palladium complexes with strained olefins, which give clean single insertion products of the "enyl" type [2].

Variable temperature studies. The low temperature ^1H NMR spectrum of the ethylene insertion product of [(*endo*-C_4Ph_4OMe)Pdhfac] (IIIa) showed the presence of two distinct species in solution (Fig. 2b, —40°C). On warming, coalescence of the peaks occurred via a concentration independent process, to give the room temperature spectrum (region of fast exchange). Similar results were observed for the other hfac and acac derivatives of the olefin insertions. At low temperatures a 3/1 ratio of isomers was seen in all cases. A process consistent with these observations is the rapid intramolecular *syn—anti* exchange of the phenyl and vinylic substituents (Fig. 5). The chloride derivatives (X = Cl), which could be obtained by reaction of Ia with the olefin or by treating the hfac derivatives of the insertion products with one equivalent of dry HCl, showed both species at room temperature, indicating that exchange was already in the slow region. Again, a 3/1 ratio of isomers was observed. It is interesting to note that the X-ray crystal structure of the isobutene insertion product, IIId, showed the vinylic group in the *anti* position [14].

Reaction of Ia—Ic with 1,2-dienes. A stoichiometric amount of the 1,2-diene was added to a $CDCl_3$ solution of the palladium complex and product formation monitored in the ^1H NMR. Resonances characteristic of the allylic complexes VIa—VIi quickly developed, and the ^1H and ^{13}C NMR and analytical data of the compounds are contained in Tables 4, 5 and 6. The order of diene

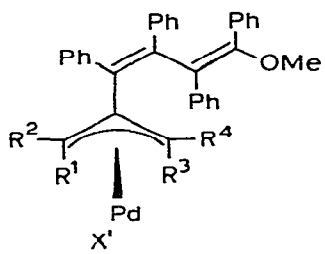


A

Fig. 5. Postulated mechanism for intramolecular *syn—anti* site exchange in olefin insertion products III (X = acac, hfac). Formation of a short-lived η^1-allylic intermediate A stabilised by anchimeric assistance from the oxygen of the side chain methoxy substituent allows for the facile *syn—anti* site exchange of Ph and PhC=CPh(OMe) substituents. Similar anchimeric assistance of *syn—anti* site exchange by side chain substituents has been observed in several allylic complexes of Pd [3].

TABLE 4

^{1}H NMR DATA FOR 1,2-DIENE INSERTION PRODUCTS VI (chemical shifts in ppm, $CDCl_3$, 60 MHz)



(VI)

VIa—VIc: R^{1-4} = H
VId—VIf: $R^1 = R^4$ = H, $R^2 = R^3$ = Me
VId—VIl: R^{1-4} = Me

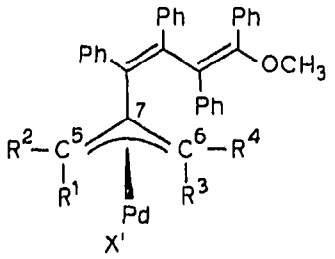
Complex	1,2-Diene	X	H^1	H^2	H^3	H^4	OMe	X
VIa	Allene	Cl [a]	2.55	3.55	2.55	3.55	3.47	
VIb	Allene	acac [a]	2.45	3.34	2.45	3.35	3.52	CH, 5.30; CH_3, 1.90
VIc	Allene	hfac [a]	2.60	3.62	2.60	3.62	3.48	CH, 6.03
VId(i)	1,3-Dimethylallene	Cl	4.73	1.25	3.90 (br)	1.18	3.52	
VId(ii)	1,3-Dimethylallene	Cl	4.58	1.02	3.82	0.23	3.47	
VIe	1,3-Dimethylallene	acac	4.24	0.90	3.50	0.47	3.48	CH, 5.16; CH_3, 1.84, 1.94
VIf(i)	1,3-Dimethylallene	hfac	2.97	0.97	2.97	0.97	3.32	CH, 5.92
VIf(ii)	1,3-Dimethylallene	hfac	4.50	0.85	3.83	0.56	3.43	CH, 5.97
VIg	Tetramethylallene	Cl	0.61	1.68	0.73	1.87	2.30	
VIh	Tetramethylallene	acac	0.62	1.64	0.70	1.86	2.31	CH, 5.13; CH_3, 1.68, 1.97
VIi	Tetramethylallene	hfac	0.66	1.67	0.75	1.92	2.37	CH, 5.88

[a] Data for spectrum at +50° C.

reactivity was roughly 1,1-dimethylallene >> allene > 1,3-dimethylallene >> tetramethylallene, and the reactivity of the anionic ligand followed, X = hfac > acac >> Cl. With 1,1-dimethylallene and complexes Ia—Ic, reaction was very rapid and multiple insertions of the diene occurred (up to five insertions of diene per palladium, as determined by mass spectra (X = hfac), and the single insertion product could not be isolated. When allene was added to a solution of [(*endo*-C_4Ph_4OMe)$PdCl]_2$, the product of insertion of a single molecule of allene predominated over the insertion of a second allene molecule (ca. 20/1 by NMR integration). If Ib (X = acac) was treated instead, the ratio of the single to double allene insertion was lower (5/1), while for X = hfac, even on reaction under dilute conditions at low temperatures, inseparable ~1/1 mixtures of the first and second insertion product were obtained. For comparative purposes the hfac complex of the single allene insertion was prepared from the chloride complex VIa by treatment with Tlhfac. Only the insertion products containing a

TABLE 5

$^{13}\{^{1}H\}$ NMR DATA FOR 1,2-DIENE INSERTION PRODUCTS VI (chemical shifts in ppm)



Complex	1,2-Diene	X	C^1	C^2	C^3	C^4	C^5	C^6	C^7	OCH_3	Other
VIc	Allene	hfac	—	—	—	—	57.9	53.6	—	55.8	CH, 89.4; CF_3, 118.2; CO, 176.5
VId(i)	1,3-Dimethylallene	Cl	17.7	—	—	18.8	75.2	78.1	121.0	58.5	
VId(ii)	1,3-Dimethylallene	Cl	—	14.5	—	17.2	73.3	74.6	116.7	58.5	
VIf(ii)	1,3-Dimethylallene	hfac	—	14.2	—	16.9	70.6	70.2	—	58.5	CH, 89.0; CF_3, 118.1; CO, 175.7
VIi	Tetramethylallene	hfac	28.9	25.8	25.8	26.4	84.5	84.4	—	54.9	CH, 88.9; CF_3, 118.1; CO, 175.9

TABLE 6

ANALYTICAL DATA FOR 1,2-DIENE INSERTION COMPLEXES VIa–VIi

Complex	X	Physical appearance	M.p. (°C)	Analysis (%) (Found (calcd.) (%))			Mass spectral data [b], major organic fragments, ion (assignment *m/e*)	Molecular weight [c] (Found (calcd.))
				C	H	Cl		
VIa	Cl	Yellow prisms [a]	131–141	64.42 (63.80) [a]	4.29 (4.61) [a]	13.69 (11.59) [a]		
VIb	acac	Yellow prisms	164–167	70.09 (70.20)	5.56 (5.41)	— —	P^+ = $[(C_3H_4)(C_4Ph_4OCH_3)]^+$ (427) $[(C_6H_8)(C_4Ph_4OCH_3)]^+$ (467)	
VIc	hfac	Yellow glass	83–86	60.05 (59.97)	3.99 (3.81)	—	P^+ = $[(C_3H_4)(C_4Ph_4OCH_3)Pdhfac]^+$ (740) [b] $[(C_3H_4)(C_4Ph_4OCH_3)^+$ (427)	
VId	Cl	Yellow prisms	171–172	68.21 (68.35)	5.15 (5.23)	5.76 (5.93)		
VIe	acac	Pale yellow prisms	129–135	70.15 (70.85)	5.54 (5.79)	— —	P^+ = $[(C_3Me_2H_2)(C_4Ph_4OCH_3)]^+$ (455)	
VIf	hfac	Pale green glass	84–86	61.00 (60.81)	4.27 (4.19)	— —	P^+ = $[(C_3Me_2H_2)(C_4Ph_4OCH_3)]^+$ (455)	
VIg	Cl	Yellow prisms [a]	168–177	66.58 (65.63) [a]	6.16 (5.43) [a]	11.06 (10.61) [a]		
VIh	acac	Yellow prisms	142–145	71.53 (71.45)	6.24 (6.14)	— —	P^+ = $[(C_3Me_4)(C_4Ph_4OCH_2)]^+$ (482)	
VIi	hfac	Pale green prisms	86–90	61.63 (61.78)	4.74 (4.55)	— —	P^+ = $[(C_3Me_4)(C_4Ph_4OCH_2)]^+$ (482)	814 (796)

[a] Contains solvent of crystallization (identified by ^{1}H NMR), $\frac{1}{2}$ CH_2Cl_2. [b] Based on ^{106}Pd. [c] In C_6H_6.

single molecule of 1,2-diene were observed with reactions of 1,3-dimethylallene and tetramethylallene and Ia—Ic. Clearly both steric and electronic factors play an important role in determining the rate of reaction and extent of multiple insertions.

The ^{1}H NMR spectra of the complexes VIa—VIi are more complex than structure VI would at first indicate. Room temperature spectra of compounds VIg—VIi derived from the reaction of tetramethylallene (R^{1-4} = Me) with Ia—Ic, show four separate methyl resonances and a single methoxy peak in the 60 MHz NMR. Similarly, the spectra of VIa—VIc, the allene insertion products (R^{1-4} = H) contained four separate allylic proton peaks at low temperatures. Thus, the ^{1}H NMR spectrum of VIb shows four distinct singlets at δ 3.73, 2.78,

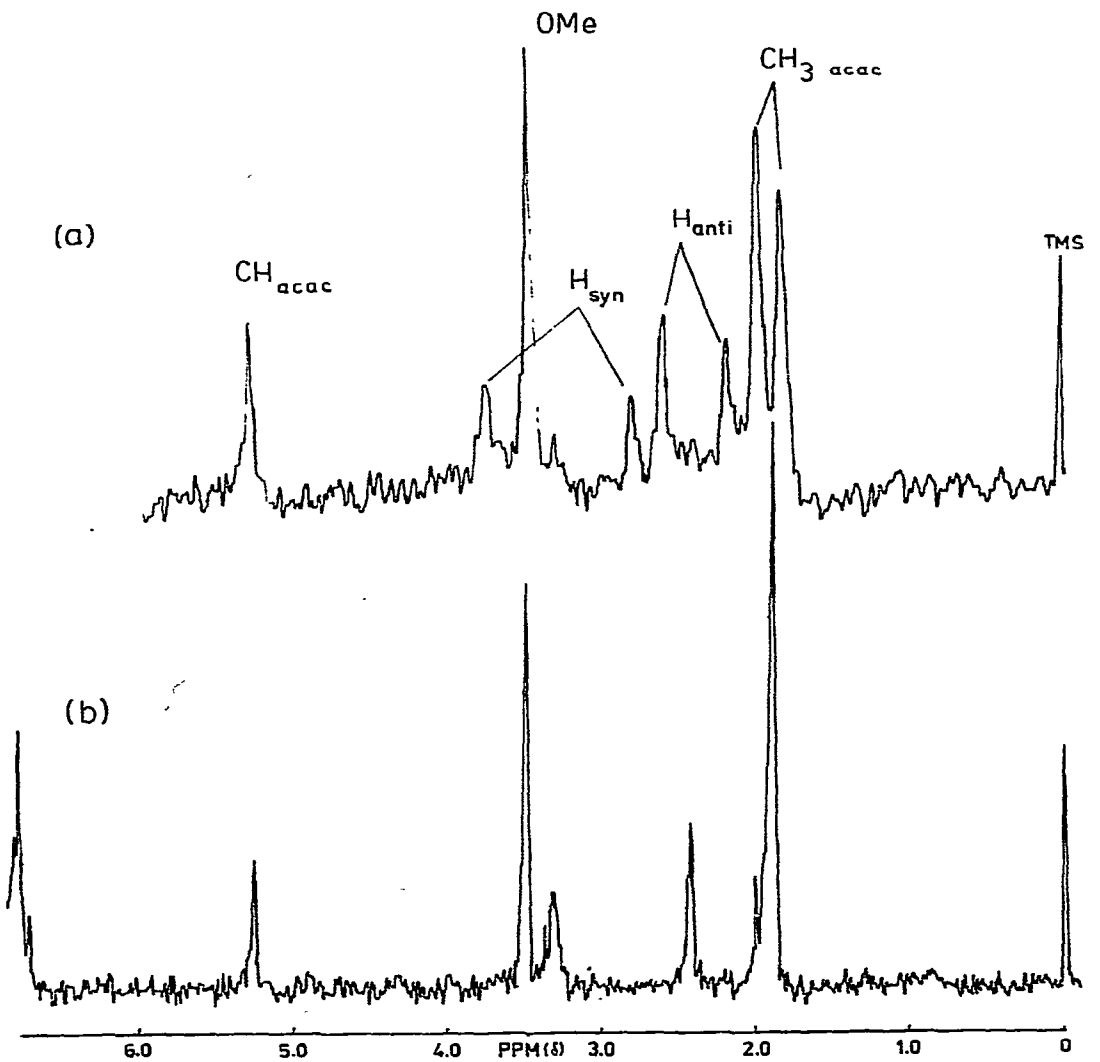


Fig. 6. ^{1}H NMR of VIb, allene insertion product of [(*endo*-C_4Ph_4OMe)Pdacac], (a) at −20°C (b) at +57°C ($CDCl_3$, 60 MHz).

2.57 and 2.19 ppm (Fig. 6a) assignable to non-equivalent *syn* and *anti* allylic protons, while the methyl groups of the acac ligand, which are also inequivalent appear as singlets at δ 1.97 and 1.80 ppm. The presence of one methoxy peak at δ 3.47 ppm indicates that a single solution species is present which contains no plane of symmetry relating both halves of the allylic function or the acac methyls. Warming the solution causes coalescence of acac methyl singlets and of the *syn* and *anti* resonances, each to a single peak (Fig. 6b). Dilution studies indicate that the process which equilibrates the protons is an intramolecular one. Furthermore, the measured activation energies for this process, $\Delta G^{\ddagger}_{Tc}$, as determined for the acac methyl groups and the *anti* proton resonances on the allyl, are the same to experimental accuracy (15.1 and 15.2 kcal/mol respectively).

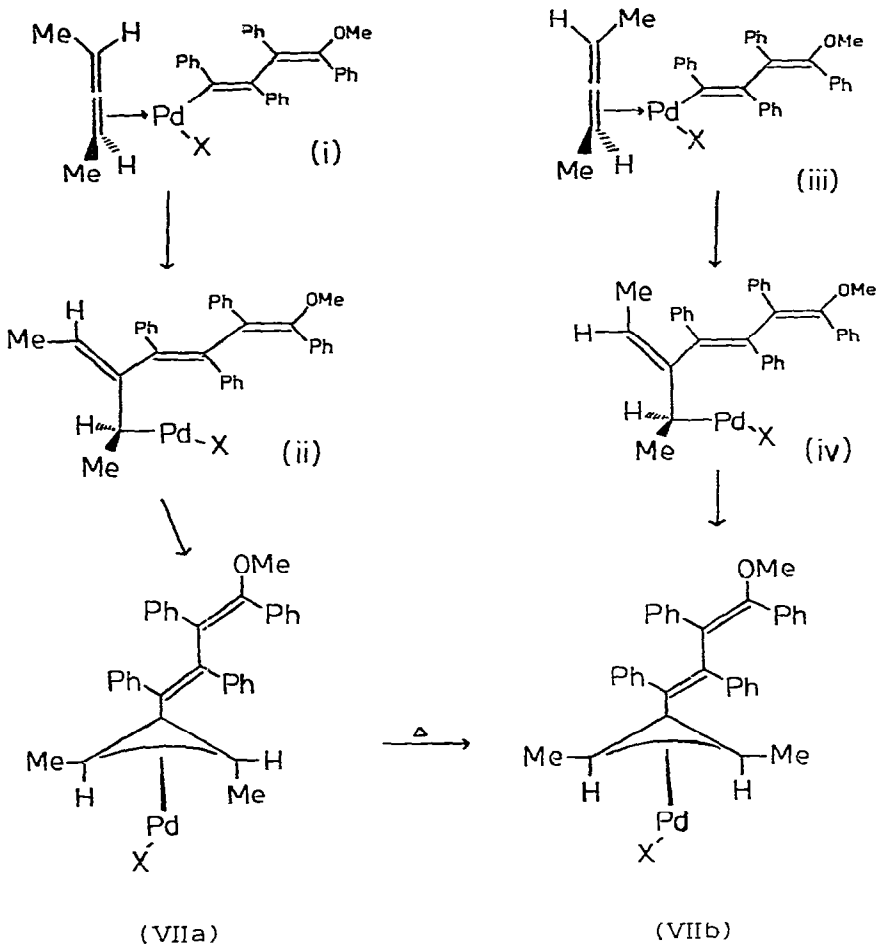
The above observations are consistent with structure VI for these compounds, where the asymmetric disposition of the tetraphenylbutadiene chain lowers the symmetry of the complex substituents. For the allene insertion products VIa—VIc this occurs at low temperatures, and on heating, free rotation of the butadienyl substituent equilibrates the *syn-syn* and *anti-anti* proton resonances at the same time that the functional groups on the β-diketonate ligand become equivalent. For the complexes VIg—VIi where the allylic substituents are all methyl groups, the energy barrier for free rotation of the chain is much greater and separate resonances for each allylic methyl are observed, even at elevated temperatures *.

The spectra of the 1,3-dimethylallene insertion products VId—VIf were further complicated by the presence of two isomers in the initial reaction mixtures (X = Cl, hfac) (Table 4, isomers (i) and (ii)), which showed two sets of allylic protons and methyl doublets as well as two distinct methoxy peaks. On warming solutions of the mixtures, conversion of the peaks associated with the (i) isomer to the (ii) isomer occurred in an irreversible manner. The hfac derivative VIf(i) underwent isomerization very rapidly in solution and attempts to obtain ^{13}C data of the isomeric mixture gave only the spectrum of the final isomer VIf(ii). The chloride compound converted much more slowly in solution, and the ^{13}C NMR of the mixture showed four distinct methyl and allylic (terminal) carbons indicative of non-equivalence of the allylic moiety in both isomers. The ^{13}C spectrum of the solution after heating contained only the two upfield methyl and allylic carbon peaks (Table 5). These results may be explained by the initial formation of a mixture of *syn,syn* and *syn,anti* isomers VIIa, VIIb (Scheme 3). Conversion of the *syn,anti* compound VIIa to the thermodynamically favoured *syn,syn* form VIIb could then occur on heating, via a $\eta^3 \rightarrow \eta^1 \rightarrow \eta^3$ rearrangement. Lukas et al. have reported the formation of both *syn*- and *anti*-1-t-butyl-2-methylallylpalladium(II) complexes in the reaction of 2,4,4-trimethyl-2-pentene with $PdCl_2$ [18]. The *anti*-t-butyl complex is kinetically favoured and may be converted to the thermodynamic *syn*-t-butyl product by refluxing with traces of phosphine.

Reaction of Ia—Ic with 1,3-dienes. Complexes Ia—Ic readily reacted with 1,3-dienes in chloroform at room temperature. Relative reactivities of the

* Rapid decomposition of the complexes VIg—VIi at higher temperatures in solution prevented estimation of this activation energy.

SCHEME 3. Mechanism of formation of *syn-anti* isomer VIIa. Coordination of 1,3-dimethylallene with the methyl group of the adjacent double bond pointing away from the metal (intermediate (i)), followed by insertion (ii), gives the *syn-anti* isomer VIIa, which converts to VIIb on heating. Alternately, a minor isomer (iii) formed by coordination of the diene with the methyl pointing towards the metal would give the *syn-syn* form (VIIb) on insertion [21].



anionic ligand again followed the order X = hfac > acac >> Cl and studies were concentrated on the hfac derivatives. The products of these reactions, obtained as yellow glasses on work-up, gave elemental analyses, molecular weights and mass spectra (β-diketonates) consistent with the insertion of a single molecule of diene per palladium (Table 7). The 60 MHz ^{1}H NMR spectra were, however, very complex owing to several factors: overlap of many of the allylic proton resonances, dynamic equilibria in solution and in some cases the presence of isomeric species (vide infra). ^{13}C and 220 MHz. ^{1}H NMR spectra were necessary to establish the allylic nature of the products. Thus, for example, the 220 MHz ^{1}H NMR spectrum of VIIIe, the insertion product derived from [(*endo*-C_4Ph_4OMe)Pdhfac] and 2,3-dimethyl-1,3-butadiene, (Fig. 7a) could be assigned as follows: δ (ppm) 2.93 (s, 3p), OMe; 3.12 (s, 1p), H_{anti}; 3.59 (s, 1p), H_{syn}; 1.56 (s, 3p), CH_3 (2-position); 0.83 (s-br, 3p), CH_3 (3-position); 5.90 (s, 1p),

TABLE 7

ANALYTICAL DATA FOR 1,3-DIENE INSERTION COMPLEX VIII

Complex	1,3-Diene	X	M.p. (°C)	Analysis (%) (Found (calcd.)(%))			Molecular weight [a] (Found (calcd.))	Mass spectral data, major organic fragments, ion (assignment, m/e)
				C	H	Cl		
VIIIa	1,3-Butadiene	hfac	80—82	61.76 (62.01) [b]	4.22 (4.19) [b]		836 (756)	P^+ = $[(C_4H_6)(C_4Ph_4OCH_3)]^+$ (441) $[(C_4H_6)(C_4Ph_4OCH_2)]^+$ (440)
VIIIb	1,3-Pentadiene	hfac	72—76	62.51 (62.42) [b]	4.30 (4.36) [b]		702 (768)	P^+ = $[(C_5H_8)(C_4Ph_4OCH_3)]^+$ (455) $[(C_5H_8)(C_4Ph_4OCH_2)]^+$ (454)
VIIIc	4-Methyl-1,3-pentadiene	hfac	74—76	62.92 (62.82) [b]	4.64 (4.54) [b]		927 (782)	P^+ = $[(C_6H_{10})(C_4Ph_4OCH_3)]^+$ (469) $[(C_6H_{10})(C_4Ph_4OCH_2)]^+$ (468)
VIIId	Isoprene	hfac	73—75	61.24 (60.91)	4.06 (4.19)			P^+ = $[(C_5H_8)(C_4Ph_4OCH_3)]^+$ (455) $[(C_5H_8)(C_4Ph_4OCH_2)]^+$ (454)
VIIIe	2,3-Dimethyl-1,3-butadiene	hfac	81—85	61.26 (61.35)	4.26 (4.38)			P^+ = $[(C_6H_{10})(C_4Ph_4OCH_3)]^+$ (469) $[(C_6H_{10})(C_4Ph_4OCH_2)]^+$ (468)
VIIIf, VIIIg	2,4-Hexadiene	hfac	71—73	61.35 (61.37)	4.38 (4.33)			P^+ = $[(C_6H_{10})(C_4Ph_4OCH_3)]^+$ (469) $[(C_6H_{10})(C_4Ph_4OCH_2)]^+$ (468)
VIIIh	1,3-Cyclohexadiene	hfac	68—73	61.66 (61.51)	4.35 (4.13)		832 (780)	P^+ = $[(C_6H_8)(C_4Ph_4OCH_3)]^+$ (467) $[(C_6H_8)(C_4Ph_4OCH_2)]^+$ (466)
VIIIi	1,3-Pentadiene	acac	83—87	69.76 (69.09) [c]	5.74 (5.69) [c]			P^+ = $[(C_5H_8)(C_4Ph_4OCH_3)]^+$ (455) $[(C_5H_8)(C_4Ph_4OCH_2)]^+$ (454)
VIIIj	4-Methyl-1,3-pentadiene	acac	83—87	69.91 (69.42) [c]	5.81 (5.86) [c]			P^+ = $[(C_6H_{10})(C_4Ph_4OCH_3)]^+$ (469) $[(C_6H_{10})(C_4Ph_4OCH_2)]^+$ (468)
VIIIk	2,3-Dimethyl-1,3-butadiene	acac	84—90	69.12 (69.42) [c]	5.86 (5.86) [c]			P^+ = $[(C_6H_{10})(C_4Ph_4OCH_3)]^+$ (469) $[(C_6H_{10})(C_4Ph_4OCH_2)]^+$ (468)
VIIIl	1,3-Butadiene	Cl	105—110	63.04 (64.28) [d]	4.76 (4.83) [d]	11.78 (11.33) [d]		
VIIIm	4-Methyl-1,3-pentadiene	Cl	118—123	67.55 (68.75)	5.39 (5.44)	7.03 (5.80)		

[a] In C_6H_6. [b] Compounds contain solvent of crystallisation: $\frac{1}{2}$-C_6H_6. [c] $\frac{1}{4}$-CH_2Cl_2. [d] $\frac{1}{2}$-CH_2Cl_2.

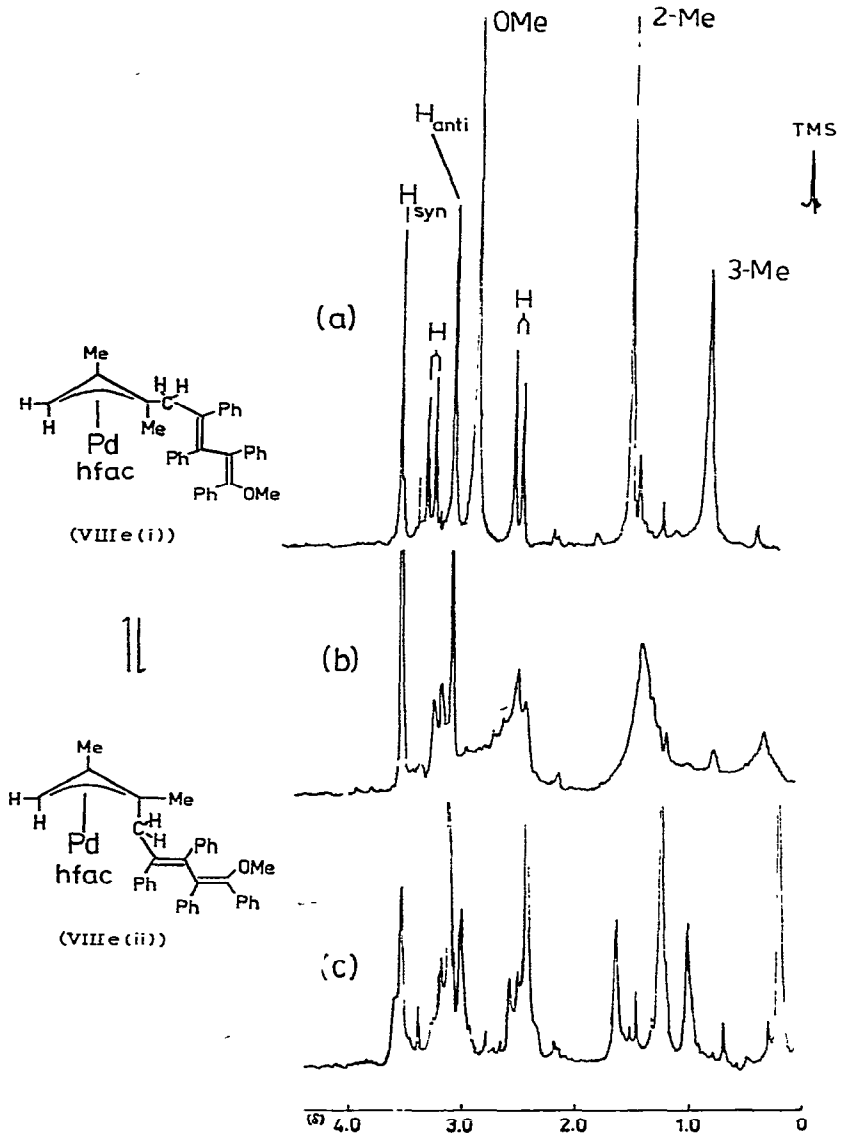


Fig. 7. ^{1}H NMR of 2,3-dimethyl-1,3-butadiene insertion product of [(*endo*-C_4Ph_4OMe)Pdhfac] (VIIIe) showing *syn—anti* exchange between isomer VIIIe(i) and VIIIe(ii); (a) at +57°C (b) at +20°C (c) at —14°C ($CDCl_3$, 220 MHz, hfac and aromatic protons omitted).

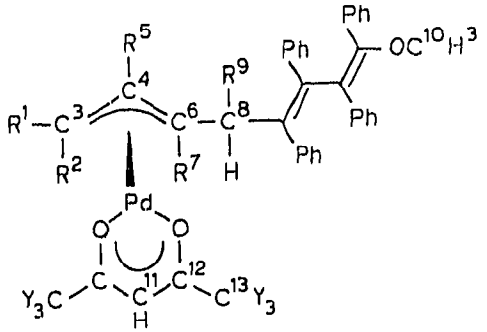
CH (hfac); 6.5—7.5 (m, 20p), Ph. In addition, the protons of the methylene group on the substituent chain of the allyl are diastereotopic, and appear at δ 2.55 and 3.32 ppm (d, 1p each), showing a geminal coupling constant of 15 Hz. The large chemical shift difference (0.77 ppm) between these protons is probably due to a through-space shielding effect by the adjacent phenyl ring.

Broadening of the upfield methyl peak is due to a dynamic *syn—anti* exchange process, shown to be intramolecular in nature by dilution studies. Cooling the solution of VIIIe to room temperature (Fig. 7b) causes broadening

TABLE 8

$^{13}C\{^1H\}$ NMR DATA FOR hfac AND acac DERIVATIVES OF 1,3-DIENE INSERTION PRODUCTS

VIII (Chemical shifts in ppm, coupling constants in Hz)



(VIII)

VIIIa: $R^{1,2,5,7,9}$ = H
VIIIb, VIIIi: R^1 = Me; $R^{2,5,7,9}$ = H
VIIIc, VIIIj: $R^{1,2}$ = Me; $R^{5,7,9}$ = H
VIIId(A), VIIId(B): $R^{1,2,5,9}$ = H; R^7 = Me
VIIId(C): $R^{1,2,7,9}$ = H; R^5 = Me
VIIIe, VIIIk: $R^{1,2,9}$ = H; $R^{5,7}$ = Me
VIIIf, VIIIg: $R^{1,9}$ = Me; $R^{2,5,7}$ = H

Complex	1,3-Diene	Y	Isomer	C^1	C^2	C^3	C^4	C^5	C^6	C^7	C^8	C^9	C^{10}	C^{11}	C^{12}	C^{13}
VIIIa	1,3-Butadiene	F		—	—	55.3	113.4	—	77.5	—	38.7	—	58.1	89.6	175.7	118.2
VIIIb	1,3-Pentadiene	F	A	16.8	—	72.4	114.1	—	73.9	—	38.8	—	55.7	89.5	175.6	118.2
			B	16.8	—	72.7	114.1		73.5	—	38.9	—	58.1	*J*(CF) 166	*J*(CF) 34	*J*(CF) 287
VIIIc	4-Methyl-1,3-pentadiene	F	A	25.9	21.7	85.6	109.1	—	71.6	—	39.3	—	55.7	89.5	175.7	118.2
			B	25.9	21.7	86.0	109.2	—	71.1	—	39.3	—	58.2	*J*(CF) 164	*J*(CF) 34	*J*(CF) 287
VIIId	Isoprene	F	A	—	—	52.9	[a]	18.3	75.9	—	36.0	—	56.0	89.5	175.5	118.2
			B	—	—	53.0	[a]	18.3	76.0	—	36.0	—	58.0	*J*(CF) 166	*J*(CF) 34	*J*(CF) 288
			C	—	—	53.0	109.5	—	91.0	ca. 17(br)	45.2	—	56.2			
VIIIe	2,3-Dimethyl-	F		—	—	54.6	[a]	19.8	85.4	19.6	42.5	—	55.9	89.5 *J*(CF) 169	175.4 *J*(CF) 34	118.1 *J*(CF) 286
VIIIf	*csi,cis-* or *trans, trans*-2,4-hexadiene			17.1	—	76.9	110.5	—	81.4	—	39.9	15.7	56.3	89.5 *J*(CF) 165	175.8 *J*(CF) 35	118.1 *J*(CF) 284
VIIIg	*cis,trans*-2,4-Hexadiene	F		17.1	—	73.6	111.0	—	81.9	—	41.0	16.9	56.0	89.5 *J*(CF) 166	175.5 *J*(CF) 34	118.1 *J*(CF) 284
VIIIi	1,3-Pentadiene	H		16.6	—	67.7	112.7	—	70.4	—	38.5	—	55.9	99.6		28.2
VIIIj	4-Methyl-1,3-pentadiene	H		25.7	21.6	68.0	107.9	—	80.5	—	38.9	—	55.9	99.5		28.4
VIIIk	2,3-Dimethyl-1,3-butadiene	H		—	—	55.1	[a]	27.9	80.9	28.3	42.0	—	56.0	99.6		28.3

[a] Falls in aromatic region.

of the methyl and methoxy resonances, while at —14°C two species in a 3/1 ratio are clearly seen (Fig. 7c), indicative of the freezing out of *syn*- and *anti*-methyl isomers VIIIe(i) and VIIIe(ii). The ^{13}C NMR of the complex (Table 8) is also consistent with the assigned structure (fast exchange limit). While allylic carbon C^4 falls in the aromatic region of the spectrum and cannot be discerned, a triplet at δ 54.6 ppm and singlet at δ 85.4 ppm are assignable, respectively, to the C^3 and C^6 carbon atoms of the allylic moiety. The ^1H NMR spectrum of the acac and Cl derivatives VIIIk, VIIIn are assigned in a similar manner (Table 9).

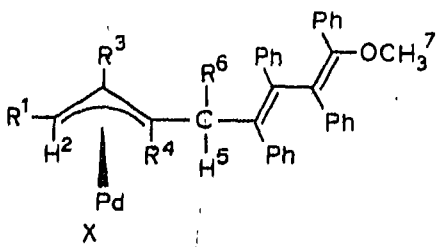
The insertion products of Ic with 2,4-hexadienes each showed ^{13}C and ^1H NMR spectra consistent with a single solution species. *cis,cis*- and *trans,trans*-2,4-hexadiene give identical products, while the insertion product of *cis,trans*-2,4-hexadiene has ^{13}C and ^1H NMR resonances with slightly different chemical shift values (Tables 8, 9, complexes VIIIf, VIIIg). These results are consistent with the stereospecific addition of the 1,3-diene to the butadienyl—palladium bond. As previously shown by Lukas et al. [9], reaction of isomeric 2,4-hexadienes with $PdCl_2$ gives the identical allylic complex with the *cis,cis* and *trans,trans* isomers, while the product of *cis,trans*-2,4-hexadiene insertion is diastereomeric. While Lukas found that these 2-chloromethyl allylic palladium diastereomers epimerised on warming, no analogous epimerisation is expected or observed in complexes VIIIf, VIIIg since carbon—carbon rather than carbon—chlorine bond formation has occurred on insertion.

The ^{13}C NMR spectra of the products VIIIa—VIIIc derived from the reaction of 1,3-butadiene, 1,3-pentadiene or 4-methyl-1,3-pentadiene with Ic are also consistent with η^3-allylic palladium(II) complexes. In the cases of the unsymmetric 1,3-dienes, the position and multiplicity of the allylic carbon resonances indicated that insertion into the less-substituted C=C double bond of the diene has occurred (Table 8). However, ^{13}C spectra of the 1,3-pentadiene and 4-methyl-1,3-pentadiene insertion products VIIIb, VIIIc showed two sets of resonances with very similar chemical shifts (Table 8, isomers A and B). These isomers were identified in the ^1H NMR spectra of the compounds by the appearance of two distinct types of methoxy peaks. Mixtures of isomers A and B could also be detected in the ^1H NMR spectra of the 1,3-butadiene, isoprene and 1,3-cyclohexadiene insertions products VIIIa, VIIId, VIIIh. The upfield methoxy resonance corresponding to isomer A falls in the region δ 2.61—2.93 ppm while B occurs from δ 3.42—3.53 ppm (the methyl group resonances of complexes VIIIb, VIIIc, VIIId were also consistent with two isomers A and B). Upon varying the relative amounts of the reacting diene and the palladium complex, the ratio of A to B peaks changed. Under highly dilute 1/1 diene/palladium conditions isomer A predominated. However, if excess diene was employed in the reaction mixture (5—7 fold excess), B could be obtained almost exclusively. Significantly, the reaction mixture of A and B obtained under dilute conditions produced no change in the ratio of the two species on reaction with excess diene; i.e., excess diene does not convert A to B. Variable temperature NMR studies further indicated that interconversion of A and B did not occur up to the decomposition point of the compounds.

The exact structures of isomers A and B have not as yet been ascertained. However, the spectroscopic and analytical data indicated that both A and B have the same stoichiometry and are η^3-allylic products derived from the

TABLE 9

^{1}H NMR DATA FOR 2,3-DIMETHYL-1,3-BUTADIENE AND 2,4-HEXADIENE INSERTION PRODUCT VIII (chemical shifts in ppm (multiplicity, coupling constants))



VIIIe, VIIIk, VIIIn: $R^{1,6}$ = H, $R^{3,4}$ = Me
VIIIf, VIIIg: $R^{1,6}$ = Me, $R^{3,4}$ = H

Complex	1,3-diene	X	H^1	H^2	H^3	H^4	H^5	H^6	H^7	X
8e	2,3-dimethyl-1,3-butadiene	hfac [a]	3.12 (s)	3.59 (s)	1.56 (s)	0.87 (s)	2.55, 3.32 (d, 15hz)		2.93 (s)	CH, 5.90
8k	2,3-dimethyl-1,3-butadiene	acac [b]	2.95 (s)	3.37 (s)	1.55 (s)	0.97 (s)	2.58, 3.30 (d, 15hz)		3.00 (s)	CH, 5.20 CH_3, 1.85
8n	2,3-dimethyl-1,3-butadiene	Cl [b]	3.40 (s)	3.48 (s)	1.50 (s)	1.04 (s)	2.93, 3.35 (d, 15hz)		3.11 (s)	
8f	*cis,cis* or *trans,trans*-2,4-hexadiene	hfac [c]	1.15 (d, 6hz)	3.4—3.9 (m)	4.87 (t, 10hz)	3.4—3.9 (m)	3.4—3.9 (m)	0.98 (d, 7hz)	3.08 (s)	CH, 5.97
8g	cis,trans-2,4-hexadiene	hfac [c]	1.13 (d, 6hz)		3.0—3.9 (m)			1.13 (d, 6hz)	2.93 (s)	CH, 5.98

[a] 220 MHz, spectrum at +57°C.
[b] 60 MHz, spectrum at +50°C.
[c] 60 MHz, spectrum at 34°C.

"insertion" of the 1,3-diene moiety into the Pd—C_4Ph_4OMe bond. In view of the significant chemical shift difference of the methoxy resonances of isomers A and B it may be that one isomer has the expected *trans*-C(Ph)=CPhOMe configuration whilst the other contains *cis*-C(Ph)=CPhOMe (similar to compound IIIc, see Fig. 3).

The ^{13}C NMR spectrum of VIIId, the isoprene insertion product of Ic, contained resonances attributable to A and B isomers as well as a minor isomer C.

^1H NMR resonances associated with C included a doublet of doublets, in the central allylic proton region, at δ 4.93 ppm (coupling constant to H_{syn} and H_{anti} of 7 and 12 Hz, respectively) and an upfield methyl singlet at δ 0.73 ppm, broadened by *syn—anti* exchange (cf. 2,3-dimethyl-1,3-butadiene insertion product VIIIe. In addition, the ^{13}C NMR spectrum showed a doublet at δ 109.5 ppm corresponding to a central allylic CH group. These results are consistent with structure VIIId(C) (Table 8, $R^{1,2,5,9}$ = H, R^7 = Me), where insertion has occurred at the less substituted C=C bond of isoprene. Integration of the methyl resonances in the proton NMR spectrum of VIIId indicated that the ratio of the isomers (A + B)/C was about 7/1.

Experimental

^1H and ^{13}C NMR spectra were recorded on Varian Associates Model A56/60D, HR220 and CFT-20 spectrometers. Mass spectra were recorded on a Bell and Howell Model 21-490 spectrometer at an ionisation energy of 70 eV. Molecular weights were measured using a Mechrolab Model 301A Vapour Pressure Osmometer. Melting points were determined on a Kofler hot stage and are uncorrected. Elemental analyses were performed by Microanalyses Laboratory (Toronto) and Canadian Microanalytical Service Ltd.

Complexes Ia—Ic were prepared as described previously [4]. Olefin, 1,2- and 1,3-dienes were obtained as commercial samples and used as received. 2,3-Norbornadiene was redistilled prior to use. Preparation of the olefin, 1,2- and 1,3-diene insertion complexes of Ia—Ic are all similar and a few examples of their reactions are given. The product yields indicated are typical (all were $\geq \sim 75\%$).

Reaction of [(endo-C_4Ph_4OMe)Pdhfac] with isobutene (Complex IIIc). 1.394 g Ic was dissolved in 20 ml CH_2Cl_2 and 1.1 ml of a saturated $CHCl_3$ solution of the olefin added. The yellow solution quickly turned blackish-green, and stirring was continued for 1 h. The product was then passed through a column filled with florisil, elution with CH_2Cl_2 to remove elemental palladium, and evaporation of solvent gave IIIc as a bright yellow glass (1.25 g, 80%). Crystals suitable for X-ray analysis were obtained by dissolving 0.5 g of the product above in n-pentane (5 ml), and passing the solution down a short alumina column. The eluate was collected in a 5 ml Erlenmeyer flask, stoppered and placed in the refrigerator. Slow evaporation of the solvent over a period of several weeks gave orange prisms of IIIc.

Reaction of [(endo-C_4Ph_4OMe)Pdhfac] with tetramethylallene (complex VIh). 1.05 g Ic was dissolved in 20 ml $CHCl_3$ and 0.21 ml of the allene added by syringe. After stirring at room temperature for 4 h the resulting pale green solution was passed down a short florisil column to remove a small amount of decomposition. Evaporation of the solvent gave 0.90 g (~75%) of VIh as a pale

green glass. The product, could be recrystallized as pale green prisms from minimum volume of dichloromethane.

Reaction of [(endo-C_4Ph_4OMe)Pdhfac] with 2,3-dimethyl-1,3-butadiene (complex VIIIe). 0.739 g Ic was dissolved in 15 ml $CHCl_3$ and 122 μl of the 1,3-diene were added via syringe. After stirring overnight at room temperature, the resulting solution was passed down a short florisil column and evaporated to a bright yellow glass (0.60 g, 85%).

Preparation of allene insertion product of [(endo-C_4Ph_4OMe)Pdhfac] (complex VIc). This was prepared from the corresponding chloride complex VIa in the following manner. 0.218 g VIa was dissolved in 5 ml CH_2Cl_2 and 0.18 g Tlhfac added. The mixture was shaken for 2 h, then centrifuged. The supernatant solution was evaporated down to a yellow glass. This was redissolved in cyclohexane and passed through a florisil column. The eluate was evaporated down, redissolved in CH_2Cl_2 and reevaporated (this last procedure was repeated several times to remove free cyclohexane). On evaporation of the solvent, VIc was obtained as a bright yellow glass (0.18 g, 64%).

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