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TRANSITION METAL PROMOTED REACTIONS OF UNSATURATED HYDROCARBONS

II*. INSERTION OF BICYCLIC OLEFINS INTO ALLYLIC–PALLADIUM AND –PLATINUM BONDS

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SUMMARY

Addition of strained olefins, based on norbornene, norbornadiene, benzonorbornadiene or bicyclo[2.2.2]octene skeletons to π-allylic(hexafluoroacetylacetonato)palladium(II) complexes [(π-All)Pd(Hfacac)], gives "enyl" products derived from "insertion" of the olefin into the least substituted terminal allylic–palladium bond. The reaction involves an initial rapid and reversible formation of (σ-allyl)(π-olefin)Pd(Hfacac). The rate-determining step involves migration of a σ-allylic carbon atom from Pd to the coordinated olefin in a concerted *cis–exo* addition of Pd–C across the double bond. Remote electronegative substituents on the olefin do not affect the coordinative ability of the olefin towards Pd. They do however inhibit the migration of the σ-allylic ligand to the coordinated olefin. This observation is interpreted in terms of a small degree of polarization of the π-olefin–Pd bond in the transition state for the σ-allyl migration.

INTRODUCTION

The insertion of olefinic functions into transition metal–carbon σ-bonds has long been recognised as a key step in the homogeneously catalysed polymerisation and oligomerisation reactions of unsaturated hydrocarbons. Mechanistic features of this reaction have in the most part been deduced from the nature of purely organic polymers, or oligomers, formed, and a *cis*-addition of the metal–carbon bond to a (presumably) coordinated olefin has frequently been postulated.

We have previously established that coordination of mono-olefins, 1,2-dienes, and 1,3-dienes to complexes of the type (π-All)Pd(Hfacac) [π-All = allylic function; Hfacac = hexafluoroacetylacetonate] occurs rapidly and reversibly in solution at room temperature[1–3]. In most cases the reaction of mono-olefinic hydrocarbons does not proceed further under the above conditions. This paper reports that introduction of a strain factor into the added mono-olefin promotes a ready insertion of

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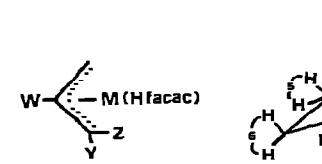
that olefin into allylic–palladium and –platinum bonds. The structures of the resultant products unambiguously define the insertion process as being a *cis*-addition of the metal–carbon bond to the olefin.

A preliminary account of this work has appeared[3].

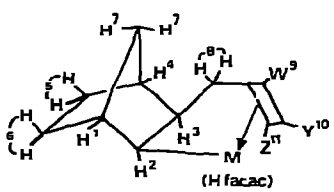
RESULTS AND DISCUSSION

The π-allylic hexafluoroacetylacetonate complexes of platinum(II) (Ia) and palladium(II) (Ib–n) react with a variety of strained bicyclic olefins to give "insertion" products of the type (II)–(X). The reaction is readily effected by allowing a solution, consisting of the stoichiometrically required amounts of the two reactants in the minimum volume of dichloromethane, to stand at room temperature for ca. 12–24 h. Chromatography of this solution gives high yields of the "enyl" products which are generally isolated as air stable, crystalline materials of remarkable thermal stability.

Reaction of norbornene, benzonorbornadiene, or norbornadiene with complexes (I) on a 1/1 molar basis readily yields complexes (II), (III), and (IV) respectively.



(I a–n)



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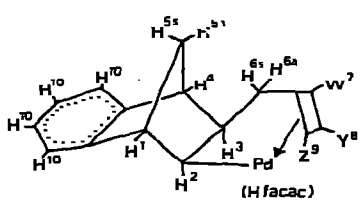

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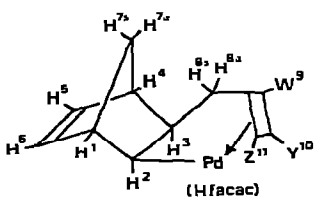

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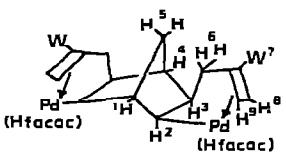

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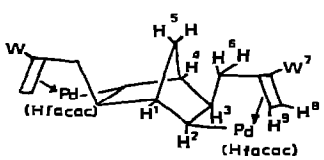

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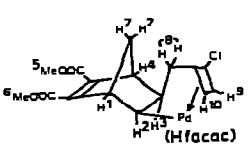
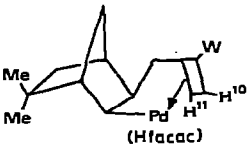
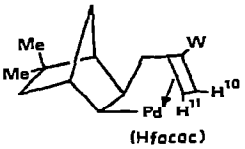


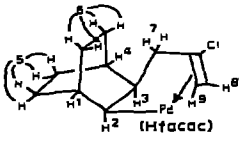
(VII)



(VIII b, d)



(IX b, d)



(X)

(a) M = Pt; W = Y = Z = H
(b) M = Pd; W = Y = Z = H
(c) M = Pd; W = CH_3; Y = Z = H
(d) M = Pd; W = Cl; Y = Z = H
(e) M = Pd; W = t-Bu; Y = Z = H
(f) M = Pd; W = t-$BuCH_2$; Y = Z = H
(g) M = Pd; W = MeEtCH; Y = Z = H
(h) M = Pd; W = Ph; Y = Z = H
(i) M = Pd; W = Z = H; Y = CH_3
(j) M = Pd; W = Z = H; Y = $COOCH_3$
(k) M = Pd; W = CH_3; Y = t-Bu; Z = H
(l) M = Pd; W = CH_3; Y = CH_2OCH_3; Z = H
(m) M = Pd; W = t-$BuCH_2$; Y = t-Bu; Z = H
(n) M = Pd; W = H; Y = Z = CH_3

Reaction of (IV) with (I) on a 1/1 molar basis, or reaction of norbornadiene with (I) on a 1/2 basis gives a mixture of isomers (V) and (VI). (V) and (VI) can be separated by fractional crystallization from dichloromethane. In the three cases studied the *cis*-isomer (V) was found to predominate over the *trans*-isomer (VI) by a ratio of ca. 3.5–4/1. Reaction of (Id) with an excess of 2,3-bis(methoxycarbonyl)norbornadiene yields only complex (VII), resulting from the addition of the 2-chloroallyl–palladium bond to the unsubstituted olefin function. The unsymmetrically substituted norbornene, 5,5-dimethyl-2-norbornene reacts with (Ib) and (Id) to yield inseparable 1/1 mixtures of (VIIIb) and (IXb), and (VIIId) and (IXd) respectively. Reaction of (Id) with bicyclo[2.2.2]octene proceeds much more slowly than with norbornene but gives an 80% yield of the analogous "insertion" product (X) after ca. 24 h.

Characterization of the insertion products (II)–(X)

The stoichiometry of the complexes (II)–(X) was established by elemental analysis and by mass spectroscopy (see Table 1). The structural features of these complexes were established primarily by their ^{1}H NMR spectra (see Tables 2–6). Supporting evidence was obtained from mass spectroscopy data. Infrared spectra were not particularly helpful as the absorptions of the Hfacac ligand masked most of the spectral regions of interest.

The ^{1}H NMR spectral features of norbornene and norbornane systems have been extensively documented in recent years[4–12]. As the bicyclic carbon skeleton in these compounds has considerable rigidity, the use of ^{1}H–^{1}H coupling constants to determine the relative positions of protons attached to this framework, and hence the overall stereochemistry, is particularly facilitated. The ^{1}H NMR spectra of complexes (IV) are considered first as these are the most straightforward to assign (see Table 4).

The ^{1}H NMR spectra of (IVc) and (IVd) are shown in Fig. 1. Protons H^5 and H^6 are readily located at ca. τ4.1 ppm since this is a typical chemical shift for the protons of a norbornene type olefin[8,9,12]. The protons attached to the coordinated olefin are readily assigned on the basis of variation of coupling patterns on changing substituents W, Y and Z on the olefin. Similarly the multiplet assigned to the H^{8s}, H^{8a} system shows a marked downfield shift on introducing an electronegative substituent at position 9 (*e.g.* W=Cl). The methylene bridge protons H^{7s} and H^{7a} exhibit a characteristic AB quartet coupling pattern[13] and are assigned on this basis. The bridgehead protons H^1 and H^4 are located as broad singlets, the resonance at lower field being tentatively assigned to H^1 since it is adjacent to the more electronegative palladium substituent, and is thus expected to experience a deshielding effect relative to H^4.[6] The remaining two resonances at ca. τ7.5 and ca. 9.0 ppm must therefore correspond to H^2 and H^3. Since H^3, which is vicinal to H^{8a} and H^{8s}, is expected to experience a more complex coupling pattern than H^2, and since H^2 is adjacent to the more electronegative palladium substituent and should therefore be shifted to low-field[6], the high-field (ca. τ 9.0 ppm) pseudo-quartet resonance in complexes (IV) is assigned to H^3, leaving H^2 as the remaining doublet of doublets. A similar set of arguments can be used to assign the spectra of complexes (III) (see Table 3).

The magnitude of the values of $J_{2,3}$ (7 Hz) in complexes (IV) and (III) indicates

(*continued on p.* 396)

TABLE 1

ANALYTICAL AND MASS SPECTRAL DATA OF THE "ENYL" INSERTION PRODUCTS OBTAINED FROM THE REACTIONS OF COMPLEXES(I) WITH STRAINED OLEFIN

Complex *Yield %*		*M.p.* (°C)	*Analysis found (calcd.)* (%)		*Mass spectral data (Pd containing fragments only)*[a] *Ion [assignment*[b]*, or m/e]*[c] (% *abundance relative to* CF_3^+ = 100%).
			C	*H*	
(IIa)	72	144–146	33.6 (33.5)	3.2 (3.0)	
(IIb)	88	160–165	40.5 (40.2)	3.5 (3.6)	P^+[448] (1.7); [P − HfacacH]$^+$ (244); [(All)Pd]$^+$(142); Pd^+(59)
(IIc)	85	134–137	41.5 (41.5)	4.0 (3.9)	P^+[462](105); [(All)Pd(Hfacac)]$^+$ (26); [(All)Pd]$^+$ (1900); Pd^+(418)
(IId)	92	173–175	37.5 (37.3)	3.0 (3.1)	P^+[482] (0.04); [P − HfacacH]$^+$(27); [(All)Pd]$^+$(8.5); Pd^+(15)
(IIe)	93	114–116	45.3 (45.2)	4.7 (4.8)	P^+[504](11); [P − Hfacac]$^+$(417); [(All)Pd]$^+$(284)
(IIf)	87	110–112	46.6 (46.3)	5.2 (5.1)	P^+[518](1.6); [P − HfacacH]$^+$(93); [(All)Pd]$^+$(28)
(IIg)	89	89–92	45.4 (45.2)	4.8 (4.8)	P^+[504](13); [P − Hfacac]$^+$(520); [(All)Pd]$^+$(326); [Pd]$^+$(118)
(IIh)	91	125–128	48.0 (48.0)	3.7 (3.8)	
(IIi)	93	87–89	41.5 (41.5)	4.2 (3.9)	P^+[462] (8.4); [P − HfacacH]$^+$ (435); [(All)Pd]$^+$ (243); Pd^+(59)
(IIj)	88	102–104	40.3 (40.3)	3.5 (3.6)	P^+ (not observed); [P − HfacacH]$^+$ (58); [(All)Pd]$^+$ (300); Pd^+(144)
(IIk)	93	94–97	46.2 (46.3)	5.0 (5.1)	P^+ [518] (15); [P − HfacacH]$^+$ (520); [(All)Pd]$^+$ 400
(III)	97	49–53	42.6 (42.7)	4.5 (4.4)	
(IIm)	37	47–50	50.3 (50.1)	5.8 (6.0)	
(IIn)	59	100–103	43.8 (42.8)	4.0 (4.2)	P^+[476](6); [(All)PdHfacac]$^+$(3); [P − HfacacH]$^+$(232); [(All)Pd]$^+$(195); [Pd]$^+$(54)
(IIIa)	90	162–165	39.1 (39.0)	2.9 (2.8)	P^+[585] (89); [P − C_9H_8]$^+$(64); [P − HfacacH]$^+$(59); [P − C_9H_8 − Hfacac]$^+$(17.5)
(IIIb)	97	107–110	46.0 (46.0)	3.1 (3.1)	P^+[496] (51); [P − C_9H_8]$^+$(7); [P − HfacacH] (267); Pd^+(70)
(IIIc)	97	128–131	46.9 (47.1)	3.4 (3.4)	P^+[510] (150); [P − C_9H_8]$^+$(36); [P − Hfacac] (580); [(All)Pd]$^+$(150); Pd^+(103)
(IIId)	95	140–143	43.2 (43.0)	2.5 (2.7)	
(IIIn)	77	135–143	48.2 (48.1)	3.9 (3.8)	P^+ [524] (123); [P − HfacacH]$^+$ (300); [P − C_9H_8 − Hfacac]$^+$(30); [(All)Pd]$^+$(54); Pd^+(44)
(IVa)	88	115–119	33.5 (33.7)	2.5 (2.6)	P^+[535] (42); [P − C_5H_6]$^+$(470); [P − HfacacH]$^+$(83); [P − HfacacH − C_5H_6]$^+$(412)
(IVb)	77	117–120	40.4 (40.3)	3.1 (3.2)	P^+[446] (29); [P − C_5H_6]$^+$(3); [P − HfacacH]$^+$(316); [P − C_5H_6 − Hfacac]$^+$ (130); [(All)Pd]$^+$(98); Pd^+(81)
(IVc)	80	155–156	41.9 (41.7)	3.6 (3.5)	P^+[480] (0.6); [P − Hfacac]$^+$(8)
(IVd)	90	d. 170–175	37.6 (37.5)	2.7 (2.7)	

(continued)

Complex *Yield %*		*M.p.* (°C)	*Analysis found (calcd.) (%)*		*Mass spectral data (Pd containing fragments only)*[a] *Ion [assignment*[b]*, or m/e]*[c] *(% abundance relative to CF_3^+ = 100%*
			C	*H*	
(IVi)	92	120–125	42.0 (41.7)	3.7 (3.5)	
(VII)	91	153–155	38.1 (38.2)	2.8 (2.9)	P^+[596] (71); [P−Hfacac]$^+$(510); [P−Hfacac−$C_9H_{10}O_4$]$^+$(106); Pd^+(206)
(VIIIb) (IXb)	91	65–75	43.0 (42.8)	4.1 (4.2)	P^+ (not observed); [P−HfacacH]$^+$(1600); [(All)Pd]$^+$ (483); Pd^+(300)
(VIIId) (IXd)	90	75–85	40.0 (39.9)	3.9 (3.8)	P^+(not observed); [P−HfacacH]$^+$ (98)
(X)	80	164–166	38.9 (38.7)	3.4 (3.5)	P^+(not observed); [P−HfacacH]$^+$(165)

[a] The mass spectra of all the complexes exhibited a peak(s) at *m/e* 207 and/or 208 assignable to the ions Hfacac$^+$ and HfacacH$^+$ respectively. [b] All=Allylic ligand regenerated by reversal of the original olefin insertion. [c] All *m/e* values are quoted for ^{106}Pd or ^{195}Pt peak. In case of ions containing chlorine, *m/e* is quoted for ^{35}Cl peak.

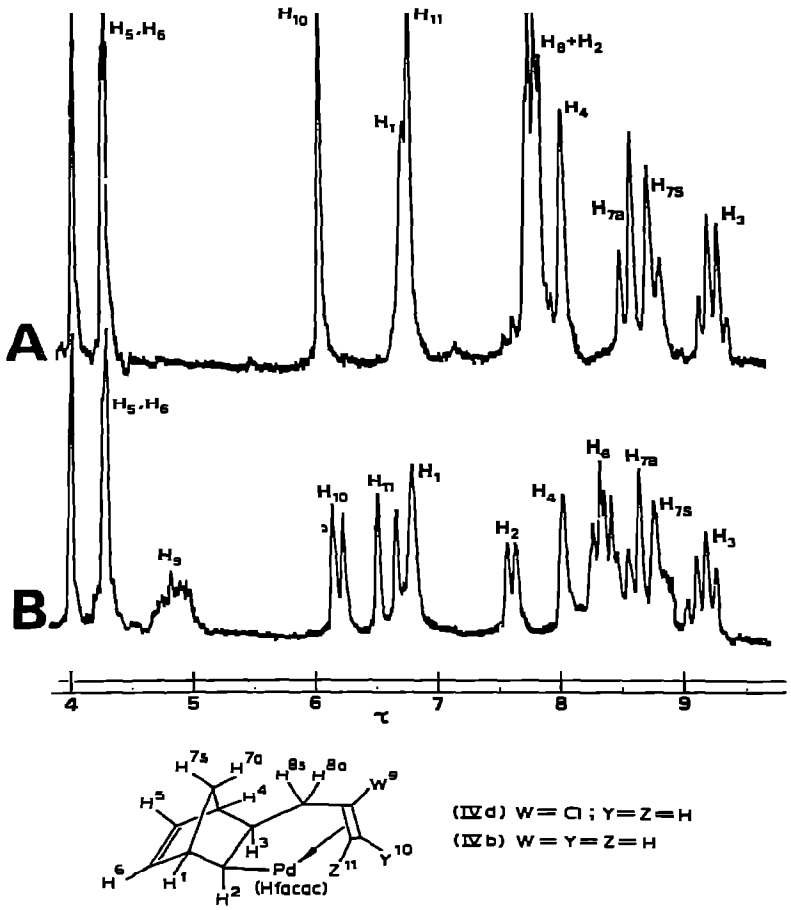


Fig. 1. ^1H NMR spectra (100 MHz; C_6D_6; 34°) of A; complex (IVd), and B; complex (IVb).

TABLE 2

^{1}H NMR DATA FOR COMPLEXES (II)[a] (60 MHz; $CDCl_3$; 34°).

Complex	*M*	*W*	*Y*	*Z*	H^2	H^9	H^{10}	H^{11}	H^1 H^3 H^4 H^5 H^6 H^7 H^8	*Hfacac*
(IIa)	Pt	H	H	H	7.20(dd) $J_{2,3}$ 7.5 $J_{2,7a}$ 2 J_{Pt-H^2} 96	5.43(m) J_{Pt-H^9} 88	6.13(d). $J_{9,10}$ 8 $J_{Pt-H^{10}}$ 92	6.51(d) $J_{9,11}$ 13.5 $J_{Pt-H^{11}}$ 82	8.0–9.0	3.95
(IIb)	Pd	H	H	H	6.70(dd) $J_{2,3}$ 7 $J_{2,7a}$ 2	4.18(m)	5.58(dd) $J_{9,10}$ 8 $J_{10,11}$ 1	5.72(dd) $J_{9,11}$ 14 $J_{10,11}$ 1	8.0–9.0	3.98(s)
(IIc)	Pd	CH_3	H	H	6.88(dd) $J_{2,3}$ 7 $J_{2,7a}$ 2	8.06(s)	5.95(s)	5.98(s)	8.0–9.0	3.98(s)
(IId)	Pd	Cl	H	H	6.82(dd) $J_{2,3}$ 7 $J_{2,7a}$ 2		5.50(s)	5.78(s)	8.0–9.0	3.96(s)
(IIe)	Pd	t-Bu	H	H	6.70(dd) $J_{2,3}$ 7 $J_{2,7a}$ 2	8.73(s)	5.66(s)	5.80(s)	8.0–9.0	4.02(s)
(IIf)	Pd	t-$BuCH_2$	H	H	6.75(bd) $J_{2,3}$ 7	(t-Bu)9.03(s)[b]	5.78(s)[c]		8.0–9.0	4.02(s)
(IIg)	Pd	$CH_3CH_2(CH_3)CH$	H	H	6.80(dd) $J_{2,3}$ 7 $J_{2,7a}$ 2	[d]	5.89(s)[c]		8.0–9.0	4.01(s)
(IIh)	Pd	C_6H_5	H	H	6.68(bd) $J_{2,3}$ 7	2.2–2.8(m)	5.30(s)	5.92(s)	8.0–9.0	4.25(s)
(IIi)	Pd	H	CH_3	H	6.80(dd) $J_{2,3}$ 7 $J_{2,7a}$ 2	8.27(d) $J_{10,11}$ 6	4.4–4.9(m)		8.0–9.0	3.98(s)
(IIj)	Pd	H	$COOCH_3$	H	6.38(bd) $J_{2,3}$ 7	3.55(dt) $J_{9,11}$ 13 $J_{9,8a}$ 4.5 $J_{9,8s}$ 2	6.30(s)	4.96(d) $J_{9,11}$ 13	8.0–9.0	3.98(s)
(IIk)	Pd	CH_3	t-Bu	H	6.98(bd) $J_{2,3}$ 7	7.99(s)	8.72(s)	5.48(s)	8.0–9.0	4.02(s)

(IIl)	Pd	CH_3		CH_2OCH_3	H	6.77(bd)	8.06(s)	$(CH_2)^f$ 5.96(dd) 6.29(dd) J_{gem} 12 $J_{11,10}$ 6	5.21(t) $J_{11,10(CH_3)}$ 6	8.0–9.0		4.02(s)
(IIm)	Pd	t-$BuCH_2$		t-Bu	H	6.77(dd) $J_{2,3}$ 7 $J_{2,7a}$ 2	[d]	[d]	5.47(s)	8.0–9.0		3.95(s)
(IIn)	Pd	H		CH_3	CH_3	6.99(dd) $J_{2,3}$ 7 $J_{2,7a}$ 2	4.62(dd) $J_{9,8a}$ 6 $J_{9,8s}$ 2.5	7.93(s)	8.22(s)	8.0–9.0		4.03(s)

[a] Chemical shifts(τ); J(Hz). Notation for peak multiplicities: s, singlet; d, doublet; m, multiplet; t, triplet; b, broad. [b] CH_2 group resonates between 8–9 τ and is obscured. [c] Both olefinic protons accidentally isochronous. [d] Resonances occur between 8–9 τ. [e] Methylene protons are diastereotopic and give rise to an AB quartet pattern.

TABLE 3

^{1}H NMR DATA FOR COMPLEXES (III) (60 MHz; 34°)

					τ(*multiplicity*)[a], *J*(*Hz*)											
Complex	*Solvent*	*W*	*Y*	*Z*	H^1	H^2	H^3	H^4	$H^{5s\,b}$	$H^{5a\,b}$	H^6	H^7	H^8	H^9	H^{10}	*Hfacac*
(IIIb)	$CDCl_3$	H	H	H	6.32(bs)	6.99(dd) $J_{2,3}$ 7 $J_{2,5a}$ 2	≈8.35[c]	7.05(bs)	8.27(d) $J_{5s,5a}$ 10	7.87(d) $J_{5s,5a}$ 10	7.43(m)	4.28(m)	5.60(d) $J_{7,8}$ 9	5.89(d) $J_{7,9}$ 15	2.88(m)	3.90(s)
(IIIc)	$CDCl_3$	CH_3	H	H	6.32(bs)	7.10(dd) $J_{2,3}$ 7 $J_{2,5s}$ 2	≈8.48[c]	7.07(bs)	8.31(d) $J_{5s,5a}$ 9	7.91(d) $J_{5s,5a}$ 9	7.43(m) $J_{6s,6a}$ 17 $J_{6s,3}$ 8 $J_{6a,3}$ 9	7.98(s)	5.93(s)	6.15(s)	2.91(m)	3.93(s)
(IIId)	$CDCl_3$	Cl	H	H	6.22(bs)	≈7[d]	≈8.4[c]	7.15(bs)	8.23(d) $J_{5s,5a}$ 9.5	7.80(d) $J_{5s,5a}$ 9.5	7.00(m)		5.52(s)	5.98(s)	2.90(m)	3.87(s)
(IIId)	C_6D_6	Cl	H	H	6.65(bs)	≈7.4[d]	8.67(q) $J_{2,3}$ 7 $J_{2,8s}$ 7 $J_{2,8a}$ 7	≈7.3[d]	8.31(d) $J_{5s,5a}$ 10	7.84(d) $J_{5s,5a}$ 10	7.43(m)		5.85(s)	6.10(s)	2.83(m)	3.80(s)
(IIIn)	$CDCl_3$	H	CH_3	CH_3	6.38(bs)	7.20(dd) $J_{2,3}$ 7 $J_{2,5s}$ 2	≈8.3[c]	7.13(bs)	≈8.2[c]	≈7.8[c]	≈7.5[c]	4.61(dd) $J_{7,6a}$ 6 $J_{7,6a}$ 2	8.19(s)	8.25(s)	2.90(m)	3.95(s)

[a] Notation: b, broad; s, singlet; d, doublet; q, quartet; m, multiplet. [b] H^{5s} assigned as broader of two resonances because of additional long range coupling $J_{2,5s}$, $J_{3,5s}$ to this proton. [c] Obscured by H^{5s}. [d] Obscured by H^6. [e] Obscured by H^8 and H^9.

TABLE 4

^{1}H NMR DATA FOR COMPLEXES (IV) (100 MHz; C_6D_6; 34°)

				τ(*multiplicity*)[a]; *J*(*Hz*)											
Complex	*W*	*Y*	*Z*	H^1	H^2	H^3	H^4	H^5+H^6	$H^{7a\,b}$	$H^{7a\,b}$	H^8	H^9	H^{10}	H^{11}	*Hfacac*
(IVb)	H	H	H	6.70(bs)	7.51(dd) $J_{2,3}$ 7 $J_{2,7a}$ 2	9.06(q) $J_{2,3}$ 7 $J_{3,8a}$ 7 $J_{3,8a}$ 7	7.93(bs)	4.18(bs)	8.72(d) $J_{7a,\,7a}$ 9	8.52(d)	8.26(m)	4.78(m)	6.10(d) $J_{9,10}$ 9	6.50(d) $J_{9,11}$ 15	3.90(s)
(IVc)	CH_3	H	H	6.58(bs)	7.48(bd) $J_{2,3}$ 7	8.97(q) $J_{2,3}$ 7 $J_{3,8a}$ 7 $J_{3,8a}$ 7	7.83(bs)	4.08(bs)	8.62(d) $J_{7a,\,7a}$ 9	≈8.4[c]	8.12(m)	8.34(s)	6.28(s)	6.58(d)	3.90(s)
(IVd)	Cl	H	H	6.61(bs)	≈7.5[d]	9.14(q) $J_{2,3}$ 7 $J_{3,8a}$ 7 $J_{3,8a}$ 7	7.90(bs)	4.14(bs)	8.66(d) $J_{7a,\,7a}$ 9	8.42(d)	7.65(m)		5.92(s)	6.65(s)	3.89(s)
(IVi)	H	CH_3	H	6.69(bs)	7.47(d) $J_{2,3}$ 7	9.00(q) $J_{2,3}$ 7 $J_{3,8a}$ 7 $J_{3,8a}$ 7	7.86(bs)	4.14(bs)	≈8.4–8.7[e]		8.20(m)	5.00(dd) $J_{9,11}$ 14 $J_{8,9}$ 4	8.59(d) $J_{9,10}$ 7	5.49(dq) $J_{9,11}$ 14 $J_{9,10}$ 7	3.92(s)

[a] Notation: b, broad; s, singlet; d, doublet; q, quartet; m, multiplet. [b] H^{7a} assigned as broader of two resonances because of additional long range coupling $J_{2,7a}$, $J_{3,7a}$ to this proton. [c] Obscured by H^9. [d] Obscured by H^8. [e] Obscured by H^{10}.

TABLE 5

^{1}H NMR DATA FOR COMPLEXES (V) AND (VI) (60 MHz; 34°)

			τ(*multiplicity*)[a]; *J*(*Hz*)									
Complex	*Solvent*	*W*	H^1	H^4	H^2	H^3	H^5	H^6	H^7	H^8	H^9	*Hfacac*
(Vb)	$CDCl_3$	H	≈7.3[b]	8.48(bs)	6.74(bd) $J_{2,3}$ 7	≈8.3[c]	8.28(bs)	7.58(m)	4.25(m)	5.64(d) $J_{7,8}$ 8	5.78(d) $J_{7,9}$ 15	3.94(s)
(VIb)	$CDCl_3$	H	7.48(bs)[d]		6.88(bd) $J_{2,3}$ 7	≈8.3[c]	8.28(bs)	7.48(m)	4.25(m)	5.55(d) $J_{7,8}$ 8	5.73(d) $J_{7,9}$ 14	3.95(s)
(Vc)	$CDCl_3$	CH_3	7.36(bs)	8.47(bs)	6.78(bd) $J_{2,3}$ 7	≈8.3[c]	8.32(bs)	7.58(m)	8.05(s)	6.04(s)[e]		3.97(s)
(Vc)	C_6D_6	CH_3	7.32(bs)	8.92(bs)	7.26(bd) $J_{2,3}$ 7	8.97(q) $J_{2,3}$ 7 $J_{3,6a}$ ≈7 $J_{3,6s}$ ≈7	8.50(bs)	8.08(m)	8.36(s)	6.31(s)	6.48(s)	3.90(s)
(VIc)	$CDCl_3$	CH_3	7.82(bs)[d]		6.98(d) $J_{2,3}$ 7	8.37(q) $J_{2,3}$ 7 $J_{3,6a}$ ≈7 $J_{3,6s}$ ≈7	8.32(bs)	7.50(m)	7.99(s)	5.87(s)	5.97(s)	4.00(s)
(VIc)	C_6D_6	CH_3	8.02(bs)[d]		7.35(d) $J_{2,3}$ 7	8.83(q) $J_{2,3}$ 7 $J_{3,6s}$ ≈7 $J_{3,6a}$ ≈7	≈8.4[f]	7.82(m)	8.37(s)	6.26(s)	6.50(s)	3.87(s)
(Vd)	$CDCl_3$	Cl	≈7.2	8.32(bs)	6.90(d) $J_{2,3}$ 7	≈8.4[c]	8.15(bs)	7.14(m)		5.51(s)	5.83(s)	3.92(s)
(VId)	$CDCl_3$	Cl	7.53(bs)[d]		≈7.0[b]	8.33(q) $J_{2,3}$ 7 $J_{3,6a}$ ≈7 $J_{3,6a}$ ≈7	8.15(bs)	7.00(m)		5.42(s)	5.76(s)	3.92(s)

[a] Notation: b, broad; s, singlet; d, doublet; q, quartet; m, multiplet. [b] Obscured by H^6 resonance. [c] Obscured by H^4 and H^5 resonances. [d] H^1 and H^4 are diastereotopic in complexes (VI). [e] H^8 and H^9 accidentally isochronous in $CDCl_3$. [f] Obscured by H^7 resonance.

TABLE 6

^{1}H N.M.R. DATA FOR COMPLEXES (VII) AND (X) [(60 MHz; $CDCl_3$; 34°)

Complex	τ(*multiplicity*)[a]; *J* (*Hz*)									
	H^1	H^2	H^3	H^4	H^5 H^6	H^7	H^8	H^9	H^{10}	*Hfacac*
VII	6.28(bs)	≈6.9[b]	≈8.1[c]	≈6.9[b]	6.20(s)	8.17(m)	6.95(m)	5.32(s)	5.70(s)	3.91(s)
	H^2	H^1	H^3	H^4	H^5	H^6	H^7	H^8	H^9	*Hfacac*
X	6.46(bd) $J_{2,3}$ 8.5	8.0-9.0						5.50(s)	5.58(s)	4.02(s)

[a] Notation: s, singlet, d, doublet; m, multiplet; b, broad. [b] Obscured by H^8 resonance. Position determined by integration. [c] Obscured by H^7 resonance. Position determined by integration.

that these two protons occupy mutually *cis*-positions. The low values of $J_{1,2}$ and $J_{4,3}$ (1 Hz) provide strong evidence that H^2 and H^3 occupy *endo*-positions since the usual values for a coupling constant from a bridgehead proton to an *exo*-proton in norbornene systems are of the order of 3–4 Hz[4,8,10]. In agreement with this a long range coupling constant $J_{2,7s}$ of 2 Hz is observed which is typical of 7s-*endo* proton coupling[4,8-10]. Long-range coupling of H^{7s} to *exo*-protons is not normally observed in systems of this type[4-12]. Thus the ^{1}H NMR spectra of complexes (III) and (IV) structurally characterize them as *cis-exo*-disubstituted norbornenes; *i.e.* the addition of the allyl–palladium bond to the olefin has occurred stereospecifically *cis*.

The ^{1}H NMR spectra of complexes (II) (see Table 2) derived from insertion of norbornene are extremely complex in the region above τ8.0 ppm, due to the greater number of aliphatic protons present in these complexes. However, the resonances below τ8.0 ppm could readily be assigned since they comprised the signals corresponding to the protons of the coordinated olefin, together with one additional resonance pattern. The assignments of the coordinated olefinic proton signals proved compatible with values obtained for complexes (III) and (IV). In addition, the spectra of complexes (II) contained a resonance at ca. τ6.5–7.0 ppm (a doublet of doublets), which exhibited exactly the same coupling pattern (*J*'s 7 and 2 Hz) as observed for H^2 in complexes (III) and (IV). As such this resonance was assigned to H^2. The magnitude of the coupling constants of the H^2 resonances indicates that the stereochemistry of complexes (II) must also be *cis–exo*.

The spectra of complexes (V)–(X) were assigned by comparison with their appropriate analogues in the series of complexes (II)–(IV) (see Tables 5 and 6). Although complexes (VIII) and (XI) could not be separated, either by column chromatography, or fractional crystallization, they were shown to be formed in ca. equal amounts by integration of the ^{1}H NMR spectrum of the product mixtures. [N.B. The proton resonances of H^{10}, and H^{11} of each isomer occur at different chemical shifts (as doublets when W = H and as singlets when W = Cl)].

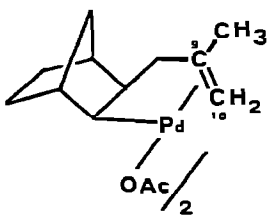
The stereochemistries of the isomeric products (V) and (VI) were readily identified by their ^{1}H NMR spectra (see Table 5). The only difference in the ^{1}H NMR spectra of these complexes is that in the *cis*-isomer (V) the two bridgehead protons are symmetrically non-equivalent and as such give rise to two anisochronous

resonances, whereas the two bridgehead protons in the *trans*-isomer (VI) are symmetrically equivalent and give rise to only one resonance of relative intensity 2. All other protons in either of the two isomers are related by symmetry [*i.e.* a mirror plane passing through H^1, H^4 and CH_2^5 in (V), and a two-fold rotation axis passing through CH_2^5 in (VI)].

The ^1H NMR spectra of those products derived from the unsymmetrically substituted allylic complexes (Ii–n) show unambiguously that the strained olefin has "inserted" into the least substituted end of the allylic moiety and that the geometry of the olefin is unchanged from that of the original π-allylic complex. Particularly diagnostic is the number of olefinic protons and the internal coupling constants of the coordinated olefinic moiety[13].

X-rays

Following a preliminary account of this work Galazzi *et al.*[14] reported that addition of sodium acetate to a mixture of (2-methylallyl)palladium chloride and norbornene gave the insertion product (XI). The structure of (XI) as determined by X-ray crystallography confirms that the mode of addition of the 2-methylallyl–Pd bond to norbornene is *cis–exo*[15]*.



(XI)

Of particular interest in the molecular structure of (XI) is the geometry of the palladium–olefin bond. The Pd–C^9–C^{10} plane lies approximately perpendicular to the square plane of coordination. The C^9–C^{10} bond axis however is not perpendicular to the square plane, as is normally found in olefin complexes of palladium(II) and platinum(II), but is tilted in towards the metal atom, such that the square plane of coordination intersects the C^9–C^{10} bond axis at a point much closer to C^{10} than C^9. Both C^9 and C^{10} however remain equidistant from the metal.

The mass spectra of the insertion products

The major metal-containing fragments in the mass spectra of representative complexes of type (II)–(IV) are listed in Table 1. In almost all cases the molecular ion is observed, providing a ready check on the molecular formula of each complex. Relative ion abundances are based on the intensity of the CF_3^+ (*m/e* 69) fragment being arbitrarily put equal to 100%. This peak should provide a good reference since its formation occurs by fragmentation of the Hfacac ligand and as such should be

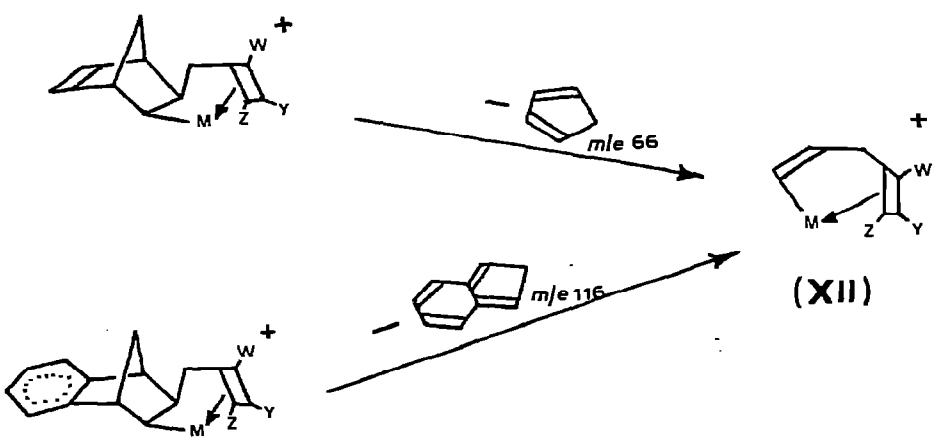
* Treatment of complex (IIc) with 1 mol of HCl (benzene solution) per Pd gave the corresponding bridged chloride dimer. Treatment of this with silver acetate gave a bridged acetate dimer with properties identical to complex (IX) synthesised by the method of Galazzi *et al.*[14].

relatively independent of the hydrocarbon ligand.

In all three classes of complex, two major breakdown routes are observed. Loss of the hexafluoroacetylacetonate radical, or hexafluoroacetylacetone from the parent ion is a highly favoured process*. One or both of these processes occurs in all the complexes investigated. The second major breakdown route appears to involve the reversal of the insertion reaction and regeneration of the π-allylic–palladium species (I). Thus the ion of the π-allylic precursor (I) usually represents an abundant ion in the mass spectra of these complexes. However, this reverse reaction is not observed in any of the complexes involving platinum.

In the mass spectra of complexes (III), and (IV) [M = Pd or Pt], a third major breakdown route is readily apparent. This involves a *retro*-Diels–Alder reaction with elimination of cyclopentadiene in the case of complexes (IV) and benzocyclopentadiene from complexes (III). This is a well-known feature of the breakdown patterns of norbornenes and benzonorbornenes, and indeed the ions $C_5H_6^+$ (*m/e* 66) and $C_9H_8^+$ (*m/e* 116) form the base peaks in the mass spectra of organic compounds of these skeletal types[18]. See Scheme 1.

SCHEME 1



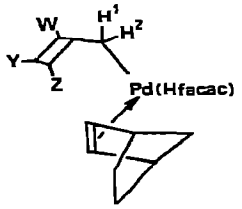
The metal containing fragment obtained by the *retro*-Diels–Alder reactions of either (III) or (IV) is presumably of structure (XII). Keeping W, Y and Z constant but varying the metal, the *retro*-Diels–Alder reaction in both (III) and (IV) is apparently much more facile when M is Pt rather than Pd. This may reflect a greater thermodynamic stability of fragment (XII) when M is Pt relative to Pd. Platinum (II) is well known to prefer σ-bonds to carbon and π-olefin bonding compared to palladium(II), where the π-allyl–palladium system is particularly stable. Of undoubted significance in this context is the observation that while (II), (III) and (IV) (M = Pd) undergo ready reversal of the insertion process under electron-impact to yield allylic–palladium species, no signs of any allylic–platinum species are observed in the mass spectra of the platinum analogues.

* This mode of breakdown is often found in the mass spectra of Hfacac complexes of transition metals[16,17].

^1H NMR studies of the insertion reaction

It has been previously established that olefins interact rapidly and reversibly in solution with π-allylic complexes of palladium(II) to generate short lived σ-allylic intermediates similar to (XIII)[1-3].

Addition of norbornene, norbornadiene or benzonorbornadiene to $CDCl_3$ solutions of complexes(I), on a 1/1 molar basis, resulted in immediate collapse of the PMR signals of the *syn* and *anti* protons H^1 and H^2 which is indicative of the rapid and reversible formation of the σ-allylic intermediate (XIII))*.



(XIII)

Since peaks in the NMR spectrum due to product formation are not observed until a later stage, it follows that coordination of the added olefin to the metal occurs rapidly and reversibly and that coordination of the olefin to the metal cannot be the rate-determining step for product formation.

For a constant allylic function, variation of the added olefin produced different extents of collapse, decreasing in the order:

norbornadiene > norbornene ≈ 1/2 (norbornadiene) ≈ complex (IVb) ≈ 2,3-bis(methoxycarbonyl)norbornadiene > benzonorbornadiene > bicyclo[2.2.2]octene, (see Fig. 2).

For a constant added olefin, variation of the 2-substituent on the allyl function of complexes (I) (M = Pd) produced significantly different extents of collapse, decreasing in the order**:

2-chloroallyl > allyl > 2-methylallyl.

Further reaction of these solutions occurred fairly rapidly (0.25–3 h) to produce peaks in the NMR spectrum characteristic of the insertion products. A kinetic investigation of the reaction of complex (Id) with norbornene to give complex (IId), by integration of the NMR spectrum at intervals of time gave a fairly good second order plot according to the rate equation (see Fig. 3):

---

* Olefins based on the bicyclo[2.2.1]heptane skeleton have two stereochemically distinct faces by which coordination to the metal can occur. Many organic reactions of norbornenes indicate that access to the *exo*-face of the olefinic function is considerably less sterically hindered than is access to the *endo*-face[19,20]. In addition X-ray structural studies of complexes of norbornadiene with Cu^{I}[21], Ag^{I}[22], and Mn^{I}[23] in which the diene acts as a monodentate ligand, invariably exhibit coordination via the *exo*-face of the olefin. Hydroformylation of norbornene by $CO/DCo(CO)_4$ has been shown to yield an *exo*-substituted product derived via the intermediacy of an *exo*-coordinated norbornene–cobalt complex[24].

** This order is similar to that observed for *syn–anti* proton exchange in $[(\pi\text{-All})Pd(OAc)Me_2PhP]$ and related systems[25,26].

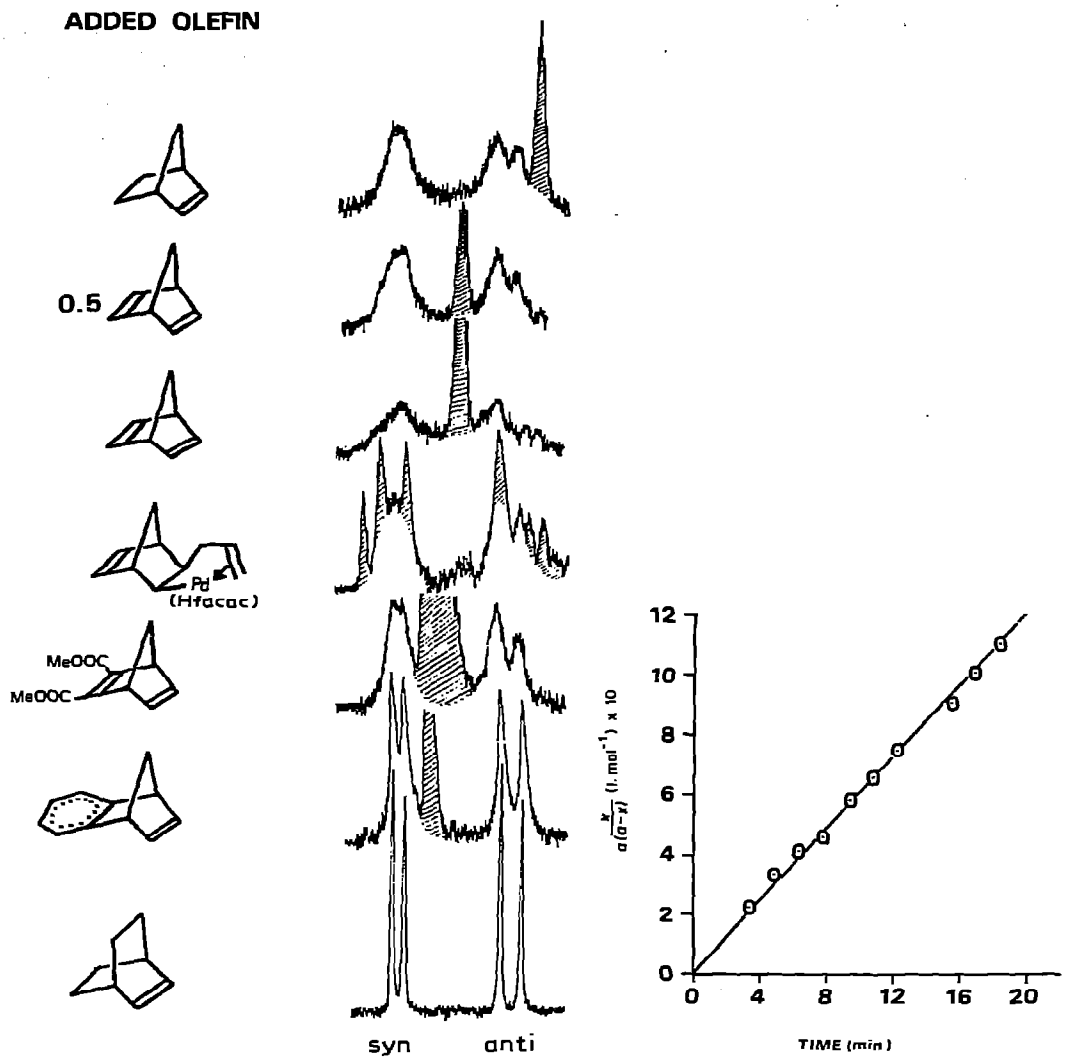


Fig. 2. ^{1}H NMR spectra (60 MHz; $CDCl_3$; 34°): Extent of collapse of the *syn*- and *anti*-proton resonances of (π-allyl)Pd(Hfacac) [0.82 *M*] on addition of various bicyclic olefins (1 molar equivalent except where stated). Resonances due to the added olefinic hydrocarbon are shaded.

Fig. 3. Second order rate plot for the reaction of (2-chloroallyl)Pd(Hfacac) [0.82 *M*] with norbornene [0.82 *M*] to give complex (IId), in $CDCl_3$ solution at 34°; [a=concentration of (2-chloro-allyl)Pd-(Hfacac) at $t=0$, x=concentration of complex (IId) at $t>0$].

$$-\frac{d[Id]}{dt} = k\cdot[\text{complex}]\cdot[\text{norbornene}]$$

The rate was found to be invariant on changing the solvent from $CDCl_3$ to C_6D_6. Thus the rate-determining step for product formation apparently involves one molecule of complex (Id) and one molecule of norbornene, and does not involve direct participation by a solvent molecule.

Although good kinetics results could not be obtained on most of these reactions, due to the complexity of the spectra and consequent integration difficulties, qualitative rates of product formation could be obtained. Assuming the same rate law to hold for all reactions approximate second order rate constants could be calculated. See Table 7. The following relative rates of product formation were observed.

TABLE 7

SECOND ORDER RATE CONSTANTS (k) FOR REACTIONS OF (π-All)Pd(Hfacac) (0.82M) AND STRAINED BICYCLIC OLEFINS (0.82 M) IN $CHCl_3$ AT 34° TO GIVE AN "ENYL INSERTION PRODUCT"

π-Allyl	*M*	*Olefin*	*Product*	$k(l \cdot mol^{-1} \cdot min^{-1}) \times 10^2$
2-Chloroallyl	Pd	Norbornadiene	(IVd)	14
2-Chloroallyl	Pd	Norbornene	(IId)	6
2-Chloroallyl	Pd	Complex (IVd)	(Vd) and (VId)	5
2-Chloroallyl	Pd	Benzonorbornadiene	(IIId)	2
2-Chloroallyl	Pd	2,3-Bis(methoxycarbonyl)-norbornadiene	(VII)	1
Allyl	Pd	Norbornene	(IIb)	3
2-Methylallyl	Pd	Norbornene	(IIc)	2
2-tert-Butylallyl	Pd	Norbornene	(IIe)	< 1
Allyl	Pt	Norbornene	(IIa)	100

(*i*). Keeping the allyl function, and the metal, in complexes (I) constant, and varying the olefin:

norbornadiene > norbornene > complex (IVd) > benzonorbornadiene > 2,3-bis(methoxycarbonyl)norbornadiene.

(*ii*). Keeping the added olefin and the metal constant, and varying the 2-substituent (W) on the allyl function:

$W = Cl > H > CH_3 >$ t-Bu

(*iii*). Keeping both the allyl function and the added olefin constant, and varying the metal:

allyl–Pt > allyl–Pd .

The concentration of the σ-allylic species (XIII) generated from different π-allylic precursors (I), as evidenced by the extent of *syn/anti*-collapse for the different allyls induced by a given olefin, parallels the facility with which insertion of the olefin occurs. This points to the probable intermediacy of a σ-allylic species in the insertion mechanism[1]. Furthermore the σ-allylic species (XIII) is expected to contain a *trans*-olefinic function, when generated from a π-1-*syn*-substituted π-allylic function[27,28]. The *trans*-geometry of such olefinic functions is retained in the products [*e.g.* (IIi, j), (IVi)].

Thus the free energy profile for the reaction may be depicted qualitatively as shown in Fig. 4. The reaction probably involves a four centre molecular addition

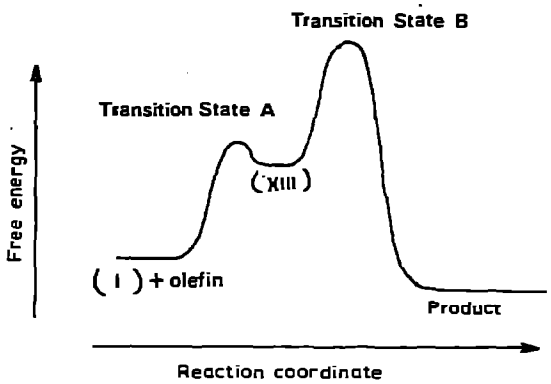


Fig. 4. Free energy profile for the insertion of bicyclic olefins into allylic palladium bonds via a σ-allylic intermediate (XIII).

with migration of the σ-bonded allylic carbon atom onto the coordinated olefin (transition state B).

The transition state B in Fig. 4 is presumably the same as that proposed by Cossee[29] for a typical olefin insertion into a transition-metal–carbon bond. Since this process is apparently first order in norbornene, and solvent independent, it is suggested that the σ-allylic olefinic function swings in to occupy the metal coordination site being vacated by the migrating carbon atom, in a concerted process. (A three-coordinate transition state appears energetically unreasonable).

The effect of remote substituents in bicyclic olefins on the rate and direction of addition of allylic–palladium bonds

The relative abilities of bicyclic olefins to effect on S_N2 substitution of the π-allyl ligand to yield (XIII) as given by the extent of collapse of *syn* and *anti* proton resonances induced by different olefins under standard conditions is probably a direct reflection of the coordinative abilities of the *exo*-face of these olefins towards palladium(II)[1,30]. The steric effect to approach on the *exo*-face of norbornene, norbornadiene, benzonorbornadiene, 2,3-bis(methoxycarbonyl)norbornadiene and complex (IV) should be constant. Thus any variations in the coordinative abilities of these olefins towards a given complex (I) must therefore stem from electronic or strain factors.

It is apparent (Fig. 2) that the extent of *syn–anti* collapse in the NMR spectrum of complex (Ib) induced by 0.5 molar equivalents of norbornadiene is approximately the same as that induced by 1 molar equivalent of either norbornene, 2,3-bis(methoxycarbonyl)norbornadiene* or complex (IVb), indicating the coordinative abilities of the unsubstituted olefinic functions in these compounds to be very similar. However there is a marked decrease in the coordinative ability of benzonorbornadiene. This may conceivably be due to homoconjugative withdrawal of electron density from the olefinic function, or due to a difference in strain energies in this olefin.

* Coordination of 2,3-bis(methoxycarbonyl)norbornadiene to palladium is assumed at this stage to occur predominantly at the *exo*-face of the unsubstituted olefin, since this is the olefin which undergoes the insertion reaction.

The ease of formation of intermediate (XIII) using different bicyclic olefins does not parallel the rate of product formation. 2,3-Bis(methoxycarbonyl)norbornadiene, which generates a σ-allylic intermediate as well as norbornene and better than benzonorbornadiene, in fact reacts to give an insertion product more slowly than does benzonorbornadiene. This may be due to remote substituents affecting the energetics of transition state B (Fig. 4). Alternatively it may be that benzonorbornadiene has a greater free energy of activation for transition state A but a lower energy σ-allylic intermediate (XIII) than is the case with 2,3-bis(methoxycarbonyl)norbornadiene. Studies of the rates of formation of complexes (VIII) and (IX), and (V) and (VI) provide some support for the former explanation.

The reaction of 5,5-dimethyl-2-norbornene with complexes (I) yielded a 1/1 mixture of the two isomeric complexes (VIII) and (IX). However, reaction of two moles of complexes (I) with norbornadiene led to the formation of the two isomeric 2/1 adducts (V) and (VI), the former being preferred by a ratio of ca. 3.5–4/1. ^{1}H NMR studies of these latter reactions showed them to proceed via almost quantitative initial formation of the 1/1 adducts (IV). The olefinic bond in complexes (IV) is slightly deactivated relative to norbornene towards further reaction with complexes (I) (Table 7), although its ability to generate a σ-allylic species by interaction with (I) remains approximately the same as for norbornene (Fig. 2). Since complexes (IV) may be regarded as substituted norbornenes having a weakly electronegative 5-substituent, "Pd(Hfacac)", this observation parallels the behaviour of 2,3-bis(methoxycarbonyl)norbornadiene. It is also apparent that it must be the electronegative palladium substituent in complexes (IV) which determines the preferential direction of addition of another mole of complex (I) to the remaining bicyclic olefin function, since the alkyl substituent should have no effect in view of the results obtained using 5,5-dimethyl-2-norbornene.

The most plausible mechanistic pathway therefore must proceed via a transition state involving a small degree of charge separation, as depicted for norbornene insertion in Fig. 5. The induced $\delta-$ charge is best accommodated on the Pd, and would

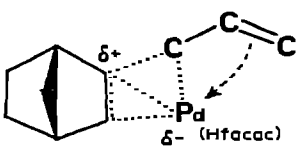
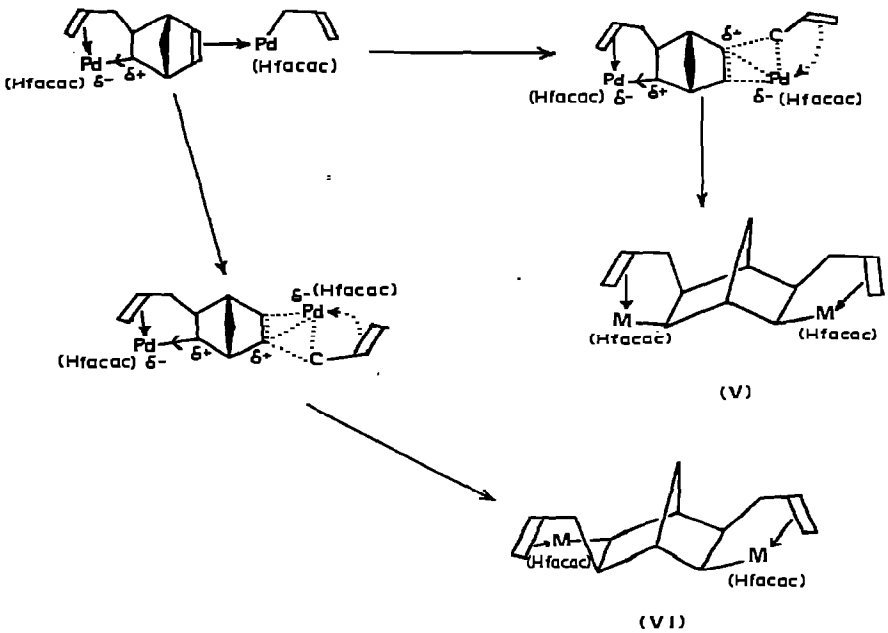


Fig. 5. Transition state for σ-allyl migration to a coordinated π-norbornene ligand. (Transition state B, Fig. 4.)

be stabilised by the electronegative Hfacac ligand. However it can be seen that introduction of electron-withdrawing groups within the norbornane skeleton would be expected to destabilise any $\delta+$ charge build up on a carbon atom within that framework. Scheme 2 depicts the proposed mechanism for preferential formation of isomer (V) over isomer (VI) in the reaction of complexes (IV) with a further mole of complexes (I). It should be noted that any charge separation in the transition states is probably small, since there is only a small preference for formation of (V) relative to (VI). However, transition state (XV) should be more energetically favourable than (XVI) since in the former case the two $\delta+$ charges in the norbornane skeleton are

SCHEME 2



further apart. Both transition states (XV) and (XVI) should be energetically less favourable than that depicted in Fig. 5. A similar polarization of the olefin–Pd bonding has been postulated to account for the relative reactivities of various 1,2-dienes towards insertion into the allyl–Pd bond of complexes (I)[31]. Remote electronegative substituents in bicyclic olefins also retard the rate of oxymercuration[20,32–35].

The increased reactivity of the platinum complex (Ia)* towards insertion relative to its palladium analogue (Ib) was initially surprising since ligand substitution reactions at Pt^{II} are generally several orders of magnitude slower than analogous reactions of Pd^{II}[37]. Indeed the extent of *syn–anti* collapse in the NMR spectrum of allylPt(Hfacac) induced by cyclopentene was found to be less than that for allylPd-(Hfacac) under identical conditions *i.e.* formation of a σ-allylic intermediate such as (XIII) is kinetically less favoured when M = Pt compared to when M = Pd. However the known organometallic chemistry of Pt^{II} compared to Pd^{II}[38] suggests that a σ-allylic(π-olefinic) Pt^{II} species analogous to (XIII) may have a considerably greater thermodynamic stability than its palladium analogue. Thus it is possible that the intermediate (XIII) (M = Pt), although kinetically less accessible than (XIII) (M = Pd), may have a considerably longer lifetime, with the result that the overall rate of product formation is greater for M = Pt than for M = Pd.

CONCLUSION

Coordination of an olefin to an allylic–palladium complex occurs readily and

* In $CDCl_3$ solution allyl(hexafluoroacetylacetonato)platinum(II) consists of a mixture of a π-allylic monomer of structure (Ia) and a μ-allyl dimer[36].

reversibly to generate a short-lived σ-allylic intermediate. Reaction of this intermediate occurs via a four-centre *cis*-addition to give the product. Introduction of substituents remote from the reaction site on the olefin can affect both the rate and direction of insertion. Our studies suggest that this electronic effect operates through a polarization of charge density on the olefinic carbon ($\delta+$) and palladium atom ($\delta-$) during migration of the σ-allyl group to the coordinated olefin. Strain in monoolefins is apparently a key factor in promoting their insertion into allyl–Pd bonds.

It is probable that similar rate-determining factors are operating in the oxy mercuration reactions of norbornenes.

EXPERIMENTAL

Instrumentation

NMR spectra were recorded on Varian A56/60D and HA100 instruments. Mass spectra were recorded on a Bell and Howell Model 21-490 spectrometer at an ionization energy of 70 eV. Melting points were determined on a Kofler hot-stage apparatus and are corrected.

Starting materials

Bicyclo[2,2,1]heptene, bicyclo[2,2,1]heptadiene and bicyclo[2,2,2]octene were commercial samples and were used without further purification. 2,3-Bis(methoxycarbonyl)bicyclo[2.2.1]heptadiene was prepared by the method of Diels and Alder[39]. We are grateful to Dr. R. Blattel for a sample of 5,5-dimethylbicyclo[2.2.1]-heptene and Dr. D. N. Butler for a sample of benzonorbornadiene.

π-Allylic–palladium chloride complexes were prepared by the method of Dent, Long, and Wilkinson[40], or by the method of Volger[41]. Conversion of the π-allylic–palladium chlorides to their hexafluoroacetylacetonates was achieved by either of two previously reported procedures[1].

Reactions of bicyclic olefins with allylic–palladium and –platinum hexafluoroacetylacetonate complexes

Complex (IIa). A solution of (1,1,1,5,5,5-hexafluoropentane-2,4-dionato)-allylplatinum(II) (0.452 g) in dichloromethane (1 ml) was treated with bicyclo[2.2.1]-heptene (0.096 g) and left to stand (2 h). The resultant solution was passed through a Florisil column (5 cm × 1 cm), eluting with dichloromethane. Evaporation of the eluate under reduced pressure yielded the *product* as golden yellow prisms (0.395 g; 72%), m.p. 144–146°. Recrystallisation from petroleum ether (b.p. 30–60°) yielded an analytical sample. (Found: C, 33.65; H, 3.21. $C_{15}H_{16}F_6O_2Pt$ calcd.: C, 33.54; H, 3.00%.)

The complexes (IIb–n), (IIIa–d, n), (IVa–d, i), (VII), (VIIIb, d) and (IXb, d) (isolated as inseparable 1/1 mixtures) and (X) were prepared in a manner similar to that used to synthesize (IIa). Reaction times varied from 2–48 h. depending on the reactivity of the added olefin and π-allylic ligand.

Complexes (Vc) and (VIc). A solution of (1,1,1,5,5,5-hexafluoropentane-2,4-dionato)-π-(2-methylallyl)palladium(II) (0.910 g) in dichloromethane (1 ml) was treated with bicyclo[2.2.1]heptadiene (125 μl), allowed to stand (24 h), and evaporated to dryness under reduced pressure. Recrystallisation of the residue from

dichloromethane (5 ml) at −30°, afforded complex (VIc), as yellow prisms (0.210 g; 20.5%), m.p. 260–262° (dec.). Evaporation of the mother liquor to dryness yielded complex (Vc), as yellow prisms (0.792 g; 79%), m.p. 205–210° (dec.). (Found: C, 36.24; H, 3.08. $C_{25}H_{24}F_{12}O_4Pd_2$ calcd.: C, 36.21; H, 2.92%.)

An analogous procedure yielded complex (VId), as yellow prisms (0.235 g; 20%), dec. 230–235°, and complex (Vd), as yellow prisms (0.812 g; 77%), dec. 185–190°, from (1,1,1,5,5,5-hexafluoropentane-2,4-dionato)-π-(2-chloroallyl)palladium-(II) (1.040 g) and bicyclo[2.2.1]heptadiene (136 μl).

(Found: C, 34.49; H, 2.29. $C_{23}H_{18}Cl_2F_{12}O_4Pd_2$ calcd.: C, 34.57; H, 2.27%.)

An analogous procedure using (1,1,1,5,5,5-hexafluoropentane-2,4-dionato)-π-allylpalladium(II) (0.92 g) and bicyclo[2.2.1]heptadiene (130 μl) yielded, on crystallisation from dichloromethane (5 ml; −30°), a crop of yellow solid (A) (0.084 g), dec. 215–220°. Evaporation of the mother liquor yielded a yellow solid (B) (0.887 g). Solid (A) was shown by its ^{1}H NMR spectrum to be pure complex (VIb). The ^{1}H NMR spectrum of solid (B) showed it to consist of a 1/7 mixture of (A) and complex (Vb), respectively. (Found: C, 34.65; H, 2.78. $C_{23}H_{20}F_{12}O_4Pd_2$ calcd.: C, 34.47; H, 2.52%.)

Monitoring of reaction rates

NMR tubes were precalibrated to a volume of 0.40 ml, and standard solutions of π-allylic–palladium complexes (0.82 *M*) were prepared by dissolving the appropriate weight of complex in this volume of $CDCl_3$ or C_6D_6. One molar equivalent of olefin was injected with a syringe, the tube was capped, shaken vigorously and quickly placed in the probe. The ^{1}H NMR spectrum was recorded and carefully integrated at intervals of time.

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REFERENCES

1 R. P. Hughes and J. Powell, *J. Amer. Chem. Soc.*, 94 (1972) 7723.
2 R. P. Hughes and J. Powell, *J. Chem. Soc. D*, (1971) 275.
3 R. P. Hughes and J. Powell, *J. Organometal. Chem.*, 30 (1971) C45.
4 P. Laszlo and P. von R. Schleyer, *J. Amer. Chem. Soc.*, 86 (1964) 1171.
5 E. I. Snyder and B. Franzus, *J. Amer. Chem. Soc.*, 86 (1964) 1166.
6 P. Laszlo and P. von R. Schleyer, *J. Amer. Chem. Soc.*, 85 (1963) 2709.
7 K. Tori, K. Aono, Y. Hata, R. Muneyuki, T. Tsuji, and H. Tanida, *Tetrahedron Lett.*, (1966) 9.
8 A. P. Marchand and J. E. Rose, *J. Amer. Chem. Soc.*, 90 (1968) 3724.
9 B. Franzus, W. C. Baird, Jr., N. F. Chamberlain, T. Hines and E. I. Snyder, *J. Amer. Chem. Soc.*, 90 (1968) 3721.
10 J. C. Davis, Jr. and T. V. Van Auken, *J. Amer. Chem. Soc.*, 87 (1965) 3900.
11 K. Tori, R. Muneyuki and H. Tanida, *Can. J. Chem.*, 41 (1963) 3142.
12 K. Tori, Y. Hata, R. Muneyuki, Y. Takano, T. Tsuji and H. Tanida, *Can. J. Chem.*, 42 (1964) 926.
13 J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "*High Resolution Nuclear Magnetic Resonance Spectroscopy*", Vols. 1 and 2, Pergamon Press, New York, N.Y., 1968.
14 M. C. Gallazzi, T. L. Hanlon, G. Vitulli, and L. Porri, *J. Organometal. Chem.*, 33 (1971) C45.

15 M. Zocchi, G. Tieghi, and A. Albinato, *J. Organometal. Chem.*, 33 (1971) C47.
16 A. L. Clobes, M. L. Morris and R. D. Koob, *J. Amer. Chem. Soc.*, 91 (1969) 3087.
17 C. Reichert, G. M. Bancroft and J. B. Westmore, *Can. J. Chem.*, 48 (1970) 1362.
18 T. Goto, A. Tatematsu, Y. Hata, R. Muneyuki, H. Tanida, and K. Tori, *Tetrahedron Lett.*, 22 (1966) 2213.
19 H. C. Brown, *Chem. Brit.*, (1966) 199.
20 T. G. Traylor, *Accounts Chem. Res.*, 2 (1969) 152.
21 N. C. Baenziger, H. L. Haight and J. R. Doyle, *Inorg. Chem.*, 3 (1964) 1535.
22 N. C. Baenziger, H. L. Haight, R. Alexander and J. R. Doyle, *Inorg. Chem.*, 5 (1966) 1399.
23 B. Granoff and R. A. Jacobson, *Inorg. Chem.*, 7 (1968) 2328.
24 W. E. Fichteman and M. Orchin, *J. Org. Chem.*, 34 (1969) 2790.
25 J. Powell, *J. Chem. Soc. A*, (1971) 2233.
26 A. Chan and J. Powell, *J. Organometal. Chem.*, 35 (1972) 203.
27 J. W. Faller, M. E. Thomson and M. J. Mattina, *J. Amer. Chem. Soc.*, 93 (1971) 2642.
28 J. W. Faller and M. E. Thomson, *J. Amer. Chem. Soc.*, 91 (1969) 6871.
29 P. Cossee, *Rec. Trav. Chim. Pays-Bas*, 85 (1966) 1161.
30 R. P. Hughes and J. Powell, *J. Organometal. Chem.*, 34 (1972) C51.
31 R. P. Hughes and J. Powell, *J. Organometal. Chem.*, 60 (1973) 409.
32 T. G. Traylor and A. W. Baker, *Tetrahedron Lett.*, (1959) 14.
33 T. G. Traylor and A. W. Baker, *J. Amer. Chem. Soc.*, 85 (1963) 2746.
34 A. Factor and T. G. Traylor, *J. Org. Chem.*, 33 (1968) 2607.
35 T. G. Traylor, unpublished observations quoted in ref. 21.
36 R. P. Hughes and J. Powell, *J. Organometal. Chem.*, 55 (1973) C45.
37 F. Basolo and R. G. Pearson, "*Mechanisms of Inorganic Reactions*", 2nd Ed., Wiley, New York, N.Y., 1967, Chapter V.
38 P. M. Maitlis, "*The Organic Chemistry of Palladium*", Vol. I, Academic Press, New York, N.Y., 1971.
39 O. Diels and K. Alder, *Justus Liebigs Ann. Chem.*, 490 (1931) 236.
40 W. T. Dent, R. Long and A. J. Wilkinson, *J. Chem. Soc.*, (1964) 1585.
41 H. C. Volger, *Rec. Trav. Chim. Pays-Bas*, 88 (1969) 225.