Transition Metal Promoted Reactions of Unsaturated Hydrocarbons. I. Mechanism of 1,3-Diene Insertion into Allyl–Palladium Bonds

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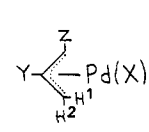
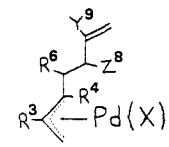
Abstract: The mechanism of "insertion" of 1,3-dienes (*e.g.*, $CH_2{=}CRCH{=}CH_2$) into the allylic palladium bonds of the complexes (π-all)Pd(X) (I) (X = hexafluoroacetylacetonate, acetylacetonate, or chloride) to give the π-allylic products II [*e.g.*, (all-$CH_2CR{=}CH{=}CH_2$)Pd(X)] has been elucidated. Addition of olefins or 1,3-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; 1,3-diene = butadiene ~ *cis*-pentadiene ~ *trans*-pentadiene > isoprene > 2,3-dimethylbutadiene ≫ 2,5-dimethyl-2,4-hexadiene; cyclic 1,3-dienes = cyclooctadiene > cyclohexadiene ~ cyclopentadiene; X = F_6acac ≫ acac > Cl. The rate of formation of insertion product II decreases in the order: all = 2-chloroallyl > allyl > 2-methylallyl > 2-*tert*-butylallyl; 1,3-diene = butadiene > isoprene > 2,3-dimethylbutadiene ~ *trans*-pentadiene > *cis*-pentadiene; cyclic 1,3-diene = cyclopentadiene > cyclohexadiene (cycloocta-1,3-diene, cycloheptatriene, and cyclooctatetraene did not insert); X = F_6acac ≫ acac ~ Cl. To account for these observations as well as the unusual stereochemical features of the insertion reaction, a mechanism is proposed in which the 1,3-diene, acting as a monodentate ligand, coordinates to the palladium through the least substituted double bond to give a σ-allylic intermediate (σ-all)(diene)Pd(X). On adopting a cis-planar orientation within this intermediate, the conjugated 1,3-diene reacts with the σ-allylic ligand to give the insertion product *via* an electrocyclic mechanism. It is envisaged that carbon–carbon bond formation occurs *outside* the coordination sphere of the palladium. Unusual features of the nmr spectra of the insertion products are discussed.

As an extension of our interest in model systems pertaining to the transition metal promoted polymerization and oligomerization reactions of unsaturated hydrocarbons, we were interested in elucidating the mechanism of 1,3-diene insertion into the allyl–palladium bond to give the insertion product II. The stereochemical features of this reaction are markedly different from those observed for the insertion of other unsaturated moieties into the allyl–palladium bond.[1-5]

Prior to the instigation of these studies, 1,3-butadiene had been shown to insert into the allyl–palladium bond of I (X = Cl, acac; Y = H; Z = CH_3) to yield the insertion product II (R^3 = R^4 = R^6 = H).[1,2] From the structure of II it is apparent that butadiene inserts into the most substituted end of an unsymmetrical allyl moiety. This is in contrast to 1,2-dienes,[2,3] strained olefins,[4] carbon monoxide,[2] alkyl isocyanides,[5] and possibly sulfur dioxide[6] which "insert"[7] into the least substituted end of the allylic ligand. An unsymmetrical 1,3-diene, such as isoprene, yielded a product II (R^3 = R^6 = H; R^4 = CH_3), in which the diene substituent invariably occupies a position on an allylic terminal carbon atom in the final π-allylic product. Originally

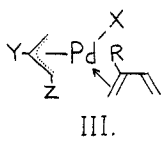


I.

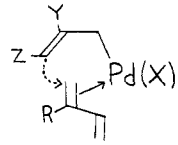


II.

Takahashi, *et al.*,[1] postulated that the 1,3-diene insertion reaction proceeds *via* coordination of the least substituted olefinic function of the diene to palladium but presented no supporting data. Kinetic data, together with some relative rate studies using differently substituted allyls and 1,3-dienes, have been interpreted by Medema, *et al.*,[2] in terms of an intermediate III containing a π-bonded allyl function and a 1,3-diene ligand coordinated to Pd through the most substituted olefin. Coordination of the diene to palladium has been envisualized as the rate-determining step for insertion.[2] It has also been shown that much more forcing conditions are required to insert a further molecule of 1,3-diene into complex II.[2] A third possible reaction mechanism, proposed by Shaw, *et al.*,[8] and based on the mode of reaction of allylic Grignards with organic carbonyl compounds, is *via* the cyclic transition state IV.



III.



IV.

Certain aspects of these proposed mechanisms and, in particular, intermediates, such as III and IV, conflict

(1) Y. Takahashi, S. Sakai, and Y. Ishii, *J. Organometal. Chem.*, 16, 177 (1969).

(2) (a) D. Medema, R. van Helden, and C. F. Kohle, *Inorg. Chim. Acta*, 3, 255 (1969); (b) D. Medema and R. van Helden, *Recl. Trav. Chim. Pays-Bas*, 90, 304 (1971).

(3) R. P. Hughes and J. Powell, unpublished results.

(4) R. P. Hughes and J. Powell, *J. Organometal. Chem.*, 30, C45 (1971).

(5) T. Kajimoto, H. Takahashi, and J. Tsuji, *ibid.*, 23, 275 (1970).

(6) (a) Insertion of SO_2 into an allyl–palladium bond has only been reported for bis-π-allylpalladium(II).[6b] Insertion of SO_2 into $[(\pi\text{-}1,1\text{-dimethylallyl})Pt(PPh_3)_2]^+Cl^-$ has been reported,[6c] but the product was not structurally characterized. (b) S. O'Brien, *J. Chem. Soc. A*, 9 (1970); (c) H. C. Volger and K. Vrieze, *J. Organometal. Chem.*, 13, 495 (1968).

(7) The word "insertion" is misleading with regard to these reactions which probably involve *migration* of a σ-bonded allylic carbon atom from Pd to the coordinated ligand (see ref 11).

(8) A. Bright, B. L. Shaw, and G. Shaw, *Amer. Chem. Soc., Div. Petrol. Chem., Prepr.*, 14, B81 (1969).

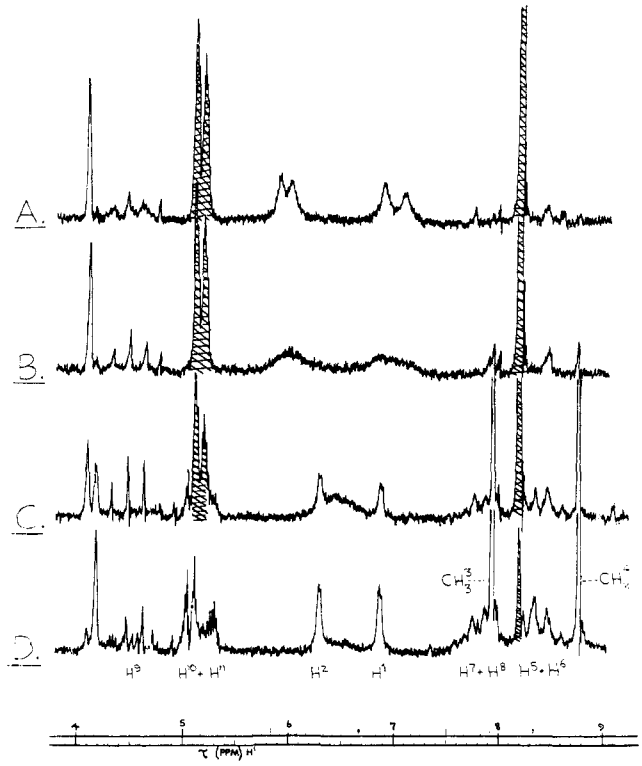


Figure 1. ^{1}H nmr spectrum ($CDCl_3$, 34°) of a solution of (π-allyl)-Pd(F_6acac) (0.82 *M*) and 2,3-dimethylbutadiene (0.82 *M*) at intervals of time, yielding complex IIc as the final product (see Table I): A, 5 min; B, 20 min; C, 18 hr; D, 138 hr. Peaks due to 2,3-dimethylbutadiene are shaded. Resonances of IIc are notated in spectrum D (see Table I).

with other previously reported experimental observations.

(i) Intermediates III and IV require coordination of the 1,3-diene to palladium *via* the most substituted olefinic function in order to obtain the observed product. Cramer[9] has shown that an increase in the number of alkyl substituents on an olefin is accompanied by a marked decrease in its ability to coordinate to Rh(I) relative to ethylene.

(ii) In III the diene must coordinate cis to a terminal substituent (Z) on the π-allylic ligand in order to obtain the observed product. It is difficult to rationalize this proposal in view of the behavior of other unsaturated moieties which presumably must coordinate cis to the least substituted allylic terminal carbon atom.[2-5] On steric grounds coordination of the 1,3-diene to the least substituted terminal allylic carbon atom would be anticipated; *cf.* [(π-1,1-dimethylallyl)PdClPPh$_3$].[10]

(iii) In general, the "insertion" of a coordinated olefin or carbon monoxide into a transition metal–carbon bond is usually a rate-determining step.[11]

(iv) A reasonable rationale is still required to explain the reluctance of insertion product II to insert a further molecule of 1,3-diene.

Bearing these observations in mind, we undertook a detailed investigation of these reactions, using ^{1}H nmr spectroscopy to monitor the reaction rates.[12] In general, our studies were confined to complexes I where X = hexafluoroacetylaceonate since these fluorinated chelate complexes gave much faster insertion rates than previously reported for X = Cl or acac.[1,2] We were thus able to conduct our studies using 1:1 diene/Pd ratios and to investigate a more extensive series of 1,3-diene/allyl systems than previously studied. A large excess of diene and elevated temperatures were previously required[1,2] to obtain reasonable reaction rates (X = Cl, acac).

Our results enable us to propose a new mechanism for 1,3-diene insertion which does not require any of the unlikely assumptions outlined above and which accounts for the different stereochemical features of 1,3-diene insertion relative to 1,2-diene insertion, etc., while invoking a common reaction intermediate.

Results

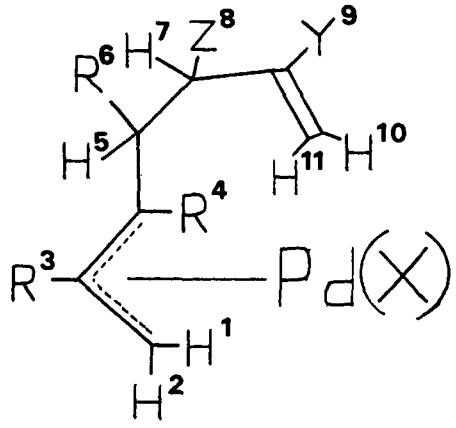
Characterization of Complexes (II). The ^{1}H nmr spectra of pure complexes II (see Table I) are quite characteristic in elucidating the structural features of the carbon skeleton. Indeed, detailed characterizations of the structural features of a series of complexes of type II (X = Cl, Br, acac) have previously been reported[1,2] including full analytical and spectroscopic details for the dimeric chloride- or bromide-bridged analogs of complexes IIa, IIb, IIf, IIh, IIi, IIk, and IIn.[2] Our ^{1}H nmr data, together with analytical data for representative complexes, clearly establish our complexes II (X = F_6acac) to be completely analogous to those previously reported.[1,2] This was further substantiated, where applicable, by conversion of complexes II (X = F_6acac) to their previously reported chloride-bridged analogs by treatment with dry HCl. Thus a detailed characterization of every complex prepared is not included in this manuscript.

Nmr Studies of 1,3-Diene Insertion. Addition of 1,3-dienes to solutions of complexes I (X = F_6acac) resulted in immediate collapse of the nmr signals of the allylic syn proton (H^2) and anti proton (H^1) indicating a rapid site exchange by these protons. The nmr spectrum of the added 1,3-diene remained unchanged from that in the absence of complex and new signals due to the insertion products II (Table I) were not observed until a later stage (see Figure 1). By keeping complex I concentration, diene concentration, and temperature all constant, the extent of collapse of the resonances of H^1 and H^2, a sensitive reflection of the rate of syn–anti proton exchange, was found to be dependent on the nature of the π-allyl moiety, the 1,3-diene, and X. Keeping any two of these variables constant and varying the third, the following orders of syn–anti proton exchange were observed: X = F_6acac $\gg$ acac > Cl; 1,3-diene = butadiene $\sim$ *cis*-pentadiene $\sim$ *trans*-pentadiene > isoprene > 2,3-dimethylbutadiene $\gg$ 2,5-dimethylhexa-2,4-diene (see Figure 2); π-allyl = 2-chloroallyl > allyl > 2-methylallyl $\gg$ 2-*tert*-butylallyl.

The relative rates of product formation[13] varied in the order: X = F_6acac $\gg$ acac $\sim$ Cl; 1,3-diene = butadiene > isoprene > 2,3-dimethylbutadiene $\sim$ *trans*-pentadiene > *cis*-pentadiene > 2,5-dimethylhexa-2,4-diene; π-allyl = 2-chloroallyl > allyl > 2-methylallyl $\gg$ 2-*tert*-butylallyl (see Figure 3).

(9) R. Cramer, *J. Amer. Chem. Soc.*, **89**, 4621 (1967).
(10) J. Powell and B. L. Shaw, *J. Chem. Soc. A*, 1839 (1967).
(11) (a) M. Kubota, D. M. Blake, and S. A. Smith, *Inorg. Chem.*, **10**, 1430 (1971), and references cited therein; (b) R. Cramer, *Accounts Chem. Res.*, 1, 186 (1968).
(12) A preliminary account of these studies has appeared: R. P. Hughes and J. Powell, *Chem. Commun.*, 275 (1971).
(13) See also ref 1 and 2 for previously reported relative rate data.

Table I. Nmr spectra of complexes (II) in $CDCl_3$ at 34° (X = F_6acac)



IIa. $R^3 = R^4 = R^6 = Z = Y = H$

IIb. $R^3 = R^6 = Z = Y = H$; $R^4 = CH_3$

IIc. $R^6 = Z = Y = H$; $R^3 = R^4 = CH_3$

IId. $R^3 = R^4 = Z = Y = H$; $R^6 = CH_3$

IIe. $R^3 = R^4 = R^6 = Z = H$; $Y = Cl$

IIf. $R^3 = R^6 = Z = H$; $R^4 = CH_3$; $Y = Cl$

IIg. $R^6 = Z = H$; $R^3 = R^4 = CH_3$; $Y = Cl$

IIh. $R^3 = R^4 = R^6 = Z = H$; $Y = CH_3$

IIi. $R^3 = R^6 = Z = H$; $R^4 = Y = CH_3$

IIj. $R^6 = Z = H$; $R^3 = P^4 = Y = CH_3$

IIk. $R^3 = R^4 = R^6 = Y = H$; $Z = CH_3$

III. $R^3 = R^6 = Y = H$; $R^4 = CH_3$; $Z = COOCH_3$

IIm. $R^6 = Y = H$; $R^3 = R^4 = CH_3$; $Z = COOCH_3$

IIn. $R^3 = R^4 = Z = H$; $R^6 = CH_3$; $Y = Cl$

Reactants			τ (multiplicity), J (Hz)										
Allyl function	1,3 - Diene	Product formed	H^1	H^2	R^3	R^4	H^5	R^6	H^7	Z^8	Y^9	H^{10}	H^{11}
π-allyl	butadiene	IIa.	ca. 6.40 (b)*		4.30(m)	6.00(dt) $J_{3,4}=11$ $J_{4,5}=6$	8.08(m)	8.08(m)	7.48(m)	7.48(m)	4.30(m)	5.00(m)	4.70(m)
π-allyl	isoprene	IIb.	ca. 6.38 (b)*		4.50(m)	8.70(s)**	8.26(m)	8.26(m)	7.63(m)	7.63(m)	4.20(m)	5.10(m)	4.90(m)
π-allyl	2,3-dimethyl-butadiene	IIc.	6.78(s)	6.21(s)	7.87(s)	8.70(s)**	8.34(m)	8.34(m)	7.73(m)	7.73(m)	4.50(m)	5.20(m)	5.00(m)
π-allyl	cis-or trans-penta-1,3-diene	IId.	ca. 6.35 (b)*		4.30(m)	6.15***	8.10(m)	8.77(d)**** 8.89(d) $J_{5,6}=7$	7.75(m)	7.75(m)	4.30(m)	5.10(m)	4.90(m)
π-2-chloroallyl	butadiene	IIe.	7.00(d) $J_{1,3}=11$	5.95(d) $J_{2,3}=6$	4.50(m)	6.15(m)	8.12(m)	8.12(m)	7.30(m)	7.30(m)	-	4.80(s)	4.80(s)
π-2-chloroallyl	isoprene	IIf.	6.74(d) $J_{1,3}=13$	5.98(d) $J_{2,3}=7$	4.74(m)	8.70(s)**	8.10(m)	8.10(m)	7.35(m)	7.35(m)	-	4.80(s)	4.80(s)
π-2-chloroallyl	2,3-dimethyl butadiene	IIg.	6.78(s)	6.12(s)	7.82(s)	8.65(s)**	8.20(m)	8.20(m)	7.43(m)	7.43(m)	-	4.82(s)	4.82(s)
π-2-methylallyl	butadiene	IIh.	6.88(d) $J_{1,3}=12$	5.85(d) $J_{2,3}=6$	4.45(m)	5.94(dt) $J_{3,4}=11$ $J_{4,5}=6$	7.96(m)	7.96(m)	7.50(m)	7.50(m)	8.10(s)	5.14(bs)	5.14(bs)
π-2-methylallyl	isoprene	IIi	6.77(d) $J_{1,3}=12$	6.00(d) $J_{2,3}=6$	4.68(m)	8.72(s)	8.22(m)	8.22(m)	7.77(m)	7.77(m)	8.30(s)	5.31(bs)	5.31(bs)
π-2-methylallyl	2,3-dimethyl butadiene	IIj	6.66(s)	6.07(s)	7.75(s)	8.60(s)**	8.20(m)	8.20(m)	7.78(m)	7.78(m)	8.24(s)	5.22(bs)	5.22(bs)
π-1-methylallyl	butadiene	IIk.	ca. 6.40 (b)*		4.40(m)	6.14(m)	8.20(m)	8.20(m)	7.5 (m)	8.9 (d) $J_{7,8}=7$	4.50(m)	5.00(m)	4.80(m)
π-1-carbomethoxyallyl	isoprene	III.	ca. 6.40 (b)*		4.50(m)	8.74(s)	7.92(m)	7.92(m)	6.52***(m)	6.35(s)	4.30(m)	5.00(m)	4.75(m)
π-1-carbomethoxyallyl	2,3-dimethyl-butadiene	IIm.	6.77(s)	6.17(s)	7.93(s)	8.67(s) 8.74(s)	8.08(m)	8.08(m)	6.50(m)	6.40(s)	4.40(m)	5.00(m)	4.75(m)
π-2-chloroallyl	cis- or trans-penta-1,3-diene	IIn.	ca. 6.20 (b)*		4.43(m)	ca.6.10***	8.10(m)	8.72(d)**** 8.81(d) $J_{5,6}=7$	7.45(m)	7.45(m)	-	4.80(s)	4.76(s)

* Resonances collapsed at 34°C due to a rapid, intermolecular exchange process (see text).

** Singlet at 34° is the result of a rapid, intramolecular exchange process between two isomers (see text).

*** Obscured by other resonances.

**** The methyl group is attached to a chiral carbon atom. Two doublets are observed of intensity ratio 1:3 due to the possibility of diastereoisomers, since the adjacent allyl-palladium system is also a chiral centre.

The rates of product formation were monitored by integration of the nmr spectrum at intervals of time, allowing the concentrations of reactants and product to be estimated.

Kinetic data indicated the rate of the insertion reaction to be approximately first order in both complex and diene, according to the rate equation $-dC/dt = k[\text{complex}][\text{diene}]$. Good second-order rate plots were

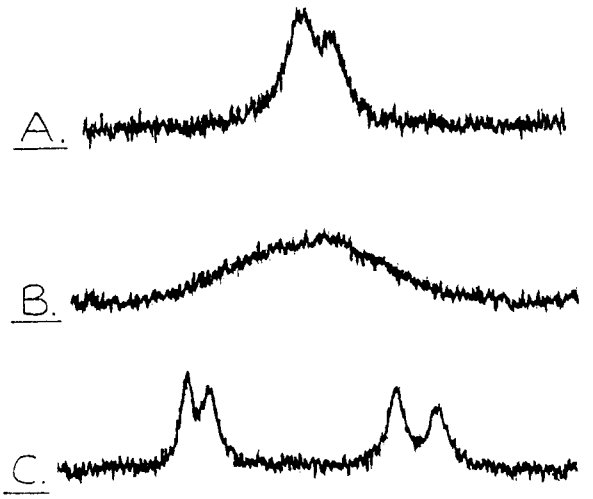


Figure 2. Collapse of the syn- and anti-proton resonances in the nmr spectrum ($CDCl_3$, 34°) of a solution of (π-allyl)Pd(F_6acac) (0.82 *M*) and 1,3-diene (0.82 *M*), varying the 1,3-diene: A, butadiene, *cis*- or *trans*-piperylene; B, isoprene; C, 2,3-dimethylbutadiene.

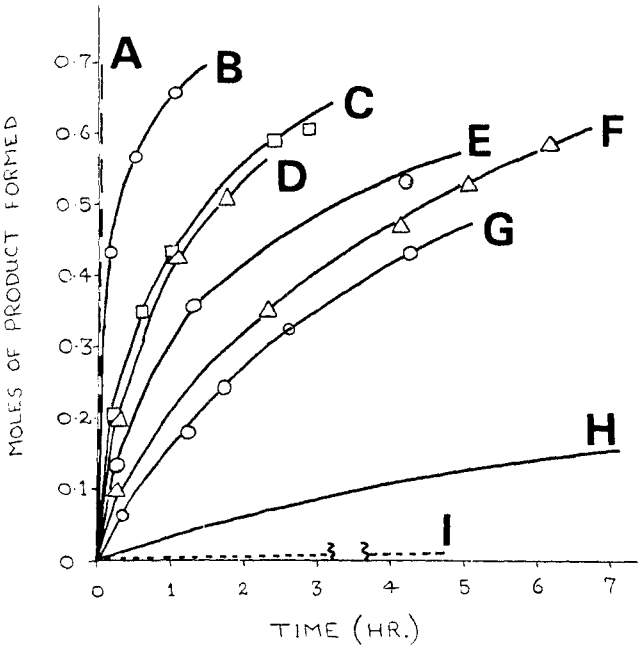


Figure 3. Rates of formation of complexes (II) from (π-all)Pd(F_6acac) (0.82 *M*) and 1,3-diene (0.82 *M*) in $CDCl_3$ at 34°: A, 2-chloroallyl + 2,3-dimethylbutadiene (estimated rate since the reaction is too fast to follow at 34°); B, 1-carbomethoxyallyl + isoprene; C, 1-carbomethoxyallyl + 2,3-dimethylbutadiene; D, allyl + butadiene; E, allyl + isoprene; F, 2-methylallyl + butadiene; G, 2-methylallyl + isoprene; H, allyl + 2,3-dimethylbutadiene (interpolated); I, 2-*tert*-butylallyl + butadiene (estimated rate; the reaction is extremely slow at 34°). (See Table I for structures of products.)

obtained from systems for which the nmr spectrum exhibited well-separated peaks, allowing more accurate integration. These second-order plots are shown in Figure 4 and cover a variety of allyl and 1,3-diene systems. The other systems examined did not provide such accurate data, owing to inaccuracies in the integration technique. However, assuming the same rate equation to hold for these systems, approximate rate constants could be extracted from the integration data. These values are sufficiently different from one another

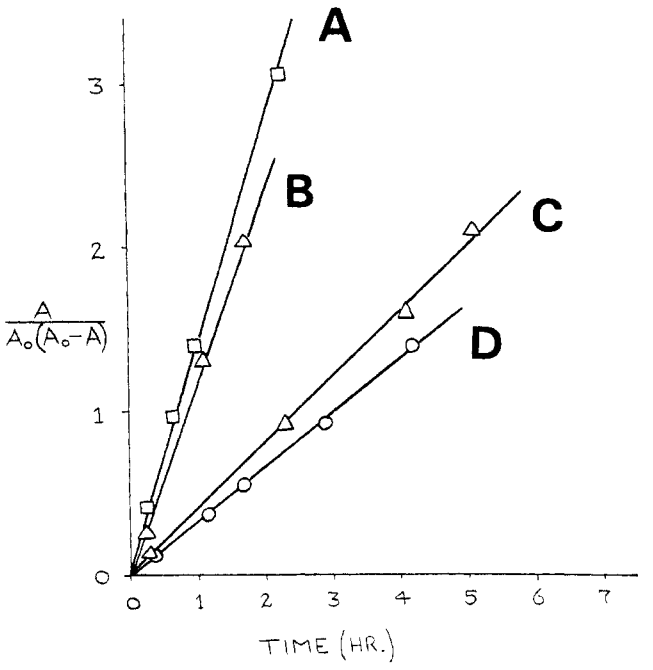


Figure 4. Second-order rate plots for formation of complexes (II) from (π-all)Pd(F_6acac) (0.82 *M*) and 1,3-diene (0.82 *M*) in $CDCl_3$ at 34°: A, 1-carbomethoxyallyl + 2,3-dimethylbutadiene; B, allyl + butadiene; C, 2-methylallyl + butadiene; D, 2-methylallyl + isoprene. (See Table I for structures of products.)

to allow definite qualitative trends to be established regarding the relative reactivities of various allyl/1,3-diene systems (see Table II).

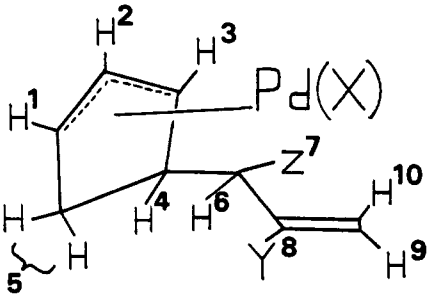
Table II. Second-Order Rate Constants (k) for Reactions of (π-all)Pd(F_6acac) (0.82 *M*) and 1,3-Dienes (0.82 *M*) in $CHCl_3$ at 34° to Give II (See Table I)

π-Allyl	1,3-Diene	k(l. mol^{-1} min^{-1}) × 10^5
Allyl	Butadiene	2010[a]
Allyl	Isoprene	828
Allyl	2,3-Dimethylbutadiene	9
Allyl	*trans*-Piperylene	70
2-Methylallyl	Butadiene	682[a]
2-Methylallyl	Isoprene	549[a,b]
2-*tert*-Butylallyl	Butadiene	<1[d]
1-Methylallyl	Butadiene	90
1-Carbomethoxyallyl	Isoprene	8000
1-Carbomethoxyallyl	2,3-Dimethylbutadiene	2500[a]
2-Chloroallyl	Butadiene	>2,500,000[e]
2-Chloroallyl	Isoprene	>2,500,000[c,e]
2-Chloroallyl	2,3-Dimethylbutadiene	>2,500,000[e]
2-Chloroallyl	*trans*-Piperylene	>2,500,000[e]
2-Chloroallyl	*cis*-Piperylene	1900
2-Chloroallyl	2,5-Dimethylhexa-2,4-diene	<0.3[f]
2-Chloroallyl	Cyclopentadiene	20,000
2-Chloroallyl	Cyclohexa-1,3-diene	15,000
2-Chloroallyl	Cycloocta-1,3-diene	*g*

[a] See Figure 4. [b] Second-order rate constants for reaction of isoprene with [(π-2-methylallyl)PdBr]$_2$ have been reported as 118 × 10^{-5} at 70° and 3.10 × 10^{-5} at 20°.[2] We estimate the value at 34° to be ~30 × 10^{-5}. [c] Second-order rate constant for reaction of isoprene with [(π-2-chloroallyl)PdCl]$_2$ has been reported as >765,000 × 10^{-5} at 20°.[2] [d] Estimated rate. Reaction <1% in 30 hr. [e] Estimated rate. Reactions complete in <5 min. [f] Reaction <5% in 15 days. [g] No observable reaction.

The ^{1}H nmr spectra of pure insertion products II (X = F_6acac) also showed collapse of the allylic syn- and anti-proton resonances (H^1 and H^2), shown by

Table III. Nmr Spectra of Complexes (XVII) in $CDCl_3$ at 34°(X = F_6acac)



XVIIa. Y = Z = H

XVIIb. Y = Cl; Z = H

XVIIc. Y = CH_3; Z = H

XVIId. Y = H; Z = $COOCH_3$

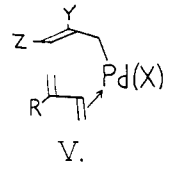
π - allyl function	Product Formed	τ (multiplicity) H^1	H^2	H^3	H^4	H^5	H^6	Z^7	Y^8	H^9	H^{10}
π - allyl	XVII a.	4.5(m)	4.2(m)	4.7(m)	7.8 —to— 8.6(bm)			7.5(bm)	4.2(m)	5.2(m)	4.9(m)
π-2-chloroallyl	XVII b.	4.6(bm)	4.2(m)	4.8(bm)	7.8(m)	8.6(bm)		7.1(m)	-	4.8(s)	4.7(s)
π-2-methylallyl	XVII c.	4.0 ——to——		4.5(bm)	7.7 —to— 8.4(bm)			7.5(bm)	8.1(s)	5.2 -to-	5.5(bm)
π-1-carbomethoxyallyl	XVII d.	4.0 ——to——		4.6(bm)	6.8 ——to——		8.5(bm)	6.3(s)	4.0-4.6(bm)	5.0(m)	4.9(m)

dilution studies to occur *via* an intermolecular mechanism. It was also observed that in reactions of complex I (X = F_6acac; Y = Z = H) with 2,3-dimethylbutadiene, the extent of syn–anti proton exchange in complex I, initially slow, increased with formation of the insertion product (see Figure 1). Addition of various complexes II to solutions of complexes I in the absence of 1,3-diene caused similar collapse of the syn- and anti-proton resonances of I. This process was also shown to be *via* an intermolecular mechanism by dilution studies. Reactions with cyclic 1,3-dienes were also carried out and similar orders of reactivity established. Extent of collapse of syn- and anti-proton resonances: cycloocta-1,3-diene > cyclopentadiene ~ cyclohexa-1,3-diene. Rate of product formation: cyclopentadiene > cyclohexa-1,3-diene (see Table III for nmr data of products obtained from cyclopentadiene). No insertion of cycloocta-1,3-diene into the allyl–palladium bond was observed. Thus, (π-2-chloroallyl)Pd(F_6-acac), the most reactive allylic complex toward insertion (Table II), failed to show any insertion reaction with cycloocta-1,3-diene after 15 days at 34°. Reactions of the 2-chloroallyl complex with aliphatic 1,3-dienes were usually complete in less than 5 min under identical conditions and with cyclopentadiene or cyclohexa-1,3-diene within 1 hr. Similarly, cycloheptatriene and cyclooctatetraene, although readily promoting syn–anti proton exchange in complexes I, showed no sign of further reaction.

Discussion

The collapse of the syn- and anti-proton resonances of complexes I on addition of 1,3-dienes is only consistent with diene-promoted formation of a short-lived σ-allylic species,[14] with rapid, reversible coordination of the diene to palladium. Since new peaks due to complexes II are not observed until a later stage, this observation proves that coordination of the diene to palladium cannot be the rate-determining step for product formation. That formation of this intermediate is not dependent on the potential bidentate character of the 1,3-diene is evidenced by ready promotion of a $\pi \rightarrow \sigma \rightarrow \pi$ process by monoolefins, such as cyclohexene and norbornene, and by 1,2-dienes.[3,15]

The rate of syn–anti proton exchange *via* a $\pi \rightarrow \sigma \rightarrow \pi$ mechanism is expected to be dependent on two major factors: the free energy of activation of formation of the σ-allylic species, which is probably a good reflection of the stability of the σ-allylic species relative to its π-allylic precursor; and the coordinative ability of the added 1,3-diene. For a particular allylic ligand our results may best be interpreted in terms of rapid and reversible formation of a σ-allylic intermediate V



V.

in which the 1,3-diene, acting as a monodentate ligand,[16] coordinates *via* the least substituted olefinic function. The formation of V may be regarded as a simple SN2 substitution of one end of the π-allyl–palladium bond by an olefin. This proposal accounts for the similar rates of diene-promoted syn–anti proton exchange observed for butadiene and *cis*- and *trans*-penta-1,3-diene where a monosubstituted olefinic function is common to all three dienes. The reason for a slightly slower rate of syn–anti proton exchange in the presence of isoprene (also has a monosubstituted olefinic function) is not clear though the extent and role of steric factors on the ease of formation of the σ-allylic species V may have some subtle effects.[17]

The extent of collapse of syn- and anti-proton resonances for various 1,3-dienes correlates very well with

(14) P. W. N. M. van Leeuwen and A. P. Praat, *Chem. Commun.*, 365 (1970), and references cited therein.

(15) Collapse of the syn- and anti-proton resonances of [(π-allyl)PdCl]$_2$ has also been observed to be induced by cyclohexyl isocyanide[5] and carbon monoxide.[10]

(16) At −40° 1,3-butadiene reacts with [(*n*-pentene)$PdCl_2$]$_2$ to give the dimeric complex [(C_4H_6)$PdCl_2$]$_2$ (stable below −20°) in which the butadiene coordinates to Pd *via* only one olefinic function: N. Donati and F. Conti, *Tetrahedron Lett.*, 1219 (1966).

(17) It should be noted that in the region of coalescence of the nmr signals of the syn and anti protons the line shape is particularly sensitive to small energy differences.

their ability to add to 6-acetoxynorbornenylpalladium-(II) hexafluoroacetylacetonate to give nortricyclenyl complexes in which the 1,3-diene is coordinated to palladium *via* its least substituted olefinic function.[18]

Thus, the values of the equilibrium constant (K) for the system (6-acetoxynorbornenyl)Pd(F_6acac) + 1,3-diene $\rightleftharpoons$ (5-acetoxynortricyclenyl)(1,3-diene)Pd(F_6-acac), which reflects the coordinative abilities of the olefinic functions of the 1,3-diene, vary as[18] 1,3-diene (K) = butadiene (2.87) ~ *cis*-penta-1,3-diene (2.32) ~ *trans*-penta-1,3-diene (3.40) > isoprene (0.16) > 2,3-dimethylbutadiene (0.02).

Effect of Allylic Substituents in Complex I on the Rate of 1,3-Diene Insertion. We have established that the free energy of activation for formation of a σ-allyl from a π-allyl precursor for a series of complexes [(π-all)Pd(OAc)(PMe_2Ph)] increases in the order[19] π-all = 2-chloroallyl < allyl < 2-methylallyl < 2-*tert*-butylallyl.

The ease of promotion of the $\pi \rightarrow \sigma \rightarrow \pi$ process with any one added 1,3-diene *decreases* in the same order, again reflecting the ease of formation of the σ-allylic intermediate V. Similarly, the rate of product formation decreases in the same order. Thus, *for a series of 2-substituted π-allyls* the rates of product formation from the same 1,3-diene may be correlated with the ease of formation of a σ-allylic intermediate, a strong implication of the intermediacy of the σ-allylic species in the insertion mechanism.

Terminal methyl substituents in complexes I greatly hinder the insertion reaction relative to an unsubstituted allyl, although the rate of the 1,3-diene-promoted exchange of the syn and anti protons H^2 and H^1 is rapid on the nmr time scale.[19,20] Thus the reaction of (π-allyl)Pd(F_6acac) with butadiene (k = 2010 × 10^{-5} l. mol^{-1} min^{-1}) is considerably faster than reaction of (π-1-methylallyl)Pd(F_6acac) with butadiene (k = 90 × 10^{-5} l. mol^{-1} min^{-1}). Thus, although the intermediate σ-allyl is readily accessible, alkyl substituents at the site of the new carbon–carbon bond formed by 1,3-diene insertion not unexpectedly hinder the insertion process. It should be noted at this point that the insertion products II invariably contain a large terminal alkyl substituent on the π-allyl function. This explains the reluctance of these products to insert a further mole of 1,3-diene.[1,2]

Insertion into a 1-carbomethoxy-substituted allyl is faster than into an unsubstituted allyl; this may reflect in part a greater stability of the σ-allylic intermediate (an α,β-unsaturated ester) in the former case. It should also be noted that electron-withdrawing groups on an olefin are known to facilitate their addition to 1,3-dienes *via* the Diels–Alder reaction.[21]

For terminally substituted π-allylic palladium complexes I, the coordination of an olefinic function to the palladium will most readily generate the σ-allylic intermediate (V; *e.g.*, Z = CH_3) in which the most substituted terminal allylic carbon atom has been displaced by the olefin.[14,19]

Effect of Substituents on the 1,3-Diene on the Rate of Insertion. Introduction of methyl substituents on aliphatic 1,3-dienes has two observable effects: it affects the rate of syn–anti proton exchange for a particular allyl group and also affects the rate of product formation.

For a constant π-allyl moiety in complexes I, the rate of syn–anti proton exchange caused by addition of different 1,3-dienes must reflect the ability of those dienes to promote formation of the σ-allylic intermediate V which in turn probably reflects the coordinative ability of the least substituted olefinic function of the diene to palladium.[22] Thus, we find that 1,3-dienes containing a monosubstituted olefinic function promote syn–anti proton exchange more readily than 2,3-dimethylbutadiene (geminal-disubstituted olefinic functions), which in turn is better than 2,5-dimethylhexa-2,4-diene (trisubstituted olefinic functions). We also find that for a series of 1,3-dienes containing internal methyl substituents, the rate of $\pi \rightarrow \sigma \rightarrow \pi$ promotion induced by the diene is mirrored by the facility with which the diene undergoes insertion into a particular allyl; *e.g.*, the rate constants for insertion of various 1,3-dienes into (π-allyl)Pd(F_6acac) vary as 1,3-diene (k) = butadiene (2010 × 10^{-5} l. mol^{-1} min^{-1}) > isoprene (828 × 10^{-5} l. mol^{-1} min^{-1}) > 2,3-dimethylbutadiene (9 × 10^{-5} l. mol^{-1} min^{-1}). As an increase in the ease of formation of the σ-allylic intermediate V probably implies an increase in the concentration of this species, the correlation of the rate constant for insertion with the rate of syn-anti proton exchange provides strong evidence that insertion occurs *via* intermediate V. Terminal methyl substituents on the diene hinder the insertion reaction. Thus, reaction of butadiene with (π-allyl)Pd(F_6acac) (k = 2010 × 10^{-5} l. mol^{-1} min^{-1}) is considerably faster than reaction of *trans*-penta-1,3-diene with the same complex (k = 70 × 10^{-5} l. mol^{-1} min^{-1}). Again this is explicable on steric and/or electronic grounds since the terminal substituent is on a carbon atom which is directly involved in forming a new carbon–carbon σ bond. However, an additional feature of terminal substitution on the diene is that the insertion rate is dependent on the geometry of the substituent relative to the diene molecule.

Stereochemical Requirement for 1,3-Diene Insertion. For a given complex I, both *cis*- and *trans*-penta-1,3-diene promote similar rates of syn–anti proton exchange, indicating that both form intermediate V with equal facility.

However, the rates of insertion of these isomeric dienes into a particular allylic complex indicate a dramatic difference in reactivity. Thus, reaction of *trans*-penta-1,3-diene with (π-2-chloroallyl)Pd(F_6acac) (k > 25 l. mol^{-1} min^{-1}) is faster than the reaction of *cis*-piperylene with the same complex (k = 1900 × 10^{-5} l. mol^{-1} min^{-1}) by a factor of at least 10^3. The observation that *cis*-penta-1,3-diene inserts less readily than *cis*-penta-1,3-diene suggests that the diene needs to

(18) R. P. Hughes and J. Powell, *J. Organometal. Chem.*, **34**, C51 (1972).

(19) (a) J. Powell, *J. Chem. Soc. A*, 2233 (1971); (b) J. Powell and A. W.-L. Chan, *J. Organometal. Chem.*, **35**, 203 (1972).

(20) $\Delta G^{\ddagger}$ for syn–anti proton exchange in [(π-allyl)Pd(OAc)PMe_2Ph] and [(π-1,1-dimethylallyl)Pd(OAc)PMe_2Ph] is of a similar magnitude.[19b]

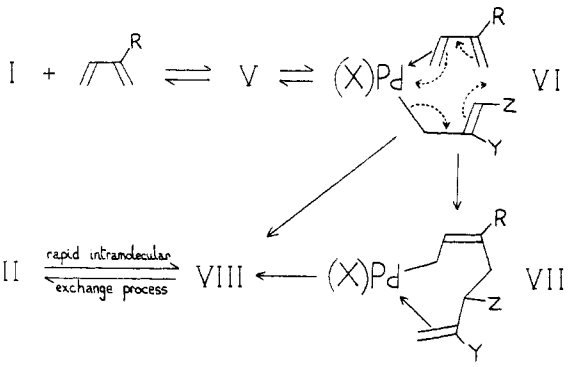
(21) A. Onischenko, "Diene Synthesis," Israel Program for Scientific Translations, Jerusalem, 1964.

(22) The extent of collapse of syn- and anti-proton resonances may be qualitatively correlated with the free energy of activation of formation of the σ-allylic intermediate. The effect of diene substituents on the free energy of the five-coordinate transition state represents an unknown factor when using the rate of syn–anti proton exchange as a qualitative measure of the coordinative ability of an olefinic function to palladium in the intermediate V.

adopt a cis-planar arrangement while coordinated to the metal in order for insertion to occur (assuming the steric effect on formation of the new carbon–carbon bond is the same in both cases). This is comparable to the stereochemical requirement of 1,3-dienes in the Diels–Alder reaction in which *cis*-penta-1,3-diene reacts less readily than the trans isomer.[21] This implication is supported by the reactions of cyclic 1,3-dienes. Thus, although cycloocta-1,3-diene promotes formation of intermediate V more readily than cyclopenta-1,3-diene or cyclohexa-1,3-diene, cycloocta-1,3-diene shows no sign of insertion. (Uv spectroscopic studies have shown that the olefinic bonds in cycloocta-1,3-diene are at 40–45° to one another;[23] similarly this diene shows a marked reluctance to undergo Diels–Alder reactions.[21]) The planar cyclopenta-1,3-diene and cyclohexa-1,3-diene molecules insert quite rapidly into the allyl–palladium bond.

Mechanism of 1,3-Diene Insertion into the Allyl–Palladium Bond. Key steps in the insertion of 1,3-dienes into allyl–palladium bonds, as indicated by our experimental observations, are the formation of a σ-allylic species V in which the diene coordinates to the palladium by the least substituted olefinic function, and adoption of a cis-planar arrangement of the 1,3-diene to give the σ-allylic species VI. In order to account for these observations we propose the reaction mechanism outlined in Scheme I. In the σ-allylic species VI,

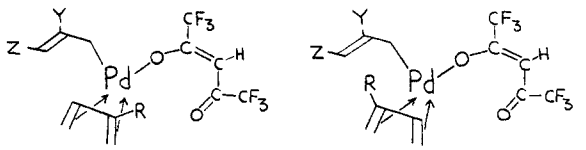
Scheme I. Mechanism of Insertion of 1,3-Dienes into the Allyl–Palladium Bond

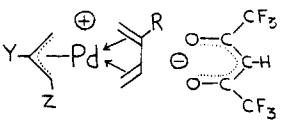


it is stereochemically feasible for the allylic olefinic function and the uncoordinated olefinic function of the cis-planar 1,3-diene to attain close proximity. Formation of the new carbon–carbon bond occurs *via* an electrocyclic mechanism outside the coordination sphere of the palladium. This process involves eight electrons and is maybe best considered as a [$_\pi$4 + $_\pi$2 + $_\sigma$2] reaction. It is not possible to distinguish whether the insertion process is completely concerted or whether a two-step mechanism, *via* an enyl intermediate VII, is operative though the facility of the reaction suggests the former. The initially formed product VIII, which contains the large $CH_2C(Z)HC(Y)=CH_2$ anti substituent, can then rearrange to the observed thermodynamically more stable insertion product II by a rapid $\pi \rightarrow \sigma \rightarrow \pi$ process induced by the side-chain olefinic function.[24] (Details of this isomerization are discussed below.) A low-temperature (−30°) pmr study of the reaction between (π-2-chloroallyl)Pd(F_6acac) and 2,3-dimethylbutadiene shows only the equilibrium concentrations of isomers IIg and VIIIg. It proved impossible to observe prior formation of one isomer and subsequent isomerization to an equilibrium mixture. Thus presumably the rate of isomerization is faster than the rate of product formation at this temperature.

Further evidence that insertion of a 1,3-diene into the allyl–palladium bond does not occur *via* direct transfer of a palladium bonded σ-allyl to a coordinated olefin is the fact that although butadiene promotes syn–anti proton exchange *via* a σ-allylic species V less readily than allene,[3,12] the rate of formation of the insertion product is much faster for butadiene.

Other Possible Intermediates. Other species which could conceivably be considered as intermediates in this reaction are illustrated as IV, IXa, IXb, and X. In-





termediate IV is analogous to V except that the diene is coordinated *via* the most substituted olefinic function. In order to produce the observed product structure II, transfer of the allyl moiety to the diene must occur *via* a cyclic bond shifting involving attack of the substituted end of the olefinic function of the σ-allyl on the coordinated olefin, followed by the noncoordinated diene olefin swinging in to form the final π-allylic product.[8] We discount this possibility for two reasons. Firstly, it does not appear to explain the cis-planar requirement for the diene to insert; cycloocta-1,3-diene might be anticipated to react by this mechanism. Secondly, we have shown that transfer of a σ-allyl to a coordinated olefin occurs *via* a direct carbon-transfer process,[4] as observed for 1,2-diene insertion;[3] this would not give the required product structure II.

Intermediates IXa and IXb can be discounted on similar grounds; *i.e.*, direct transfer of the σ-bonded allylic carbon to the coordinated olefin is expected. The species X involving displacement of F_6acac$^-$ by a chelating 1,3-diene is not favored. We have shown that the tendency for the ionic species [(π-2-R-C_3H_4)-Pd(PMe_2Ph)$_2$]$^+$[X]$^-$ to be formed on addition of Me_2-PhP to $CHCl_3$ solutions of I (X = F_6acac or $O_2CC_5H_4N$) decreases in the order 2-*tert*-butylallyl ~ 2-methylallyl > allyl[19b,25] which is the reverse to the ease of 1,3-diene insertion into these allylic–palladium bonds. No signs of formation of cationic intermediates such as X were observed in the nmr spectrum, even at low temperature. However, with 1,5-cyclooctadiene (1,5-COD), a better chelating agent, low-temperature nmr

(23) E. A. Braude, *Chem. Ind. (London)*, 1557 (1954).
(24) D. J. S. Guthrie, R. Spratt, and S. M. Nelson, *Chem. Commun.*, 935 (1971).
(25) J. Powell, A. Chan, and R. P. Hughes, manuscript in preparation.

studies indicated reversible formation of [(π-2-methylallyl)Pd(1,5-COD)]$^+$[F_6acac]$^-$.[25,26]

However, the fact that this species can only be observed at low temperatures (*ca.* −60°) is presumably due to the higher solvating capacity of $CHCl_3$ at these temperatures. At the temperatures of our experiments (+34°) the nmr spectrum of [(2-methylallyl)-PdF_6acac] in the presence of 0.5 mol of 1,5-COD per Pd atom contained a sharp singlet resonance of relative intensity 4 due to the syn and anti protons situated approximately at the mean position of the syn- and anti-proton resonances of [(π-2-methylallyl)PdF_6acac] in the absence of olefin-induced exchange. The resonances due to the 1,5-COD were little changed from the resonance pattern of 1,5-COD in the absence of complex. This is in marked contrast to the salt [(2-methylallyl)Pd(1,5-COD)]$^+$[F_6acac]$^-$ where the olefinic proton resonances of the 1,5-COD ligand are moved well downfield.[25,26]

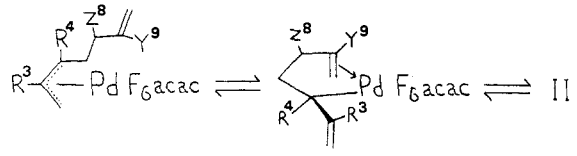
Effect of the Anionic Ligand X on the Rate of 1,3-Diene Insertion. Both from these and other studies it has been observed that fluorinated anionic ligands such as F_6acac and CF_3COO[2] increase the rate of 1,3-diene insertion. Thus the rate of reaction of isoprene with [(π-2-methylallyl)PdBr]$_2$ ($k = 30 \times 10^{-5}$) is slower than the reaction of (π-2-methylallyl)Pd(F_6acac) with the same diene ($k = 549 \times 10^{-5}$) by a factor of approximately 20 (see Table II). This is probably due to the electron-withdrawing effect of these fluorinated ligands increasing the electrophilicity of the palladium atom and hence increasing the stability of the σ-allylic–π-olefinic palladium intermediate V. (Electron-withdrawing anionic ligands would stabilize both the C–Pd and olefin–Pd σ bonds.) When X = Cl the rate of 1,3-diene insertion is first order in diene and first order in [(π-all)PdCl]$_2$ dimer.[2] The reaction probably occurs *via* a dimeric σ-allylic intermediate [(σ-all)(diene)-$PdCl_2$Pd(π-all)] which is similar to the proposed intermediate [(σ-all)(PPh_3)$PdCl_2$Pd(π-all)] for [(π-all)-PdCl]$_2$ promoted syn–anti proton exchange in the complexes [(π-all)(PPh_3)PdCl].[10,27a]

Interconversion of Syn and Anti Isomers II and VIII. Nelson, *et al.*,[24] have shown by variable temperature pmr spectroscopy that rapid interconversion of the chloride-bridged analogs of IIf and VIIIf occurs *via* intramolecular formation of a chelating 4-enyl intermediate analogous to XIf. The value of $\Delta G^{\ddagger}_{T_c}$ for the process found in their system was 17.3 kcal mol^{-1}. We have investigated this interconversion using the isomeric F_6acac complexes IIf and VIIIf and have calculated a value of 14.8 kcal mol^{-1} for this process, using the usual coalescence method[27b] (Scheme II).

The lower $\Delta G^{\ddagger}_{T_c}$ for the hexafluoroacetylacetonates IIf and VIIIf relative to the chloride analogs (14.8 and 17.3 kcal mol^{-1}, respectively) is a further example of the way in which the electrophilicity–reactivity of palladium complexes toward olefins is increased by electron-withdrawing anionic ligands.

Effect of Substituents on the Syn/Anti Isomer Ratio and Rate of Interconversion of Complexes II and VIII.

Scheme II



VIII XI.

b, $R^3 = Z = Y = H$; $R^4 = CH_3$
f, $R^3 = Z = H$; $R^4 = CH_3$; Y = Cl
g, $R^3 = R^4 = CH_3$; Y = Cl; Z = H
i, $R^3 = Z = H$; $R^4 = Y = Cl$

Low-temperature pmr studies show that the insertion products derived from isoprene contain syn and anti isomers in approximately equal amounts. However, the nature of the substituent Y on the terminal olefinic function markedly affects the facility of the intramolecular interconversion of complexes II and VIII, as evidenced by the coalescence temperature for collapse of the *syn*- and *anti*-methyl proton resonances. Thus, when Y = Cl (isomers IIf and VIIIf) $T_c = +12°$ but when Y = H (isomers IIb and VIIIb) or Y = Me (isomers IIi and VIIIi) the value of T_c is in both cases lowered to *ca.* −62°, the line separations in the region of no exchange being virtually identical in all three cases (*ca.* 11.5 Hz). The calculated values of $\Delta G^{\ddagger}_{T_c}$ are 14.8 kcal mol^{-1} (Y = Cl) and 10.5 ± 0.2 kcal mol^{-1} (Y = H, Me). The reasons for the higher value in the case of Y = Cl are not clear.

The insertion products derived from 2,3-dimethylbutadiene, however, show unequal proportions of syn and anti isomers, as evidenced by two resonances in the low-temperature pmr spectrum attributable to the methyl group (R^4) of unequal intensity (ratio 2.5–3:1), the higher field resonance being the lower intensity. Nuclear Overhauser enhancement experiments[28] have shown that the *anti*-methyl group in (π-1,1-dimethylallyl)PdCl[(*S*)-α-phenylethylamine] absorbs at higher field than the *syn*-methyl group. We thus assign the lower intensity methyl resonance in these insertion products to isomer II. Evidently introduction of a methyl group (R^3) on the central allylic carbon atom alters the relative thermodynamic stabilities of the two isomers, presumably for steric reasons, the more bulky alkyl side chain preferring to adopt an anti configuration (isomer VIII).

It is interesting to note that the coalescence temperature for the methyl (R^4) resonances of isomers IIg and VIIIg is +30°, compared to +12° for isomers IIf and VIIIf (derived from isoprene), implying a higher $\Delta G^{\ddagger}_{T_c}$ value in the former case, the line separations at no exchange being equal. Thus, introduction of a methyl group (R^3) on the central carbon of the allyl raises the free energy of activation for intramolecular formation of the σ-allylic intermediate XIg compared to that for XIf, an observation consistent with our previous data concerning formation of σ-allylic species.[19]

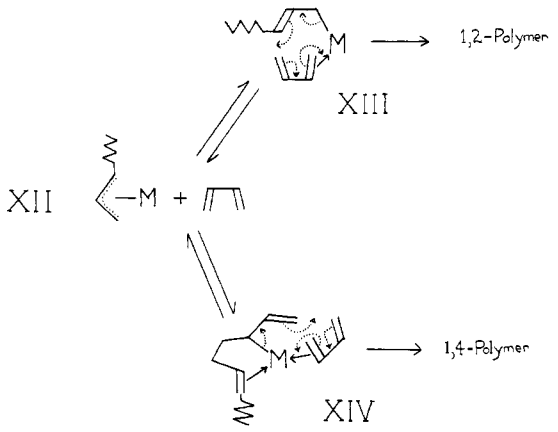
Possible Mechanism of Homogeneous Polymerization of 1,3-Dienes *via* π-Allylic Intermediates (See Scheme III). Successive electrocyclic insertions of 1,3-dienes into allyl–transition metal bonds, *via* an intermediate

(26) The cations [(π-all)Pd(1,5-COD)]$^+$ can be isolated as BF_4^- salts: B. F. G. Johnson, J. Lewis, and D. A. White, *J. Amer. Chem. Soc.*, 91, 5186 (1969).

(27) (a) K. Vrieze, A. P. Praat, and P. Cossee, *J. Organometal. Chem.*, 12, 533 (1968); (b) H. S. Gutowsky and C. H. Holm, *J. Chem. Phys.*, 25, 1228 (1956).

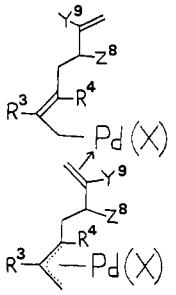
(28) J. W. Faller, M. E. Thomsen, and M. J. Mattina, *J. Amer. Chem. Soc.*, 93, 2642 (1971).

Scheme III. Postulated Mechanism for 1,2 or 1,4 Polymerization of 1,3-Dienes by Successive Electrocyclic Insertions into Allyl–Transition Metal Bonds

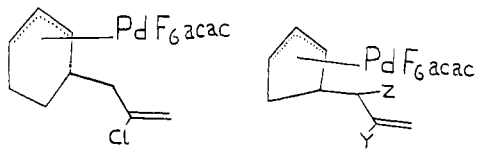


such as XIII, provide a plausible mechanism for 1,2-polymerization of 1,3-dienes. Changes in known catalyst systems which lead to an increased number of available coordination sites generally change the mode of polymerization from 1,2 to 1,4.[29] The electrocyclic insertion mechanism may thus conceivably lead to a 1,4-polymeric chain, *via* anchimerically assisted formation of an intermediate such as XIV, since intramolecular coordination of the α olefin has been shown here and elsewhere[24] to occur with great facility.

Nmr Spectra of Complexes (II) (See Table I). It is noteworthy that the nmr spectra of pure complexes IIa, IIb, IId, IIj, and IIk show collapse of the proton signals of H^1 and H^2 at room temperature. This occurs *via* an intermolecular process involving a σ-allylic species of the type XV. A ready $\pi \rightarrow \sigma \rightarrow \pi$ process is only observable in these complexes when $R^3 = Y = H$. When $R^3 = CH_3$, or when $Y = CH_3$ or Cl, the rate of exchange of protons H^1 and H^2 is slowed considerably. These observations can be reconciled in the light of our previous arguments concerning the coordinative ability of olefins and the ease with which a σ-allylic species is formed from a π-allylic precursor;



XV



XVI XVII

i.e., when the π-allylic function in these complexes has a 2-methyl substituent ($R^3 = CH_3$), a $\pi \rightarrow \sigma \rightarrow \pi$ process occurs less readily than in the analogous complexes where $R^3 = H$. When $Y = CH_3$ or Cl, the side-chain olefinic function in complexes II corresponds to a geminal-disubstituted olefin, supporting our conclusions that disubstituted olefins of this type coordinate less readily than monosubstituted olefins (*i.e.*, $Y = H$).

Thus the observed increase in the rate of syn–anti proton exchange in the (π-allyl)Pd(F_6acac)–2,3-dimethylbutadiene system with longer reaction times (Figure 1) is due to the fact that the insertion product IIc, containing a monosubstituted olefinic function, is a better promoter of syn–anti exchange than 2,3-dimethylbutadiene (geminal-disubstituted olefinic functions).

Conclusions

The "insertion" of unsaturated ligands L into allyl–palladium complexes may be rationalized in terms of initial formation of a σ-allylic intermediate "$RCH_2{=}C\text{-}HCH_2PdL$." The unusual stereochemical features of 1,3-diene insertion are due to the ability of the initially formed σ-allylic intermediate to undergo an electrocyclic reaction in which carbon–carbon bond formation occurs outside the coordination sphere of the palladium atom. Similar electrocyclic reactions may well be involved in transition metal promoted oligomerization and 1,4-polymerization reactions of 1,3-dienes and in ligand-induced coupling reactions of coordinated allyl groups with other unsaturated ligands.[30]

Experimental Section

Instrumentation. Nmr spectra were run on a Varian A56/60D instrument.

Starting Materials. 1,3-Dienes were commercially available and were used without further purification, with the exception of cyclopentadiene, which was freshly distilled before use. π-Allylic complexes I (X = Cl) were prepared by the method of Dent, Long, and Wilkinson[31] or by the method of Volger.[32] Conversion to complexes I (X = F_6acac) was achieved by one of two procedures, either of which is generally applicable. Full details of physical and spectroscopic properties, together with analytical data for these F_6acac complexes, will be published shortly.[33]

Method A. 1,1,1,5,5,5-Hexafluoropentane-2,4-dionato(π-2-chloroallyl)palladium(II). Di-μ-acetato-bis(π-2-chloroallyl)dipalladium (II) was prepared *in situ* by treatment of a solution of the corresponding chloride bridged dimer (0.760 g) in chloroform (50 ml) with silver acetate (0.600 g), shaking (1 hr), and filtration of the precipitated silver chloride. 1,1,1,5,5,5-Hexafluoropentane-2,4-dione (0.760 ml) was added to the filtrate and resultant solution was evaporated to dryness under reduced pressure. The residue was freed of liberated acetic acid by pumping at high vacuum (1 hr). Recrystallization from petroleum ether (bp 30–60°) yielded the product as pale yellow needles (1.350 g, 99%), mp 85–87°.

Anal. Calcd for $C_8H_5ClF_6O_2Pd$: C, 24.71; H, 1.30; Cl, 9.12; F, 29.30. Found: C, 24.78; H, 1.33; Cl, 9.14; F, 29.71.

Method B. 1,1,1,5,5,5-Hexafluoropentane-2,4-dionato-(π-1-methylallyl)palladium(II). A solution of di-μ-chloro-bis(π-1-methylallyl)dipalladium(II) (1.225 g) in chloroform (50 ml) was treated with 1,1,1,5,5,5-hexafluoropentane-2,4-dionatothallium(I) (2.700 g) and the resultant mixture was shaken (5 min). The precipitated thallous chloride was filtered and the filtrate evaporated to dryness under reduced pressure. Recrystallization of the residue from petroleum ether (bp 30–60°) yielded the product as pale yellow needles (2.070 g, 90%), mp 65–67°.

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Anal. Calcd for $C_9H_8F_6O_2Pd$: C, 29.34; H, 2.19. Found: C, 29.13; H, 2.01.

Monitoring of Reaction Rates. Nmr tubes were precalibrated to a volume of 0.40 ml. Standard solutions of complexes I (0.82 *M*) were prepared by dissolving the appropriate weight of complex I in this volume of $CDCl_3$. One molar equivalent of diene was injected with a syringe, and the tube was sealed, shaken vigorously, and quickly placed in the probe. The nmr spectrum was recorded and carefully integrated at intervals of time.

For reactions involving butadiene, a solution of butadiene in ethanol-free chloroform was prepared by bubbling butadiene through a sample of chloroform which had been passed down an alumina column. This solution was standardized by dissolving a known molar amount of $[(\pi\text{-}C_3H_5)PdCl]_2$ in a known volume of solution in an nmr tube. Careful integration of the nmr spectrum allowed the molarity of butadiene in the $CHCl_3$ to be calculated.

Characterization of Complexes. Structural characterization of complexes II (X = Cl, acac) has been reported by other authors.[1,2] We have characterized complexes II (X = F_6acac) by analysis of their ^1H nmr spectra and (where available) by comparison of their nmr spectra with those previously reported for the analogous chloride and/or acac complexes.[1,2] Chemical shift data for some representative complexes are listed in Table I. Yields of complexes II were quantitative in the nmr reaction tube. The complexes were generally isolated on evaporation as yellow volatile oils, with a pungent smell.

Complexes XVII, arising from reactions between complexes I and cyclopentadiene, were likewise isolated as yellow oils, which decomposed slowly at room temperature depositing a palladium mirror. Nmr data are listed in Table III. Large-scale preparations of complexes II could also be effected with relative ease. Experimental details for preparation of complexes derived from a representative series of 1,3-dienes are presented below.

Reaction of 1,1,1,5,5,5-Hexafluoropentane-2,4-dionato(π-2-chloroallyl)palladium(II) with Butadiene. Butadiene was bubbled through a solution of 1,1,1,5,5,5-hexafluoropentane-2,4-dionato(π-2-chloroallyl)palladium(II) (0.626 g) in dichloromethane (5 ml) for 5 min. The resultant solution was passed down a short Florisil column, eluting with dichloromethane. Evaporation of the eluate under reduced pressure yielded a yellow oil (0.700 g, 98%), shown by its ^1H nmr spectrum to be 1,1,1,5,5,5-hexafluoropentane-2,4-dionato-π-1-*syn*-(3-chlorobut-3-en-1-yl)allylpalladium(II) (complex IIe).

Anal. Calcd for $C_{12}H_{11}ClF_6O_2Pd$: C, 32.54; H, 2.50. Found: C, 32.45; H, 2.32.

Reaction of 1,1,1,5,5,5-Hexafluoropentane-2,4-dionato(π-2-chloroallyl)palladium(II) with Isoprene. A solution of 1,1,1,5,5,5-hexafluoropentane-2,4-dionato(π-2-chloroallyl)palladium(II) (0.576 g) in dichloromethane (0.5 ml) was treated with isoprene (0.200 ml) and left to stand (5 min). The resultant solution was passed through a short Florisil column, eluting with dichloromethane. Evaporation of the eluate under reduced pressure yielded a yellow oil (0.650 g, 96%), shown by its low-temperature ^1H nmr spectrum to consist of a 1:1 mixture of 1,1,1,5,5,5-hexafluoropentane-2,4-dionato-π-1-*syn*-(3-chlorobut-3-en-1-yl)-1-*anti*-methylallylpalladium(II) (complex IIf) and 1,1,1,5,5,5-hexafluoropentane-2,4-dionato-π-1-*anti*-(3-chlorobut-3-en-1-yl)-1-*syn*-methylallylpalladium(II) (complex VIIIf).

Anal. Calcd for $C_{13}H_{13}ClF_6O_2Pd$: C, 34.16; H, 2.87. Found: C, 34.25; H, 2.71.

Similarly prepared were the following.

A 1:3 mixture of 1,1,1,5,5,5-hexafluoropentane-2,4-dionato-π-1-*syn*-(3-chlorobut-3-en-1-yl)-1-*anti*-2-dimethylallylpalladium(II) (complex IIg) and 1,1,1,5,5,5-hexafluoropentane-2,4-dionato-π-1-*anti*-(3-chlorobut-3-en-1-yl)-1-*syn*-2-dimethylallylpalladium(II) (complex VIIIg) (97%) was prepared from 1,1,1,5,5,5-hexafluoropentane-2,4-dionato-π-2-chloroallylpalladium(II) and 2,3-dimethylbutadiene.

Anal. Calcd for $C_{14}H_{15}ClF_6O_2Pd$: C, 35.70; H, 3.21. Found: C, 35.97; H, 3.24.

1,1,1,5,5,5-Hexafluoropentane-2,4-dionato-π-1-*syn*-(3-chloro-1-methylbut-3-en-1-yl)allylpalladium(II) (complex IIn) (96%) was prepared from 1,1,1,5,5,5-hexafluoropentane-2,4-dionato-π-2-chloroallylpalladium(II) and *trans*-penta-1,3-diene.

Anal. Calcd for $C_{13}H_{13}ClF_6O_2Pd$: C, 34.16; H, 2.87. Found: C, 34 25; H, 2.79.

1,1,1,5,5,5-Hexafluoropentane-2,4-dionato-π-4-*exo*-(2-chloroprop-2-en-1-yl)cyclohexenylpalladium(II) (complex XVI) as yellow prisms (94%), mp 99–102°, was prepared from 1,1,1,5,5,5-hexafluoropentane-2,4-dionato-π-2-chloroallylpalladium(II) and cyclohexa-1,3-diene.

Anal. Calcd for $C_{14}H_{13}ClF_6O_2Pd$: C, 35.87; H, 2.79; Cl, 7.56. Found: C, 35.84; H, 2.92; Cl, 7.46.

Treatment of complexes II (X = F_6acac) with an equimolar amount of dry HCl in benzene yielded the previously characterized chloride-bridged analogs.[2] *E.g.*, a solution of 1,1,1,5,5,5-hexafluoropentane-2,4-dionato-1-(3-chlorobut-3-en-1-yl)-1-methylallylpalladium(II) (0.280 g) in benzene (10 ml) was treated with a benzene solution of HCl (1.20 ml, 0.54 *M*). The resultant solution was passed down an alumina column (1 × 1 in.), eluting with dichloromethane. Evaporation of the eluate to dryness under reduced pressure yielded the previously reported[2] di-μ-chloro-bis[1-(3-chlorobut-3-en-1-yl)-1-methylallyl]dipalladium(II) (0.141 g, 80%), identified by its ^1H nmr spectrum.

Similarly, treatment of complexes IIa, IIb, IIh, and IIi (X = F_6acac) with an equimolar amount of HCl in benzene yielded the chloride-bridged dimeric analogs, whose ^1H nmr spectra were identical with those of authentic samples.[2]

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