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TRANSITION METAL-PROMOTED REACTIONS OF UNSATURATED HYDROCARBONS

IV*. REACTIONS OF NORBORNENYL COMPLEXES OF PALLADIUM(II) WITH GROUP V DONOR LIGANDS, OLEFINS, 1,3-DIENES AND 1,2-DIENES

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Summary

6-Acetoxynorbornenylpalladium-hexafluoroacetylacetonate and -benzoyltrifluoroacetonate complexes (I) react with neutral donor ligands containing Group V atoms to yield 5-acetoxynortricyclenylpalladium complexes. Reactions of (I) with mono-olefins or 1,3-dienes produce analogous nortricyclenyl complexes containing a coordinated olefinic ligand, which are in equilibtrium with the starting materials. The role of steric and electronic factors in the olefinic ligand in determining the equilibrium constant in these systems has been evaluated. Reactions of (I) with 1,2-dienes at —10° generate σ-nortricyclenyl (π-1,2-diene) palladium complexes which rapidly rearrange above 0° to yield new 2-(5'-acetoxynortricyclenyl)allyl complexes of palladium(II). A comparison of these reactions to the known interactions of allylic palladium complexes with olefins, 1,3-dienes, and 1,2-dienes is presented.

Introduction

Reaction of the norbornenyl complexes (I) [Y = OMe, OAc; X = Cl, OAc] with a variety of donor ligands to yield σ-nortricyclenyl complexes has been demonstrated by a number of authors [1-6]. Consideration of a π—σ enyl bonding model for norbornenyl complexes has led to the proposal [2] that the ring-closure reaction observed in the carbon skeleton might be regarded as an "internal insertion" of the coordinated olefin into the metal—carbon σ-bond. An alternative representation of these reactions would be in terms of a π-homoallyl/σ-homoallyl system. Recent ^{1}H and ^{13}C NMR studies of complexes (I) have shown the norbornenyl ligand to be considerably distorted relative to a simple

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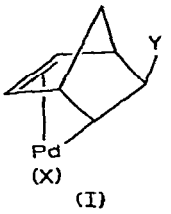
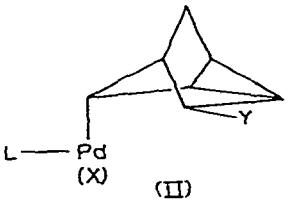
SCHEME 1.



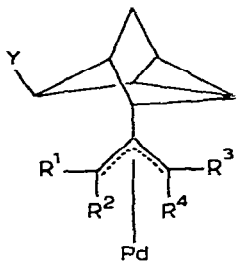
(I)

(Ia), Y = OAc; X = hfacac
(Ib), Y = OAc; X = btfac
(Ic), Y = OMe; X = hfacac



(II)

(IIa), X = hfacac; L = pyridine
(IIb), X = hfacac; L = Ph_3P
(IIc), X = hfacac; L = $PhMe_2P$
(IId), X = hfacac; L = Ph_3Sb
(IIe), X = btfac ; L = pyridine
(IIf), X = btfac ; L = Ph_3P
(IIg), X = btfac ; L = Ph_3As



(III)

(IIIa), $R^1 = R^2 = R^3 = R^4 = H_4$; Y = OAc
(IIIb), $R^1 = CH_3$; $R^2 = R^3 = R^4 = H$; Y = OAc
(IIIc), $R^1 = R^2 = CH_3$; $R^3 = R^4 = H$; Y = OAc
(IIId), $R^1 = R^3 = CH_3$; $R^2 = R^4 = H$; Y = OAc
(IIIe), $R^1 = R^2 = R^3 = R^4 = CH_3$; Y = OAc
(IIIf), $R^1 = R^2 = R^3 = R^4 = H_4$ Y = OMe
(IIIg), $R^1 = R^2 = CH_3$; $R^3 = H$; Y = OMe

norbornene [7]. The nature of this distortion is consistent with the changes in conformation expected on going from a 'norbornenyl' to a 'homo-allyl' skeletal arrangement. Thus such systems could be considered analogous to the π-allyl/σ-allyl systems of palladium(II). However a recent X-ray structural study of di-μ-chloro-bis(*endo*-3-phenylnorbornen-2-yl-*endo*-palladium) has shown this molecule to have a ground state structure more typical of a π—σ enyl bonding mode rather than a π-homoallylic one [8]. Thus it is probable that the π-homoallylic mode of bonding is either a transition state or an intermediate in the conversion of norbornenyl complexes into nortricyclenyl derivatives. The major differences of the π-allyl/σ-allyl and the norbornenyl/nortricyclenyl systems lies in the stability of the σ-nortricyclenyl palladium species, and the absence of a double bond in the σ-nortricyclenyl species. In contrast to σ-nortricyclenyl complexes of palladium, σ-allylpalladium species cannot, in most cases be directly observed in solution [9].

We have investigated the reactions of the norbornenyl complexes (I) with a variety of neutral donor ligands to yield σ-nortricyclenyl complexes of palladium(II). The reactions of complexes (I) with hydrocarbon olefins and dienes have also been studied [10] and a comparison with previous studies [11—14] of the reactivity of allylic palladium complexes towards these hydrocarbons has been made.

Results and discussion

Reactions of norbornenyl palladium complexes with neutral donor ligands

Complexes (I) [X = hexafluoroacetylacetonate (hfacac); benzoyltrifluoroacetonate (btfac): Y = OAc] reacted readily with one molar equivalent of pyridine, Ph_3P, $PhMe_2P$, Ph_3As or Ph_3Sb in chloroform solution to yield complexes exhibiting ^1H NMR spectra characteristic of complete conversion to the σ-nortricyclenyl structure [2—6]. These complexes were thus formulated in terms of structure (II) (X = hfacac; btfac). ^1H NMR data for complexes (II) are presented in Table 1.

Complexes (IIa,e,f,g) were isolated as air stable yellow crystals and satisfactory microanalytical data were obtained. Complexes (IIb,c,d) however, could only be isolated from solutions as oils, which showed some tendency to decompose at room temperature, and as such microanalytical data could not be obtained.

The formulation of complexes (II) as nortricyclenylpalladium derivatives is further supported by ^{13}C NMR studies. The change observed in the ^{13}C NMR spectrum of complex (Ia) on addition of one mole of pyridine [to give (IIa)] is shown in Fig. 1. Of particular interest is the disappearance of the low field reso-

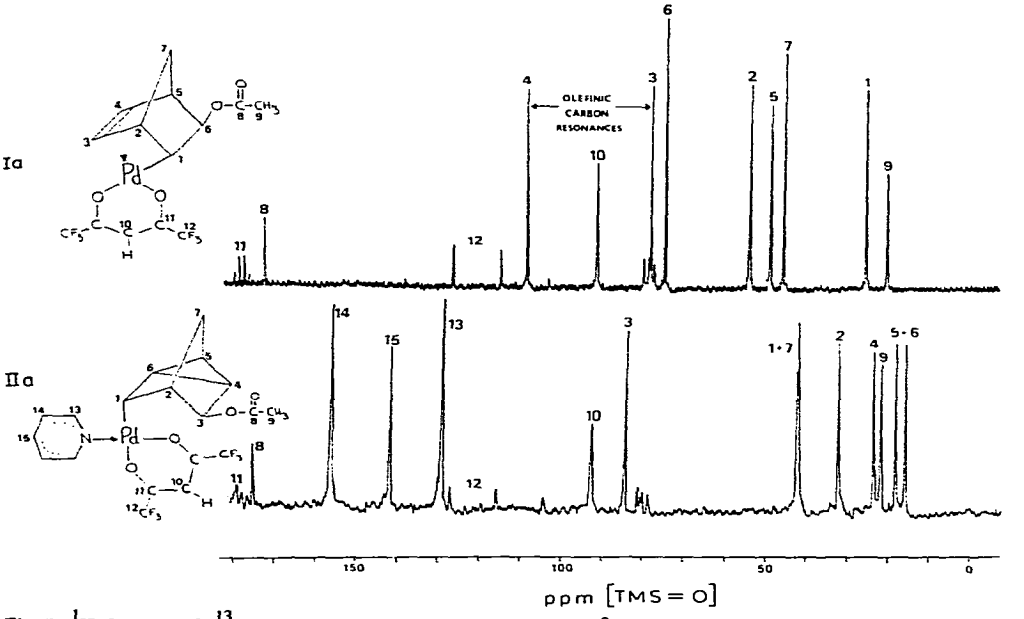
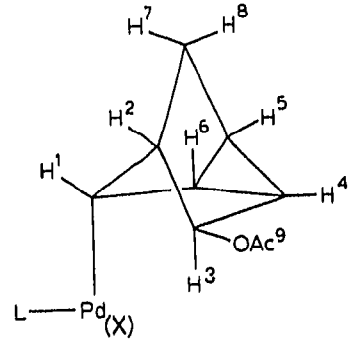


Fig. 1. ^1H-decoupled ^{13}C NMR spectra (25.2 MHz; $CDCl_3$; 34°) of the norbornenyl complex (Ia) and the nortricyclenyl complex (IIa).

TABLE 1

^{1}H NMR DATA FOR COMPLEXES (II)

[$CDCl_3$; 60 MHz; 34°]



Complex	X	L	τ (multiplicity)[a] J(Hz)						
			H^1	H^2	H^3	H^4 H^5 H^6 H^7 H^8	H^9	X	L
(IIa)	hfacac	pyridine	7.71 (bs)	7.90 (bs)	4.45 (bs)	8.2 - 8.8 (m)	8.00 (s)	3.98 (s)	1.5 - 2.7 (m)
(IIb)	hfacac	Ph_3P	8.0 - 8.3 (b)		4.65 (bs)	8.5 - 8.8 (4H,m) 9.33 (1H,d) J = 10	8.02 (s)	3.96 (s)	2.0 - 2.8 (m)
(IIc)	hfacac	$PhMe_2P$	7.95 (bs)	8.06 (bs)	4.44 (bs)	8.4 - 8.8 (m)	8.00 (s)	3.86 (s)	Ph 1.8 - 2.6 (m) Me[b] 8.17 (d) J(P—H) = 9 8.20 (d) J(P—H) = 9
(IId)	hfacac	Ph_3Sb	7.70 (bs)	8.10 (bs)	4.48 (bs)	8.4 - 9.2 (m)	8.03 (s)	3.91 (s)	2.2 - 2.7 (m)
(IIe)	btfac	pyridine	7.77 (bs)	7.90 (bs)	4.37 (bs)	8.3 - 8.8 (m)	8.00 (s)	3.60 (s) 2.50 (m)	1.5 - 2.7 (m)
(IIf)	btfac	Ph_3P	8.0 - 8.2 (b)		4.52 (bs)	8.4 - 8.8 (4H,m) 9.25 (1H,d) J = 10	8.04 (s)	3.60 (s) 2.50 (m)	2.0 - 2.8 (m)
(IIg)	btfac	Ph_3As	8.00 (bs)	8.24 (bs)	4.45 (bs)	8.4 - 9.2 (m)	8.10 (s)	3.60 (s) 2.50 (m)	2.0 - 2.8 (m)

[a] s, singlet; d, doublet; b, broad; m, multiplet. [b] The PMe_2Ph methyl groups are diastereotopic since the σ-nortricyclenyl ligand is chiral.

nances of the olefinic carbons C^3 and C^4 in the spectrum of (Ia) and the appearance of new resonances at high field in the region expected for a nortricyclene structure [15], in the spectrum of (IIa). An analogous situation occurs in the ^1H NMR spectrum of (Ia) (Y = OAc; X = hfacac) on addition of increasing amounts of Ph_3Sb (see Fig. 2). Disappearance of the resonances typical of complex (Ia) occurs, with generation of high field resonances [2—6] of complex (IId). It should be noted that the ^1H NMR spectrum obtained in this system at molar ratios of Ph_3Sb/Pd between 0 and 1 is therefore characteristic of a mixture of complex (I) and complex (II).

Reactions of norbornenyl palladium complexes with mono-olefins

The ^1H NMR spectra obtained upon addition of one molar equivalent of ethylene or styrene to a 0.82 *M* $CDCl_3$ solution of complex (Ia) at 34° are

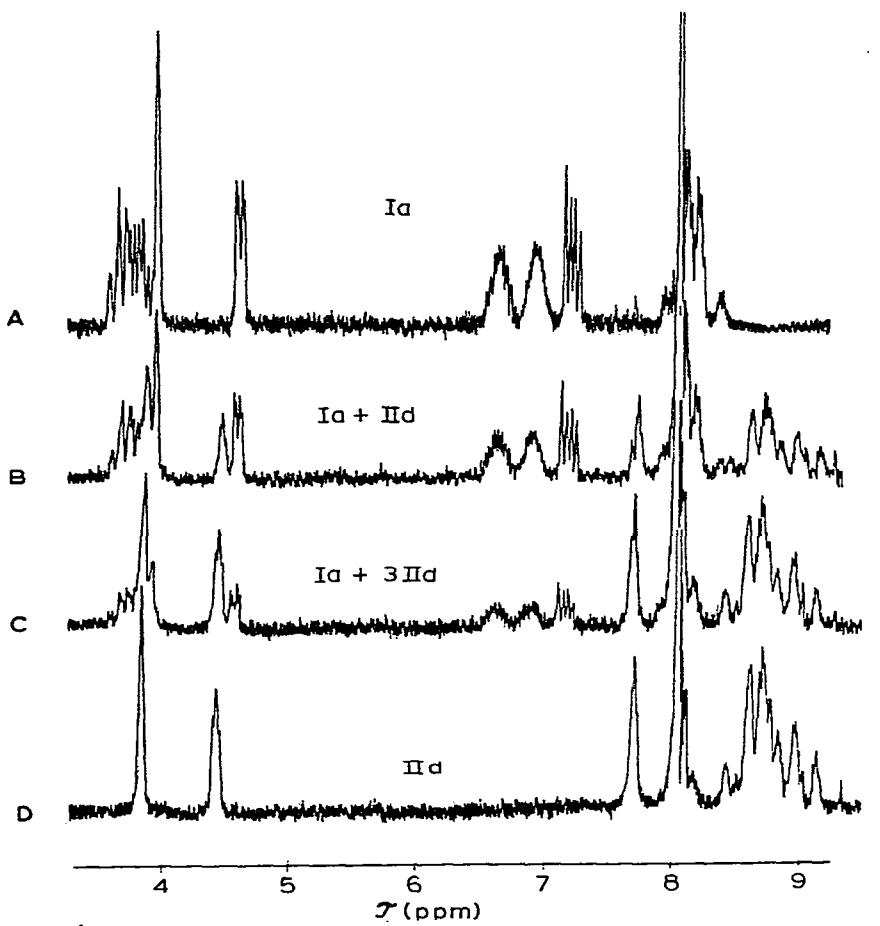


Fig. 2. ^1H NMR spectra [60 MHz; $CDCl_3$; 34°] obtained on adding increasing amounts of Ph_3Sb to a solution of complex (Ia), to yield as the final product (spectrum D), complex (IId): A, Ph_3Sb/Pd = 0; B, Ph_3Sb/Pd = 0.5; Ph_3Sb/Pd = 0.75; D, Ph_3Sb/Pd = 1.

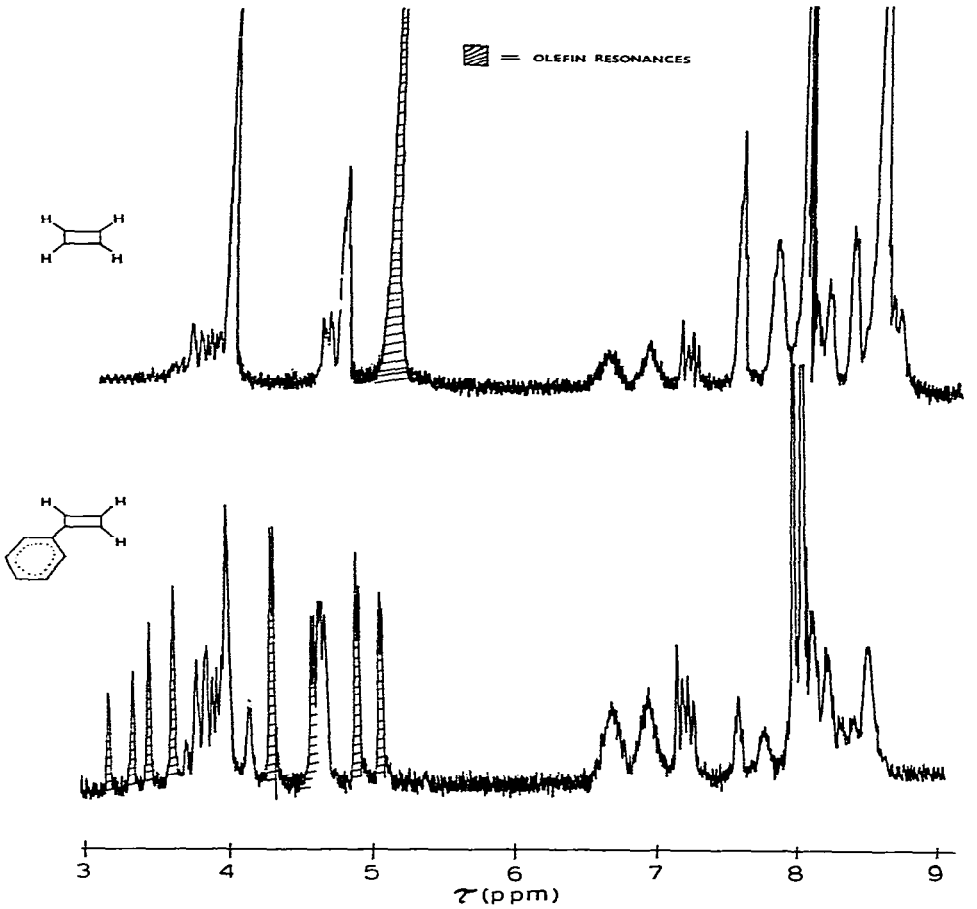
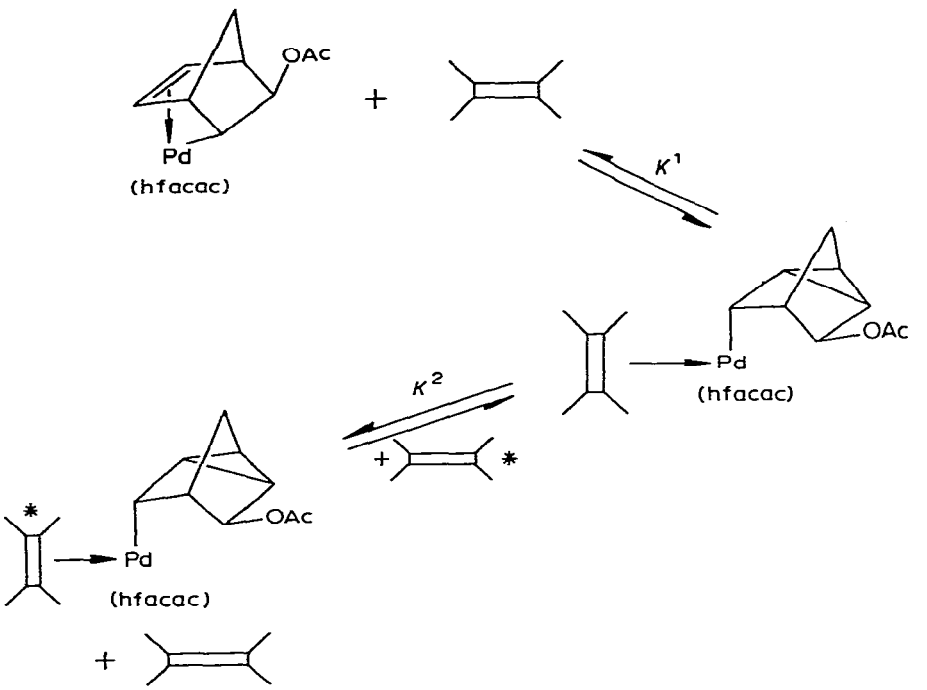


Fig. 3. ^{1}H NMR spectra [60 MHz; $CDCl_3$; 34°] obtained on addition of one molar equivalent of ethylene, or styrene, to a solution of complex (Ia) [0.82 *M*]. [Resonances of the added olefin are shaded. See Fig. 2A for spectrum of pure complex (Ia)].

shown in Fig. 3. The spectra are entirely compatible with the existence in solution of a mixture of complex (Ia) and a σ-nortricyclenyl complex by simple comparison to Fig. 2. The relative amount of the σ-nortricyclenyl complex formed as evidenced from relative peak intensities is dependent upon the structure of the added olefin. For example, one molar equivalent of added ethylene gives a spectrum consistent with appreciably more formation of a σ-nortricyclenyl complex than does styrene. The nortricyclenyl complexes could not be isolated from these solutions. Evaporation of the solution containing the added ethylene gave a virtually quantitative return (> 95%) of the norbornenyl complex (Ia). Thus the reaction in solution leading to formation of the σ-nortricyclenyl complex must be completely reversible.

SCHEME 2. Equilibria operating in a solution of complex (Ia) in the presence of an added olefin.



These results are compatible with the equilibria shown in Scheme 2, with formation of an σ-nortricyclenyl complex analogous to (II) (L = olefin). The equilibrium denoted by the equilibrium constant K^2 must be dynamic, (i.e. substitution of coordinated olefin by free olefin must be rapid on the NMR time scale) since resonances assignable to a coordinated olefin are not observed and no major chemical shift change in the resonance(s) of the added olefin (usually present in excess) is observed. Low temperature NMR studies of the interaction of ethylene with complex (Ia) indicated that this exchange process was still rapid at −60° *. The equilibrium denoted by K^1 however must be relatively static, since the NMR resonances of the π-norbornenyl palladium complex (Ia) and those of the σ-nortricyclenyl moiety are sharp and clearly defined. By integrating the spectrum obtained on addition of olefin, the absolute final concentrations of (Ia), the σ-nortricyclenyl complex, and the total olefin concentration can easily be calculated from the integration. Assuming that the σ-nortricyclenyl complex incorporates one molecule of coordinated olefin [i.e. it is analogous to (II) (L = olefin)], the concentration of *free olefin* in the system is obtained.

This represents a direct and simple method of measuring the relative coordinative abilities (i.e. K^1) of differently substituted olefins towards palladium(II) in a position *trans* to the hfacac ligand.

The equilibrium constants for a variety of mono-olefins calculated by this method are presented in Table 2.

* It has been shown that the coordinated ethylene molecules in $(C_2H_4)_2Rh(acac)$ are kinetically labile to substitution by traces of free ethylene even at −60° (see ref. 17 and 30).

TABLE 2

EQUILIBRIUM CONSTANTS (K^1) [$CDCl_3$; 34°] FOR THE REACTION OF COMPLEX (I) [0.82 *M*] AND OLEFIN[≈0.82 *M*] ⇌ COMPLEX (II) [L = OLEFIN]

Olefin	K^1		Olefin	K^1	
	X = hfacac	X = btfac		X = hfacac	X = btfac
CH_2=CH_2	33 ±3	27 ±3	Styrene	0.56±0.06[a]	0.55±0.05
CH_3CH=CH_2	4.42±0.4	4.46±0.4	*p*-Nitrostyrene	0.20±0.02	0.17±0.02
cis-CH_3CH=$CHCH_3$	3.93±0.3	3.67±0.3	*p*-Methoxystyrene	1.43±0.1	1.67±0.2
trans-CH_3CH=$CHCH_3$	0.29±0.03	0.32±0.03	*p*-Methylstyrene	0.66±0.06	—
$(CH_3)_2C$=CH_2	< 0.02	< 0.03	*p*-Fluorostyrene	0.45±0.04	0.52±0.05
n-BuCH=CH_2	6.91±0.7	4.98±1.0	*p*-Chlorostyrene	0.49±0.05	—
i-BuCH=CH_2	2.72±0.3	3.35±0.3	*p*-Bromostyrene	0.44±0.05	—
t-BuCH=CH_2	0.37±0.04	0.48±0.1	*p*-(Trimethylsilyl)-styrene	0.81±0.08	—
			p-N,N-Dimethyl-aminostyrene	4.19±0.4	3.95±0.4

[a] This value was found to be invariant over a range [0.4 - 1.0 *M*] of styrene concentrations.

Increasing methyl substitution on the added mono-olefin causes a significant reduction in the value of K^1 relative to that obtained for ethylene. In addition to the number of methyl groups, their relative positions on the olefin also play a significant role in determining the coordinative ability of the olefinic function. Thus the value of K^1 obtained for *cis*-2-butene (3.93) is significantly larger than that obtained for *trans*-2-butene (0.29), which in turn is significantly larger than that obtained for *iso*-butene (< 0.02) (Table 2). The equilibrium constants for a number of silver—olefin complexes have been determined by gas chromatography and show precisely the same trends regarding the effects of methyl substitution [16]. Cramer [17] has reported the relative stabilities of a number of olefin complexes of Rh^I and the same trend is again observed. However, in the latter case the equilibrium constants obtained for *cis*- and *trans*-2-butene are of the same order of magnitude. A rationale for the significantly different values for these olefins obtained in our system may lie in the extreme bulkiness of the σ-nortricyclenyl ligand in the position *cis* to the coordinated olefin. *cis*-2-Butene can coordinate to palladium in such a way that both methyl groups point away from the nortricyclenyl moiety. Coordination of *trans*-2-butene however must result in one methyl substituent on the olefin pointing towards the bulky *cis*-ligand with a resultant steric interaction.

For a series of monosubstituted olefins there is a decrease in the value of K^1 as the extent of branching in the olefin substituent is increased, as observed for the series n-Bu > i-Bu > t-Bu. This has again been noted in silver olefin complexes [16], and presumably reflects increased steric interactions at the olefin—metal coordination site.

*Electronic effects on thermodynamic parameters for coordination of para-substituted styrenes to palladium(II)**

In recent reviews [18] it has been concluded that the major factor determining the thermodynamic stabilities of olefin—Pt^{II} and —Pd^{II} bonds is the

* A preliminary account of these findings has been published, see ref. 31.

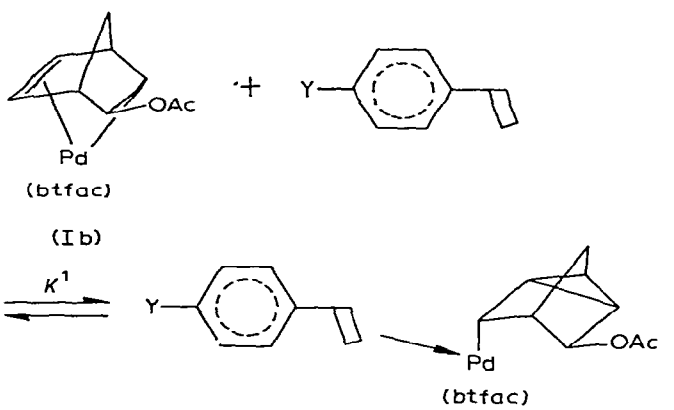
metal-d→olefin-π^* component of the Dewar—Chatt—Duncanson model. Studies of the effect of polar substituents on the enthalpy of formation of complexes $\{[CH_2{=}CH(CH_2)_n Q^+R'R''_2]PtX_3^-\}$(R', R'' = H, alkyl; Q = N,P,As; X = Cl,Br; n = 1,2) [19] have been interpreted in these terms, even though variations in n, Q, R' and R'' create a concommitant variation in steric factors close to the olefin—metal coordination site. A recent study of bond strengths [20] has led to the conclusion "that the Pd—N bond must have considerably more π-character than the Pd—olefin bond, a result that is unacceptable to the currently held view of metal ligand bonding in these compounds" [20]. Some reassessment of the thermodynamic significance of the metal-d→olefin-π^* component of Pd^{II}—olefin bonds is clearly indicated by the results presented below.

^{1}H NMR studies of the system:

[Ia or b] + p-$YC_6H_4CH{=}CH_2$ ⇌ (IIh) (X = hfacac or btfac; L = p-$YC_6H_4CH{=}CH_2$)

provide an extremely simple route to values of the equilibrium constant (K^1), see Scheme 3. For this system steric variations at the olefin—metal coordination site on changing the styrene substituent (Y) are expected to be negligible. $Log_{10}K^1$, at constant temperature (T), exhibits a linear dependence upon the σ_p^+ parameter [21] of Y (ρ = 0.54 at 34°) [see Fig. 4]. Plots of $\log_{10}K^1$ against $1/T$ are linear over the temperature range studied (T = 273 — 312°K). Variations in ΔG^o, ΔH^o and ΔS^o as a function of Y are presented in Table 3. There is a linear relationship between ΔH^o and ΔS^o.

SCHEME 3



btfac = benzoyltrifluoroacetonate (IIh)

The linear dependence of $\log_{10}K^1$ upon the σ_p^+ parameter of Y, rather than the Hammett σ_p value, indicates that resonance effects of Y are of importance in determining the value of K. The olefin-π→metal-d σ-bonding component must be of predominant importance in determining the thermodynamic stability of the olefin—Pd bond in (IIh) since the reaction becomes more exothermic as the π-donor ability of Y increases. The observed changes in ΔS^o on changing Y indicate an increased solvation requirement for (IIh) with increasing π-donor capability of Y. Increasing contributions from the ionic canonical forms shown in

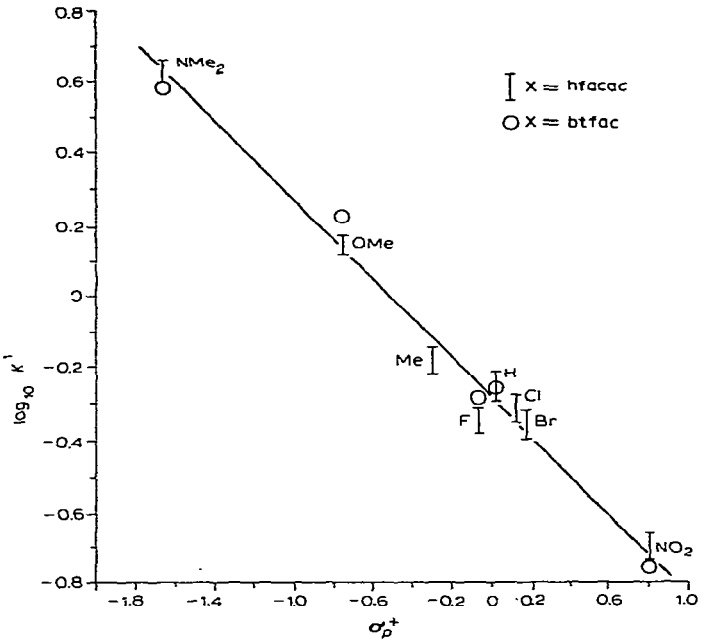


Fig. 4. Plot of $\log_{10} K^1$ for various *p*-substituted styrenes against the σ_p^+ parameter [21] of the *p*-substituent.

Scheme 4 (i.e. Pd closer to the terminal olefinic C atom) as the donor properties of Y increases provides a reasonable rationalization of this feature. Similar proposals provide a rationalization of the ^{13}C NMR and IR spectra of a series of styrene—Pt^{II} complexes [22]. An X-ray study of $[(PhCH{=}CH_2)PdCl_2]_2$ shows the terminal olefinic carbon C^1 to be closer to the coordination plane than C^2 (see Scheme 3) [23]. Similar trends in ΔH^0 and ΔS^0 have long been known for substituted styrene complexes of Ag^I [24]. If metal-*d*→olefin-π^* back bonding was of prime importance in complexes (IIh) a reverse trend to that observed would have been anticipated for the ΔH^0 and ΔG^0 values.

TABLE 3

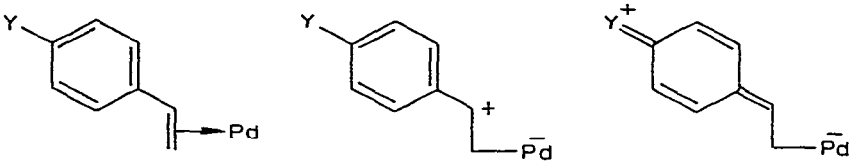
THERMODYNAMIC PARAMETERS OBTAINED FOR THE EQUILIBRIUM: COMPLEX (Ib) + *p*-$YC_6H_4CH{=}CH_2$ ⟷ COMPLEX (IIh)

[$CDCl_3$ solution; 273 - 312 K][a]

Y	ΔG^0 (kJ·mol^{-1})	ΔH^0 (kJ·mol^{-1})	ΔS^0 (J·deg.$^{-1}$·mol^{-1})
NO_2	3.3 ± 0.4	−11.7 ± 2	−50 ± 4
F	1.5 ± 0.4	−26.0 ± 2	−92 ± 4
H	1.0 ± 0.4	−27.8 ± 2	−96 ± 4
OCH_3	−1.0 ± 0.4	−33.0 ± 2	−105 ± 4
$N(CH_3)_2$	−4.5 ± 0.4	−43.1 ± 2	−126 ± 4

[a] $[(Ib)]_{initial} = [p\text{-}YC_6H_4CH{=}CH_2]_{initial} = 0.82\ M$; errors estimated from reproducibility of data for the equilibrium system with Y = H, varying the concentration range of the styrene from 0.40 - 1.00 *M*.

SCHEME 4. Canonical forms contributing to the styrene—palladium bond.



These results suggest that the π-acceptor properties of olefins may have been overemphasised in the interpretation of thermodynamic parameters. Supporting evidence for the dominance of the σ-donor properties of olefins has been recently obtained from ^{13}C NMR data [22,25], which indicate that the conclusions reached above should be equally applicable to olefin—Pt^{II} bonds since both Pd^{II} and Pt^{II} have comparable electronic requirements in their bonding to σ-carbon [25], π-olefinic [25,26], and π-allylic ligands [25].

There is however the possibility that steric factors between the aromatic ring and other coordinated ligands are sufficient to cause a considerable reduction in metal-*d*—olefin-π^* overlap with a consequent reduction in the importance of π-backbonding in these complexes. However in the complex $[(p\text{-}NO_2C_6H_4CH{=}CH_2)PtCl_2(NC_5H_4Me)]$ the ^{13}C NMR parameters and particularly $J(^{195}Pt—^{13}C)$ of the two olefinic carbons are very similar to one another suggesting a similarity of environment of the two olefinic carbons relative to the metal centre. This observation does not appear consistent with the above argument concerning steric factors. X-ray structural studies of the complexes $[(p\text{-}YC_6H_4CH{=}CH_2)PtCl_2(NC_5H_4Me)]$ (Y = NO_2, NMe_2) are currently in progress in order to elucidate the magnitude of the changes in conformation and bonding associated with changes in the *para*-substituent.

Reactions of norbornenylpalladium complexes with 1,3-dienes

In order to explain the relative rates of *syn-anti*-proton exchange observed in the ^1H NMR spectra of π-allylic palladium(II) complexes on addition of 1,3-dienes [13,14], it was necessary to propose [14] that preferential coordination of an unsymmetrically substituted 1,3-diene to palladium in the intermediate σ-allylic species must occur via the least substituted olefinic function. The observation that isoprene generated a σ-allylic species less readily, compared to butadiene or *cis*- or *trans*-piperylene, was attributed to a steric factor although it could not be distinguished whether this factor operated in the transition state leading to formation of the σ-allylic species (i.e. a kinetic effect), or whether it resulted in a lower thermodynamic stability of the σ-allylic species by steric destabilisation of the olefin—palladium bond in this moiety [14].

The values of K^1 obtained from the ^1H NMR spectra of the norbornenyl complex (Ia) in the presence of various 1,3-dienes are shown in Table 4. Comparison of these values with those obtained for mono-olefins (Table 2) reveals that the value of K^1 for butadiene (2.87) is significantly lower than that obtained for propene (4.42) and 1-hexene (6.91) even though butadiene contains twice as many monosubstituted olefinic functions per mole than does propene or hexene. Introduction of internal methyl substituents, as in 2,3-dimethylbutadiene, severly reduces the value of K^1. The values of K^1 observed for butadiene, *cis*-piperylene, and *trans*-piperylene are all of a similar magnitude, a feature

TABLE 4

EQUILIBRIUM CONSTANTS (K^1) [$CDCl_3$; 34°] FOR THE REACTION OF COMPLEX (I) [0.82 *M*] AND 1,3-DIENE [0.82 *M*] ⇌ COMPLEX (II) [L = 1,3-DIENE]

1,3-Diene	K^1	
	X = hfacac	X = btfac
Butadiene	2.87 ± 0.3	2.92 ± 0.3
trans-Piperylene	3.42 ± 0.3	2.76 ± 0.4
cis-Piperylene	2.32 ± 0.3	2.66 ± 0.3
Isoprene	0.16 ± 0.01	0.17 ± 0.01
2,3-Dimethylbutadiene	< 0.02	—

which can only be explained by monodentate coordination of these 1,3-dienes via their least substituted olefinic functions. An X-ray structural study of the complex [(4-methylpenta-1,3-diene)$_2$RhCl]$_2$ has shown the 1,3-diene to be functioning as a monodentate ligand coordinated to rhodium via its less substituted double bond [27]. A significantly lower value of K^1 is observed for isoprene, compared to butadiene or the piperylenes. It has been demonstrated above that increased branching of a substitutent close to the olefinic coordination site results in a lower K^1 for mono-olefins. Considering the least substituted olefinic function of isoprene as the coordinating olefin, the lower value of K^1 observed for this olefin can also be rationalised in terms of branching [i.e. a $-C(CH_3)=CH_2$ substituent in isoprene compared to a $-CH=CH(CH_3)$ substituent in the piperylenes].

The same trends in the values of K^1 for 1,3-dienes are also found in the argentation constants [16].

The values of K^1 obtained for various 1,3-dienes in the norbornenyl/nortricyclenyl system parallel their ability to generate a σ-allylic intermediate in their reactions with π-allylic complexes of palladium(II) [14]. Since the K^1 values reflect the thermodynamic stability of the coordinated olefin (or 1,3-diene) complex it is therefore apparent that differences in the rate of *syn-/anti*-proton exchange induced by the different 1,3-dienes in the ^{1}H NMR spectra of allylic—palladium complexes are due to changes in the thermodynamic stability of the σ-allylic intermediate rather than to stabilisation or destabilisation of the transition state leading to that intermediate. The above results therefore justify the use [13,14] of the extent of the *syn-/anti*-proton collapse in a particular allyl/unsaturated hydrocarbon system as a qualitative measure of the concentration of a given σ-allylic intermediate.

Complex (II) [L = olefin] is structurally analogous to the short-lived σ-allylic species generated in the π-allylic—palladium(II)—olefin systems [12—14]. As with σ-allyl(π-olefin)palladium complexes [12], no further reaction of complex (II) [L = olefin] was observed. In contrast to the allylic—palladium—1,3-diene system [13,14], where insertion of the 1,3-diene into the allyl—Pd bond occurs readily, no further reaction of complex (II) (L = 1,3-diene) was observed over a period of seven days at 34°.

In view of the proposed "[π4 + π2 + σ2] electrocyclic mechanism" for insertion of 1,3-dienes into the allyl—palladium bond [14], this latter observation is not surprising since the σ-nortricyclenyl moiety in complex (II) (L = 1,3-

diene), in contrast to a σ-allylic moiety, does not incorporate the allylic olefin function which is required for the [π4 + π2 + σ2] electrocyclic mechanism. Thus the non-reactivity of complex (II) (L = 1,3-diene) towards insertion is consistent with the proposed mechanism for the insertion of 1,3-dienes into the allyl—palladium bond [14].

Reaction of π-homoallylic complexes of palladium(II) with 1,2-dienes, and bicyclic olefins

Those reactions of σ-allylic complexes which have been postulated to proceed via a direct migration of the σ-bonded carbon to a coordinated olefinic function [11--14] should be paralleled by the σ-nortricyclenyl system. To test this postulate the reactions of strained bicyclic olefins and 1,2-dienes with complexes (Ia,c) were therefore examined.

Reaction of complex (Ia) with norbornadiene in $CDCl_3$ at 34° as monitored by ^1H NMR spectroscopy, showed rapid disappearance of the olefinic proton resonances both of complex (Ia) and the diene, with generation of new resonances at high field. Evaporation of the solution yielded a polymeric gelatinous material which was not characterised further. Presumably insertion of norbornadiene into the σ-nortricyclenyl—palladium bond occurs readily, and since the product derived from this insertion contains no olefin capable of chelating the metal (in contrast to insertion of norbornadiene into the allyl—palladium bond) [12,28,29], a vacant coordination site is generated which presumably leads to further, consecutive insertions of norbornadiene.

Reaction of complexes (Ia,c) with allene, 1-methylallene, 1,1-dimethylallene or 1,3-dimethylallene on a 1/1 molar basis, occurred rapidly (< 10 min in $CDCl_3$ solution) in an NMR tube, to yield complexes (III) (Scheme 1), derived from insertion of the 1,2-diene into a σ-nortricyclenyl—palladium bond [10]. Low temperature ^1H NMR studies of the reaction indicated that formation of a complex (II) (L = 1,2-diene) was essentially quantitative at —10°. The relative coordinative abilities of the various 1,2-dienes could therefore not be determined. However, they must all be significantly better coordinating ligands than any of the mono-olefins or 1,3-dienes examined above. This is in contrast to the silver(I)-system, where the argentation constant of allene is much lower than those of ethylene or butadiene [16].

Similarly the relative rates of insertion of the 1,2-dienes could not be accurately monitored in the NMR tube since the reaction was too fast to follow by integration of the NMR spectrum. Tetramethylallene, which showed no observable formation of a complex (II) (L = tetramethylallene) at 34°, did insert slowly over a period of 24 h to yield an analogous product (IIIe). 1,3-Di-tert-butylallene showed no tendency to insert over a period of one week at 34°.

The enhanced rate of insertion of 1,2-dienes in this system compared to allene insertion into the allyl—palladium bond can be rationalised in terms of a greater concentration of complex (II) (L = 1,2-diene) compared to a σ-allylic analogue [13,14].

Complexes (III) were characterised by their ^1H NMR spectra (Table 5), and by the mass spectra of representative complexes (Table 6), together with microanalytical data. The ^1H NMR spectra of complexes (IIIa) and (IIIf) show four anisochronous resonances for the four protons of the π-allylic system. (The nor-

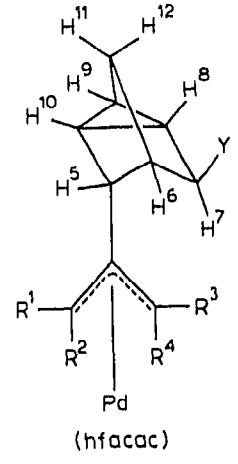


TABLE 5

^{1}H NMR DATA FOR COMPLEXES (III)

[60MHz; $CDCl_3$; 34°]

Complex	Substituents					τ (multiplicity)[a]; J(Hz)									
	R^1	R^2	R^3	R^4	Y	H^1	H^2	H^3	H^4	H^5	H^6	H^7	$H^8H^9H^{10}H^{11}H^{12}$	Y	hfacac
(IIIa)	H	H	H	H	OAc	5.83(d) $J_{1,3}$ 3	7.00(s)	6.05(d) $J_{1,3}$ 3	7.05(s)	7.30(bs)	7.91(bs)	4.97(bs)	8.3-8.7(4H,m) 7.97(1H,d); J 10	8.00(s)	3.92(s)
(IIIb)	CH_3	H	H	H	OAc	8.72(d) $J_{1,2}$ 7	6.22(q) $J_{1,2}$ 7	5.87(s)	7.22(s)	6.99(bs)	7.87(bs)	5.05(bs)	8.3-8.8(4H,m) ≈7.9[b](1H)	7.97(s)	3.95(s)
(IIIc)	CH_3	CH_3	H	H	OAc	8.59(s)	8.73(s)	5.85(d) $J_{3,4}$ 1	6.70(d) $J_{3,4}$ 1	6.98(bs)	7.92(bs)	5.11(bs)	8.3-8.8(4H,m) ≈7.9[b](1H)	7.97(s)	3.97(s)
(IIId)	CH_3[c]	H[c]	CH_3[c]	H[c]	OAc	8.65(d) $J_{1,2}$ 7	5.12(q) $J_{1,2}$ 7	8.89(d) $J_{1,2}$ 7	5.77(q)	6.99(bs)	7.89(bs)	5.18(bs)	8.3-8.8(4H,m) ≈7.9[b](1H)	7.97(s)	3.97(s)
(IIIe)	CH_3	CH_3	CH_3	CH_3	OAc	8.21(s)[d]	8.33(s)[d]	8.29(s)[d]	8.40(s)[d]	6.76(bs)	7.74(bs)	5.23(bs)	8.3-8.8(4H,m) ≈7.9[b](1H)	7.96(s)	4.01(s)
(IIIf)	H	H	H	H	OMe	5.85(d) $J_{1,3}$ 2.5	7.00(s)	6.03(d) $J_{1,3}$ 2.5	7.03(s)	7.30(bs)	8.05(bs)	6.08(bs)	8.4-8.8(4H,m) 7.85(1H,d) J 9	6.71(s)	3.93(s)
(IIIg)	CH_3	CH_3	H	H	OMe	8.63(s)	8.78(s)	5.95(bs)	6.81(bs)	7.07(bs)	8.05(bs)	6.39(bs)	8.4-8.8(4H,m) 7.9[e](1H)	6.70(s)	4.01(s)

[a]Notation: s, singlet; d, doublet; q, quartet; b, broad. [b]Obscured by Y resonance. [c]The allyl substitution pattern (*syn,syn*; *syn,anti*; *anti,anti*) is unknown in this complex. Hence the assignments as shown may be subject to change. [d]The individual assignment of each methyl resonance is not definite. [e]Obscured by H^6 resonance.

TABLE 6

MASS SPECTRAL DATA FOR COMPLEXES (III)

Complex	Ion (assignment (m/e)[a] [% abundance relative to CF_3^+ = 100%])
(IIIa)	P^+ (504) [31]; P—hfacac$^+$ (297) [200]; $C_3H_5Pd^+$ (147) [54]; P—hfacac—Pd—AcOH$^+$ (131) [19]; Pd^+ (106) [58]
(IIIe)	P^+ (560) [0.7]; P—hfacacH$^+$ (352) [73]; P—hfacac—Pd^+ (246) [16]
(IIIf)	P^+ (476) [11]; P—hfacac$^+$ (269) [89]; P—hfacac—Pd^+ (163) [790]; $C_3H_5Pd^+$ (147) [100]; P—hfacac—Pd—MeOH$^+$ (131) [113]; Pd^+ (106) [111]
(IIIg)	P^+ (504) [1.5]; P—hfacac$^+$ (297) [26]; P—hfacac—Pd^+ (191) [98]

[a] All m/e values for palladium containing species are quoted for the ^{106}Pd peak.

tricyclenyl substituent in these complexes is a chiral group and thus all four allylic protons are diastereotopic). A problem arises in assigning the total geometry of complex (IIId), derived from insertion of 1,3-dimethylallene, since there appears to be no unambiguous way of distinguishing between a *syn,syn*-, *syn,anti*-, or an *anti,anti*-configuration for the two methyl groups. Two doublet methyl resonances are observed, together with two quartet resonances for the remaining two π-allylic protons. Any of the three possible methyl group configurations could give rise to the observed spectrum because of the asymmetry of the 2-nortricyclenyl substituent. The resonances of the nortricyclenyl moiety were assigned by comparison with complexes (IIa,b,c,d) and with literature data [2—6].

Conclusions

Those insertion reactions of σ-allylic—palladium species which have been postulated to proceed via a direct carbon migration to a coordinated olefin [11—13] find a parallel in the reactions of the analogous σ-nortricyclenyl—palladium species. However, the insertion of 1,3-dienes into allylic—palladium bonds, which has been proposed to occur via an electrocyclic mechanism with participation by the σ-allylic olefin function [14], does not find a parallel in the σ-nortricyclenyl system. The results presented above therefore constitute strong supporting evidence for the mechanisms put forward for the insertion of unsaturated hydrocarbons into allylic—palladium bonds.

The data pertaining to the relative coordinative ability of *para*-substituted styrenes towards palladium(II) suggest that the role of π-acceptor properties of hydrocarbon olefins has been overemphasized in the interpretation of thermodynamic parameters.

Experimental

Instrumentation

^1H NMR spectra were run on a Varian Associates A56/60D spectrometer, ^{13}C NMR spectra were recorded on a Varian XL100-15 spectrometer operating in the fourier transform mode. Mass spectra were recorded on a Bell and Howell Model 21-490 instrument at an ionisation energy of 70 eV.

Complexes (I)

1,1,1,5,5,5-Hexafluoropentane-2,4-dionato-2,3-π-5-*endo*-σ-(6-*exo*-acetoxybicyclo[2.2.1]heptenyl)palladium(II) and 1,1,1,5,5,5-Hexafluoropentane-2,4-dionato-2,3-π-5-*endo*-σ-(6-*exo*-methoxybicyclo[2.2.1]heptenyl)palladium(II) were prepared by previously reported methods [7].

Benzoyltrifluoroacetonato-2,3-π-5-endo-σ-(6-exo-acetoxybicyclo[2.2.1]-heptenyl)palladium(II). A suspension of dichloro(norbornadiene)palladium(II) (2.15 g) in anhydrous diethyl ether (50 ml) was stirred with 2 molar equivalents of silver acetate (2.69 g) for 1 h. The silver chloride formed was filtered and benzoyltrifluoroacetone (1.73 g) was added to the resultant yellow solution. Evaporation of the solvent at reduced pressure gave a yellow solid. Recrystallization from dichloromethane/light petroleum (b.p. 30-60°) gave the product as yellow prisms (3.50 g, 91%), m.p. 104-105°. (Found: C, 48.43; H, 3.88. $C_{19}H_{17}F_3O_4Pd$ calcd.: C, 48.27; H, 3.62%.)

Complexes (II)

1,1,1,5,5,5-Hexafluoropentan-2,4-dionato-3-endo-σ-(5-exo-acetoxynortricyclenyl)(pyridine)palladium(II). Pyridine (28 μl) was added dropwise to a solution of 1,1,1,5,5,5-hexafluoropentan-2,4-dionato-2,3-π-5-*endo*-σ-(6-*exo*-acetoxybicyclo[2.2.1]heptenyl)palladium(II) (0.159 g) in benzene (2 ml). The resultant solution was evaporated to dryness under reduced pressure, and the residue was recrystallised from diethyl ether/petroleum ether (b.p. 30-60°), to yield the *product* as yellow needles (0.150 g, 80%), m.p. 122-124° dec. (Found: C, 40.80; H, 3.18; N, 2.64. $C_{18}H_{17}F_6NO_4Pd$ calcd.: C, 40.66; H, 3.22; N, 2.64%.) The triphenylphosphine, dimethylphenylphosphine, and triphenylstibine analogues of the above complex were similarly prepared as unstable yellow oils, which could not be crystallised, and were identified by their ^1H NMR spectra (see Table 1).

Benzoyltrifluoroacetonato-3-endo-σ-(5-exo-acetoxynortricyclenyl)(pyridine)-palladium(II). Pyridine (0.025 ml) was added to a solution of benzoyltrifluoroacetonato-2,3-π-5-*endo*-σ-(6-*exo*-acetoxybicyclo[2.2.1]heptenyl)palladium(II) (0.149 g) in dichloromethane (10 ml). The resultant yellow solution was evaporated to dryness under reduced pressure to give a yellow oil. Recrystallisation from dichloromethane/hexane gave the product as yellow prisms (0.135 g, 78%), m.p. 91-96°. (Found: C, 52.39; H, 4.27. $C_{24}H_{22}F_3NO_4Pd$ calcd.: C, 52.23; H, 4.02%.)

Similarly prepared were:

Benzoyltrifluoroacetonato-3-endo-σ-(5-exo-acetoxynortricyclenyl)(triphenylphosphine)palladium(II) as yellow prisms from dichloromethane/hexane (70%), m.p. 128-136°. (Found: C, 60.39; H, 4.51. $C_{37}H_{32}F_3O_4PPd$ calcd.: C, 60.46; H, 4.39%.)

Benzoyltrifluoroacetonato-3-endo-σ-(5-exo-acetoxynortricyclenyl)(triphenylarsine)palladium(II) as yellow prisms from dichloromethane/hexane (75%), m.p. 117-121°. (Found: C, 57.33; H, 4.08. $C_{37}H_{32}AsF_3O_4Pd$ calcd.: C, 57.03; H, 4.14%.)

Determination of the equilibrium constants for the reactions of mono-olefins and 1,3-dienes with norbornenyl complexes of palladium(II) to give σ-nortricyclenyl derivatives.

Aliphatic olefins and 1,3-dienes were commercial samples, used without

further purification. We are grateful to Drs. W.F. Reynolds and G.K. Hamer for samples of *p*-substituted styrenes.

NMR tubes were precalibrated to a volume of 0.40 ml. Standard solutions (0.82 *M* in $CDCl_3$) of 1,1,1,5,5,5-hexafluoropentan-2,4-dionato-2,3-π-5-*endo*-σ-(6-*exo*-acetoxybicyclo[2.2.1]heptenyl)palladium(II) were made up in the NMR tube. Liquid olefins or 1,3-dienes were injected with a microsyringe. Gaseous olefins or 1,3-dienes were introduced by bubbling the gas through the solution in the NMR tube using a fine capillary, until a satisfactory concentration of olefin or diene was dissolved, as evidenced by the ^1H NMR spectrum. The ^1H NMR spectrum was recorded and integrated at 34°. Values of the equilibrium constant (K^1) were calculated from the integrated spectra.

Complexes (III)

Allene, 1,1,-dimethylallene, 1,3-dimethylallene and tetramethylallene were commercial samples. We are grateful to Drs. J.C. Thompson and C.S. Liu for a sample of 1-methylallene.

1,1,1,5,5,5-Hexafluoropentan-2,4-dionato-π-{2-[endo-3'-(5'-exo-acetoxynortricyclenyl)]allyl} palladium(II). Allene was bubbled through a solution of 1,1,1,5,5,5-hexafluoropentan-2,4-dionato-2,3-π-5-*endo*-σ-(6-*exo*-acetoxybicyclo[2.2.1]heptenyl)palladium(II) (0.135 g) in dichloromethane (2 ml) for 5 min, and the resultant solution was evaporated to dryness under reduced pressure. Recrystallisation of the residue from petroleum ether (b.p. 30-60°) yielded the product as pale yellow prisms (0.140 g, 92%), m.p. 95-99°. (Found: C, 40.71; H, 3.18. $C_{17}H_{16}F_6O_4Pd$ calcd.: C, 40.46; H, 3.20%.)

Similarly prepared were:

1,1,1,5,5,5-Hexafluoropentan-2,4-dionato-π-{2-[endo-3'-(5'-exo-methoxynortricyclenyl)]allyl} palladium(II), as a pale yellow oil (0.200 g, 90%) from 1,1,1,5,5,5-hexafluoropentan-2,4-dionato-2,3-π-5-*endo*-σ-(6-methoxybicyclo[2.2.1]heptenyl)palladium(II), (0.200 g) and allene. (Found: C, 40.24; H, 3.18. $C_{16}H_{16}F_6O_3Pd$ calcd.: C, 40.32; H, 3.38%.)

1,1,1,5,5,5-Hexafluoropentan-2,4-dionato-π-{2-[endo-3'-(5'-exo-acetoxynortricyclenyl)]-1-methylallyl} palladium(II), as a yellow oil (0.230 g, 88%) from 1,1,1,5,5,5-hexafluoropentan-2,4-dionato-2,3-π-5-*endo*-σ-(6-*exo*-acetoxybicyclo[2.2.1]heptenyl)palladium(II) (0.240 g) and 1-methylallene. (Found: C, 41.77; H, 3.62. $C_{18}H_{18}F_6O_4Pd$ calcd.: C, 41.69; H, 3.50%.)

1,1,1,5,5,5-Hexafluoropentan-2,4-dionato-π-{2-endo-3'-(5'-exo-acetoxynortricyclenyl)]-1,1-dimethylallyl} palladium(II). 1,1-Dimethylallene (60 μl) was injected into a solution of 1,1,1,5,5,5-hexafluoropentan-2,4-dionato-2,3-π-5-*endo*-σ-(6-*exo*-acetoxybicyclo[2.2.1]heptenyl)palladium(II) (0.200 g) in dichloromethane (2 ml). After standing at room temperature for 2 h the solution was passed down a Florisil column (5 cm × 1 cm) eluting with dichloromethane. Evaporation of the eluate to dryness under reduced pressure yielded the *product,* as a pale yellow oil (0.210 g, 92%). (Found: C, 42.86; H, 4.02. $C_{19}H_{20}F_6O_4Pd$ calcd.: C, 42.84; H, 3.78%.)

Similarly prepared were:

1,1,1,5,5,5-Hexafluoropentan-2,4-dionato-π-{2-[endo-3'-(5'-exo-methoxynortricyclenyl)]-1,1-dimethylallyl} palladium(II) as a yellow oil (0.250 g, 83%), from 1,1,1,5,5,5-hexafluoropentan-2,4-dionato-2,3-π-5-*endo*-σ-(6-*exo*-methoxy-

bicyclo[2.2.1]heptenyl)palladium(II) (0.259 g) and 1,1-dimethylallene (100 μl). (Found: C, 42.78; H, 4.27. $C_{18}H_{20}F_6O_3Pd$ calcd.: C, 42.85; H, 3.99%.)

1,1,1,5,5,5-Hexafluoropentan-2,4-dionato-π-{2-[endo-3'-(5'-exo-acetoxynortricyclenyl)]-1,3-dimethylallyl}palladium(II), as yellow prisms (0.200 g, 88%), m.p. 95-99°, from 1,1,1,5,5,5-hexafluoropentan-2,4-dionato-2,3-π-5-*endo*-σ-(6-*exo*-acetoxybicyclo[2.2.1]heptenyl)palladium(II) (0.200 g) and 1,3-dimethylallene (40 μl). (Found: C, 42.78; H, 4.06. $C_{19}H_{20}F_6O_4Pd$ calcd.: C, 42.84; H, 3.78%.)

1,1,1,5,5,5-Hexafluoropentan-2,4-dionato-π-{2-[endo-3'-(5'-exo-acetoxynortricyclenyl)]-1,1,3,3-tetramethylallyl}palladium(II), as pale yellow prisms (0.230 g, 87%), m.p. 102-105°, from 1,1,1,5,5,5-hexafluoropentan-2,4-dionato-2,3-π-5-*endo*-σ-(6-*exo*-acetoxybicyclo[2.2.1]heptenyl)palladium(II) (0.220 g) and tetramethylallene (60 μl), after a reaction time of 24 h.

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