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A ^{13}C AND ^{1}H NMR INVESTIGATION OF THE BONDING IN NORBORNENYL COMPLEXES OF PALLADIUM(II) AND PLATINUM(II)

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SUMMARY

The modes of bonding in several norbornenyl complexes of palladium(II) and platinum(II) has been investigated by both ^{1}H and ^{13}C NMR spectroscopy. Analysis of internal ^{1}H–^{1}H, ^{13}C–^{1}H, and ^{195}Pt–^{13}C coupling constants indicate considerable distortion of the norbornenyl ligand in these complexes relative to organic norbornenes. The nature of this distortion is compatible with a π-homoallylic bonding scheme.

INTRODUCTION

Reactions of chelating diene complexes of Pd^{II} and Pt^{II} with nucleophilic reagents have been the subject of much study in recent years[1–13]. Of particular interest is the nature of the olefin–metal bond and the stereochemistry of nucleophilic attack at the coordinated olefin. Reaction of dichloro(norbornadiene)M^{II} (M = Pd, Pt) with alkoxide[3,5,11] or carboxylate[12,13] nucleophiles (Y) has been shown to yield norbornenyl complexes (I) (M = Pd, Pt; Y = OCH_3; $OCOCH_3$) in which the nucleophile Y occupies an *exo*-position. Similar reactions occur with the analogous complexes of 1,5-cyclooctadiene and *endo*-dicyclopentadiene to yield complexes (II) and (III) respectively[2–4,6–12]. The stereochemistries of the latter two complexes have been determined by X-ray crystallographic studies[14,15]. It is noteworthy that nucleophilic attack on coordinated dicyclopentadiene to give complexes (III) occurs exclusively at the norbornene-type olefin[3].

On the basis of ^{1}H NMR studies of complex (I) (M = Pd; Y = OMe; X = Cl),

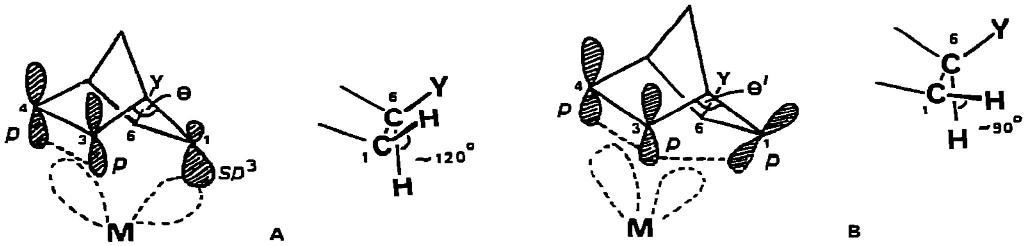
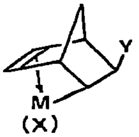
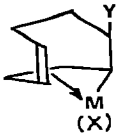


Fig. 1. Extremes of bonding orbital models for the norbornenyl ligand: A. π–σ enyl; B. π–homoallyl.

Hancock and Green[11] have suggested that the bonding in the norbornenyl–metal system might be better represented in terms of a "π-homoallylic" structure (Fig. 1b), rather than the π–σ enyl structure (Fig. 1a). Indirect chemical evidence for a π-homoallylic interaction has been provided by reaction of complex (I) (M = Pd, Pt; Y = OMe, OAc; X = Cl, Hfacac) with a variety of donor ligands to yield σ-nortricyclenyl complexes, or organic products derived from the decomposition of such complexes[5,12,16-21]. If the π-homoallylic description (Fig. 1b) is indeed correct, then these nortricyclenyl derivatives may be considered as "σ-homoallylic" complexes by analogy to π-allyl/σ-allyl transition metal systems[16]. Recently however, on the basis of ^{1}H NMR studies of complexes (I) (M = Pd, Pt; Y = X = OAc), Haszeldine *et al.*[12] and Lewis *et al.*[13] have disputed the ^{1}H NMR assignments of Hancock and Green[11], and as such the validity of the π-homoallylic bonding description (see Fig. 1b) remains an open question.



(I)



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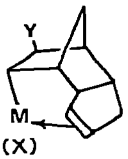
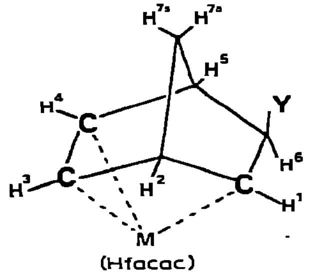
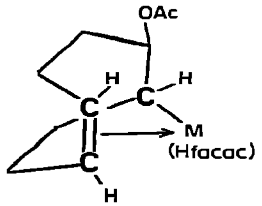


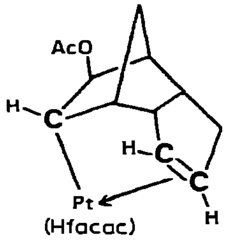
(III)



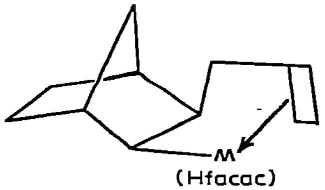
(IV) (a) M = Pd; Y = OMe
(b) M = Pd; Y = OAc
(c) M = Pt; Y = OAc



(V) (a) M = Pd
(b) M = Pt



(VI)



(VII) (a) M = Pd
(b) M = Pt

We here report detailed studies of the ^{1}H and ^{13}C NMR spectra of the hexafluoroacetylacetonate complexes (IV) (M = Pd, Y = OMe; M = Pd, Pt; Y = OAc) together with those of (V) (M = Pd, Pt), (VI) and (VII) (M = Pd, Pt) which were recorded for comparative purposes. The ^{1}H NMR spectra of complexes (IV) are far better resolved than any of the previously reported spectra of the dimeric complexes (I) (X = Cl or OAc)*. The results, some of which are at variance with the previously reported spectral assignments, provide compelling evidence that the "π-homoallylic" bonding scheme (Fig. 1b) provides a significant contribution to the overall bonding in norbornenyl transition metal complexes.

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* In all cases to date the reported ^{1}H NMR spectra of complexes (I) comprise rather broad, featureless resonances, and the decoupling experiments performed were only capable of determining line width changes[11-13]. It should be noted that in complex (I) where X = Cl there are four possible geometric isomers, and for X = OAc, there is a total of six possible geometric isomers.

EXPERIMENTAL

Instrumentation

^1H NMR spectra were run on Varian Associates A56/60D and HA-100 instruments. ^{13}C NMR spectra were obtained using a Varian Associates XL–100–15 spectrometer, operating in the Fourier Transform Mode, and utilising a Varian 620*i* computer with a 16K memory.

Starting materials

Dichloro(Diene)M^{II} complexes (M = Pd: Diene = norbornadiene, 1,5-cyclooctadiene: M = Pt; Diene = norbornadiene, 1,5-cyclooctadiene, *endo*-dicyclopentadiene) were prepared by standard procedures[1–13].

Di-μ-chlorobis[2,3-π-5-*endo*-σ-(6-*exo*-methoxybicyclo[2.2.1]heptenyl)]dipalladium(II) was prepared by the method of Hancock and Green[11].

Conversion to enyl (Hfacac) complexes

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*). A suspension of dichloro(bicyclo[2.2.1]heptadiene)palladium(II) (1.328 g) in anhydrous diethyl ether (75 ml) was treated with silver acetate (2.550 g). The mixture was stirred vigorously (30 min) and filtered. 1,1,1,5,5,5-Hexafluoropentan-2,4,-dione (1.050 ml) was added to the golden yellow filtrate, causing it to pale considerably, and the resultant solution was evaporated to dryness under reduced pressure. The residue was freed of acetic acid by exposing it to high vacuum (ca. 1h) and recrystallised from petroleum ether (b.p. 30–60°) to yield the product as cream coloured prisms (1.870 g; 82%), m.p. 90–95° dec. (Found: C, 36.20; H, 2.58. $C_{14}H_{12}F_6O_4Pd$ calcd.: C, 36.19; H, 2.60%.)

Similarly prepared were:

1,1,1,5,5,5-*Hexafluoropentan*-2,4-*dionato*-2,3-π-5-*endo*-σ-(6-*exo-acetoxybicyclo*[2.2.1]*heptenyl*)*platinum*(*II*), as yellow prisms (75%), m.p. 87–91°, from dichloro(bicyclo[2.2.1]heptadiene)platinum(II). (Found: C, 30.63; H, 2.41. $C_{14}H_{12}F_6O_4Pt$ calcd.: C, 30.38; H, 2.18%.)

1,1,1,5,5,5-*Hexafluoropentan*-2,4-*dionato*-2,3-π-5-*endo*-σ-(6-*exo-methoxybicyclo*[2.2.1]*heptenyl*)*palladium*(*II*), as pale yellow prisms (65%), m.p. 53–60°, identified by its ^1H NMR spectrum, from di-μ-chlorobis[2,3-π-5-*endo*-σ-(6-*exo*-methoxybicyclo-[2.2.1]heptenyl)]dipalladium(II).

1,1,1,5,5,5-*Hexafluoropentan*-2,4-*dionato*-1,2-π-5-*endo*-σ-(6-*exo-acetoxycyclooctenyl*)*palladium*(*II*), as pale yellow prisms (85%), m.p. 91–94°, from dichloro(1,5-cyclooctadiene)palladium(II). (Found: C, 37.46; H, 3.34. $C_{15}H_{16}F_6O_4Pd$ calcd.: C, 37.49; H, 3.36%.)

1,1,1,5,5,5-*Hexafluoropentan*-2,4-*dionato*-1,2-π-5-*endo*-σ-(6-*exo-acetoxybicyclooctenyl*)*platinum*(*II*), as yellow prisms (80%), m.p. 84–87°, from dichloro(1,5-cyclooctadiene)platinum(II). (Found: C, 31.51; H, 2.75. $C_{15}H_{16}F_6O_4Pt$ calcd.: C, 31.65: H, 2.83%.)

1,1,1,5,5,5-*Hexafluoropentan*-2,4-*dionato*-2,3-π-5-*endo*-σ-(6-*exo-acetoxycyclopentadienyl*)*platinum*(*II*), as a yellow oil (90%), which could not be crystallised, from dichloro(dicyclopentadiene)platinum(II).

The complexes 1,1,1,5,5,5-hexafluoropentan-2,4-dionato-2′,3′-π-3-*exo*-σ-(*exo*-2-prop-2′-enylbicyclo[2.2.1]heptyl)M^{II} (M = Pd, Pt) were prepared by previously reported methods[22].

RESULTS AND DISCUSSION

^1H *NMR spectra of complexes (IV)*

The ^1H NMR spectra of complexes (IVb) and (IVc) are shown in Fig. 2. Chemical shift data for these two complexes together with that of (IVa) are shown in Table 1. Excluding the resonances of the Hfacac, OAc, or OMe moieties, the spectra consist of eight resonance patterns. The first, most striking, observation is that, although chemical shift changes occur on changing M from Pd to Pt, (or Y from OAc to OMe) no change in the internal ^1H–^1H coupling constants is observed, as evidenced by peak multiplicities and line-widths. It is thus evident that on changing M from Pd to Pt *no angular changes of the C–H bonds relative to one another must occur in the organic group.* Chemical shift changes on varying M from Pd to Pt are expected to be greatest for those protons attached to carbon atoms which are directly involved in bonding to the metal[12]. Similarly the largest values of $J(^{195}Pt–H)$ are expected for the protons on carbon atoms directly involved in bonding to Pt.

On changing M from Pd to Pt, the resonance patterns denoted A, B and F (Fig. 2) experience the largest shifts to high field and also exhibit the largest values of $J(^{195}Pt–H)$ in (IVc) (see Table 1). These resonances are thus attributed to protons H(1), H(3) and H(4). On the basis of chemical shift the low field resonances A and B are attributed to H(3) and H(4), thus identifying resonance F as the signal of proton H(1), which, according to the π–σ enyl bonding model is attached to the carbon atom forming a σ-bond to the metal.

Examination of the ^1H NMR spectra of complexes (IVa) and (IVb) (see Table 1) reveals that the only major spectral change on varying Y from OAc to OMe is in the chemical shift of resonance C (Y = OAc; τ 4.60 ppm; Y = OMe, τ 5.82 ppm). This resonance must therefore be assigned to the proton (H(6)) directly bonded to the substituent (Y)-bearing carbon. The high-field resonances G and H (Fig. 2) are readily assigned to the methylene bridge protons H(7a) and H(7s), both on the basis of chemical shift and the characteristic AB quartet coupling pattern exhibited by diastereotopic protons in this environment[23]. (The magnitude of J_{7a-7s} 10 Hz *in this bicyclic system* can only be ascribed to two geminally coupled protons[23].)

The above analysis of the ^1H NMR data of (IVb) and (IVc) gives an unambiguous assignment of H(1) and H(6) together with the pairs of protons (H(3) and H(4)) and (H(7a) and H(7s)). By a process of elimination the broad resonances denoted D and E must correspond to the pair of bridgehead protons (H(2) and H(5)). In order to obtain a complete assignment, the ^1H NMR spectrum of (IVb) was subjected to a detailed analysis by means of double resonance. Decoupled spectra are shown in Fig. 3.

Irradiation of resonance F(H(1)) has no effect on C(H(6)) but cause sharpening of D and E(H(2) and H(5)) (Fig. 3b). Likewise irradiation of C(H(6)) has no effect on F (H(1)) (Fig. 3c). Thus H(1) and H(6) are not coupled significantly (i.e. $J(H(1)–H(6)) \approx 0$), an initially surprising result in view of the fact that $J(H_{exo}–H_{endo})$ in norbornene systems is usually of the order of 2–3 Hz[23,24]. Indeed, assumption of a coupling constant $J_{1,6} \approx 2.5$ Hz has been a basis for previous attempts to assign the

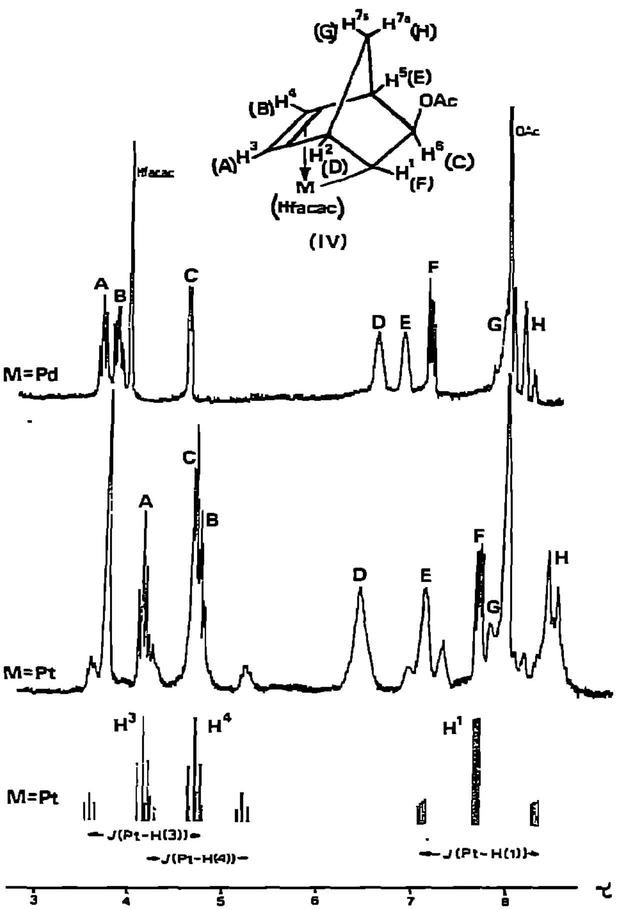


Fig. 2. ^{1}H NMR spectra [100 MHz; $CDCl_3$; 34°] of the acetoxynorbornenyl complexes (IVb) and (IVc). [Values of J(Pt–H) for H(1), H(3) and H(4) were confirmed by running the spectra at 100 and 60 MHz in $CDCl_3$ and C_6D_6.]

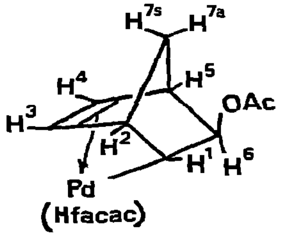
TABLE 1

^{1}H NMR DATA [100 MHz; $CDCl_3$; 34°] FOR COMPLEXES (IV)
(See Fig. 2 for numbering of protons)

Y	*M*	*τ(ppm) (multiplicity)*[a], *J(Pt–H) (Hz)*[b,c]							
		H^1	H^2	H^3	H^4	H^5	H^6	H^{7s}	H^{7a}
(IVa) OMe	Pd	7.13 (dd)	6.77 (bs)	3.77 (t)	3.91 (dt)	6.97 (bs)	5.82 (dd)	8.22 (bd)	7.90 (bd)
(IVb) OAc	Pd	7.16 (dd)	6.60 (bs)	3.68 (t)	3.85 (dt)	6.87 (bs)	4.60 (dd)	8.19 (bd)	7.99 (bd)
(IVc) OAc	Pt	7.75 (dd) J(Pt–H) 124[c]	6.52 (bs)	4.21 (t) J(Pt–H)108[c]	4.80 (dt) J(Pt–H)100[c]	7.20 (bs)	4.73 (dd)	8.56 (bd)	8.10 (bd)

[a] s, Singlet; d, doublet; t, triplet; b, broad. [b] Full internal ^{1}H–^{1}H couplings given in Fig. 4. [c] Values of J(Pt–H) were confirmed by obtaining spectra of this complex at 60 and 100 MHz in two different solvents ($CDCl_3$, C_6D_6).

spectra of norbornenyl complexes[11-13]. Irradiation of resonance D (H(2) or H(5)) (Fig. 3d) collapses resonance F (H(1)) to a doublet ($J \approx 2$ Hz), demonstrating a coupling of 4.4 Hz between D and H(1). The largest coupling expected to be experienced by H(1) is from the vicinal bridgehead proton H(2). Resonance D is thus assigned to H(2) with the result that resonance E must be assigned to H(5). Irradiation of resonance D (H(2)) also collapses resonance A to a 1/1 doublet ($J \approx 4$ Hz) and resonance



(IVb)

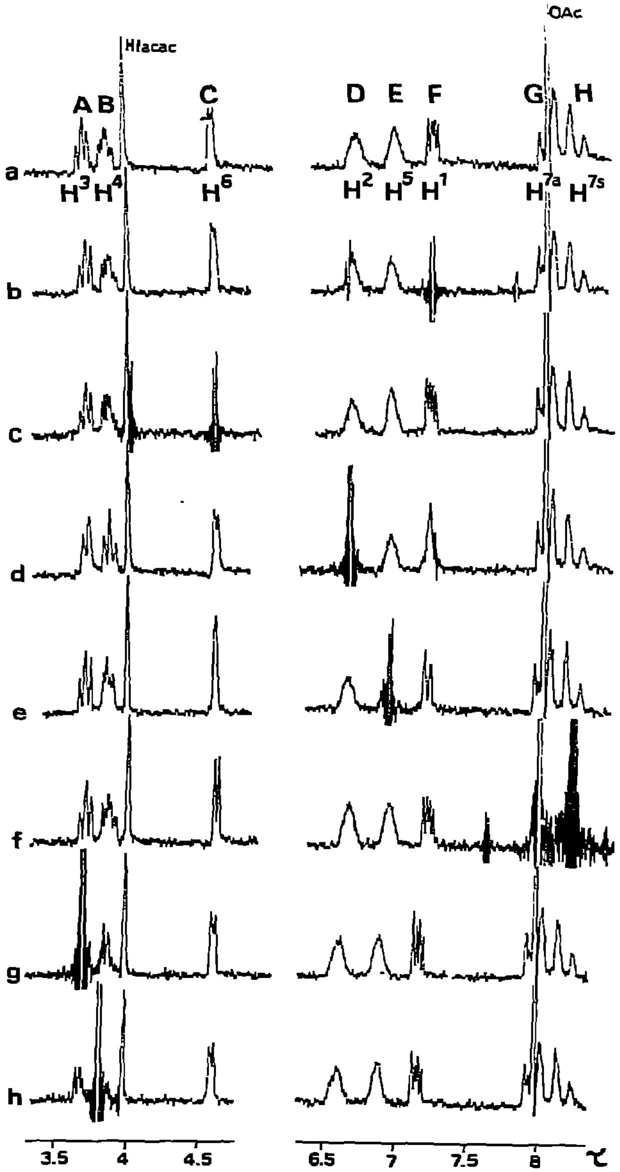


Fig. 3. ^{1}H NMR spectra [100 MHz; $CDCl_3$; 34°] of complex (IVb) with homonuclear decoupling of the individual proton resonances.

B to a 1/2/1 triplet ($J \approx 4$ Hz). The olefinic proton which should couple most strongly with H(2) is H(3)[23,24]. Resonance A is thus assigned to H(3) ($J_{3,2} = 3.8$ Hz) leaving resonance B to be assigned to H(4) ($J_{4,2} = 1.9$ Hz). In agreement with this assignment, irradiation of resonance E (H(5)) (Fig. 3e) collapses resonance B (H(4)) to a doublet of 1/1 doublets ($J \approx 4$, $J \approx 2$) demonstrating $J_{5,4} = 4.2$ Hz, whilst causing only a slight sharpening of the A (H(3)) triplet resonance. Irradiation of resonance E (H(5)) also collapses F(H(1)) to a doublet ($J \sim 4.5$ Hz) while C(H(6)) is collapsed to a broad singlet, demonstrating $J_{1,5} = 2.3$ Hz and $J_{5,6} = 2.6$ Hz. The value of $J_{5,6}$ was initially surprising since there is usually zero coupling between a bridgehead proton and an *endo*-proton[23,24]. Irradiation of the high field resonance (H) (Fig. 3f) collapses the C (H(6)) resonance to a 1/1 doublet ($J = 2.6$ Hz) demonstrating a small (1.2 Hz) coupling between (H) and (C) (H(6)). Resonance (H) is thus assigned to H(7s) as long range coupling between H(7s) and *endo*-protons is a well known feature of norbornene systems[24]. A coupling constant $J_{3,4} = 3.8$ Hz is demonstrated by irradiation of A (H(3)) or B (H(4)) (Figs. 3g and 3h). An unequal coupling of the bridgehead protons H(2) and H(5) to the methylene bridge protons has also been demonstrated. Irradiation of E (H(5)) (Fig. 3e) causes sharpening of both the H(7a) and H(7s) resonances (G and H) whereas irradiation of D (H(2)) (Fig. 3d) only causes sharpening of the H(7a) resonance (G). This unequal coupling effect has been noted previously in unsymmetrically substituted norbornenes[25].

Full internal $^1H-^1H$ coupling constants data are summarized in Fig. 4. Besides the unusual values of J_{1-6} and J_{5-6} noted above another interesting feature of the data is the four bond couplings J_{1-5}, J_{2-4}, and J_{3-5}. Long range couplings of this type between bridgehead and olefinic protons (*e.g.* J_{2-4}) are well known in norbornene systems where the four bonds involved lie in an approximate planar W-configuration[24]. The similar values of $J_{1,5}$ (2.3 Hz) and J_{2-4} (1.9 Hz) imply similar environments, in an angular sense, for H(1) and H(4) relative to the bridgehead protons H(5) and H(2)

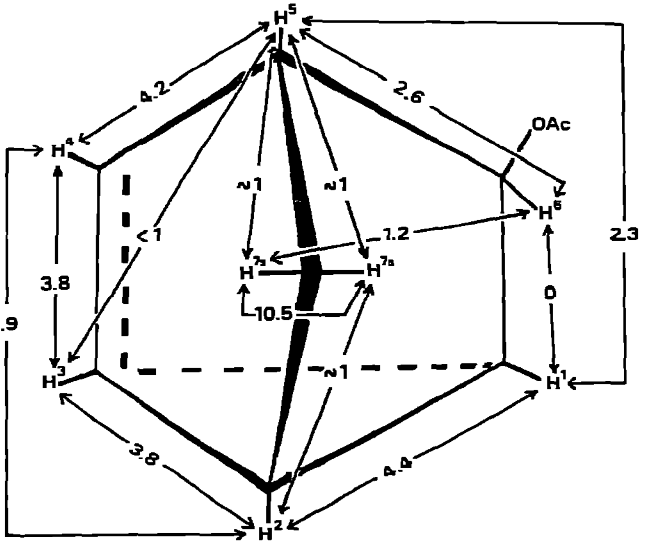


Fig. 4. Internal $^1H-^1H$ coupling constants (Hz) for the norbornenyl ligand in complexes (IVb) and (IVc).

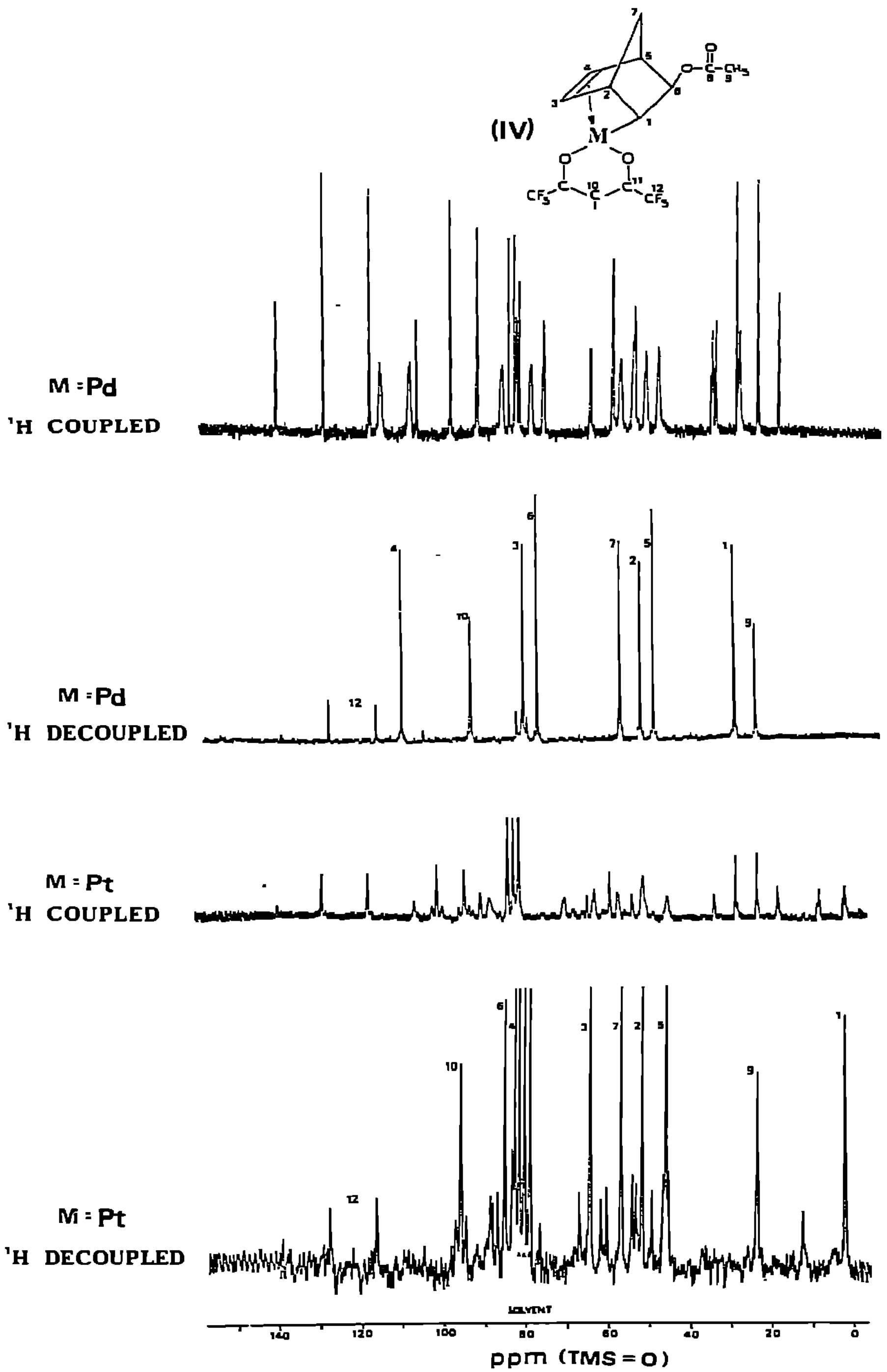


Fig. 5. ¹H-decoupled and ¹H-coupled ^{13}C NMR spectra [25.2 MHz; $CDCl_3$; 34°] of complexes (IVb) and (IVc).

respectively. The relatively small value of $J_{3,5}$ (< 1 Hz) implies that this similarity does not extend to H(3) in its angular relationship to H(5).

As pointed out above several features of the proton NMR spectra of (IVb) and (IVc) are not wholly compatible with the π–σ norbornenyl bonding scheme (Fig. 1a)*. Now let us consider the π-homoallylic bonding scheme (Fig. 1b). One consequence of the π-homoallylic bonding scheme is that H(1) is attached to a C-atom via a carbon hybrid orbital which is more sp^2 than sp^3 in character. This feature would account for the observed similarity in the angular environments of the C–H(1) and C–H(4) bonds. Secondly the dihedral angle between the C–H(1) and C–H(6) bonds would be ca. 90° in the π-homoallylic bonding model compared to ca. 120° in the extreme π–σ enyl model. In accord with the Karplus relationship[26], this accounts for the value of J_{1-6} being ca. 0 instead of ca. 2.5–3.0 Hz as observed in substituted norbornenes. A further consequence of (Fig. 1b) is that relative to (Fig. 1a) the *s*-character in the C–H(1) orbital must increase and the *s*-character of the carbon orbital used in bonding H(1)–C to the metal must be less than that in a typical norbornyl–metal σ-bond. Examination of the ^{13}C NMR spectra of (IVb), (IVc) and related "enyl" complexes provides compelling evidence that this is indeed the case.

^{13}*C NMR studies*

The ^{1}H-decoupled and ^{1}H-coupled ^{13}C NMR spectra of complexes (IVb) and (IVc) are shown in Fig. 5. In order to assist in the assignment of the spectra of these complexes, the spectra of the enyl complexes (IVa), (IVb), (V), (VIa), (VIb), (VIIa) and (VIIb) were also recorded. δ^{13}C, $J(^{13}$C–H) and $J(^{195}$Pt–^{13}C) data are presented in Table 2. We shall first discuss the ^{13}C NMR spectra of (Va) and (Vb) since these may be considered typical examples of π–σ bonded enyl complexes.

Excluding the carbon resonances of the OAc and Hfacac moieties the ^{1}H-decoupled ^{13}C NMR spectra of complexes (Va) and (Vb) exhibit the expected eight resonances, together with satellites due to ^{195}Pt–C coupling in (Vb). The resonances due to C(1), C(4), C(5), and C(8) are readily identified by examination of the ^{1}H-coupled spectra since they exhibit doublet splitting, the other four methylene carbons exhibiting triplet splitting. The most significant chemical shift changes on changing M from Pd to Pt are expected to occur for carbon atoms C(1), C(4), and C(5) (*i.e.* those directly involved in bonding to the metal). Similarly these carbon atoms should exhibit the largest values of $J(^{195}$Pt–^{13}C). In fact only three major chemical shift changes are observed on changing M from Pd to Pt. These resonances are assigned to C(1), C(4) and C(5) on this basis, leaving the remaining doublet resonance as that of C(8). The resonance at δ 25.9 ppm in (Vb) is assigned to C(1) on the basis of the value of $J(^{195}$Pt–^{13}C) 730 Hz observed for this carbon. Clark *et al.*[27] have shown that $J(^{195}$Pt–^{13}C) for a methyl carbon σ-bonded to Pt^{II} lies between 600 and 700 Hz for neutral complexes. Assignment of C(1) allows the remaining two carbon resonances to be assigned to C(4) and C(5), although there appears to be no way of obtaining an unambiguous assignment apart from specific ^{1}H-decoupling experiments. The lower

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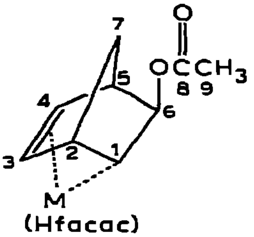
* Whilst coordination of the olefin to M in bonding model A (Fig. 1) is expected to change the stereochemistry of the olefinic H's and result in a slight increase in the olefinic C=C bond length[33] these changes in themselves are insufficient to account for the observed H–H coupling constants and in particular J_{1-6} and J_{5-6}.

(*continued on p.* 438)

TABLE 2

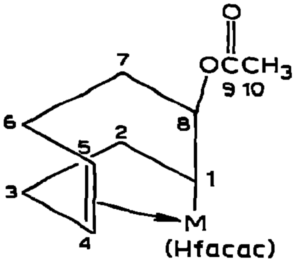
^{13}C NMR DATA [25.2 MHz; CDCl$_3$; 34°] FOR COMPLEXES (IV)-(VII).

(IV)



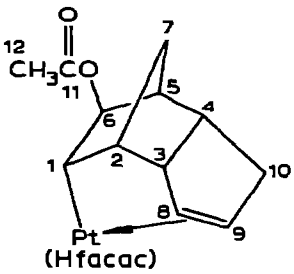
M	C_1	C_3	C_4	C_6	C_2	C_5
Pd δ^a	25.9	76.4	105.7	73.1	48.3*	45.2*
J(C–H)^b	166	174	181	167	155	151
δ^a	0.3	61.3	79.2	81.5	48.8	43.0
Pt J(C–H)^b	160	178	181	168	153	153
J(Pt–C)	470	132	296	88	117	29

(V)



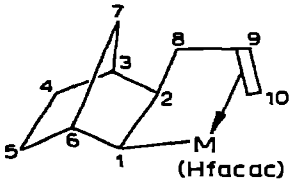
	C_1	C_4	C_5	C_8	(C_2,	C_3,
δ^a	49.0	97.1*	103.5*	74.5	(33.8,	29.7,
Pd J(C–H)^b	144	160	157	148		
δ^a	25.9	77.9*	82.2*	75.0	(33.4,	28.4,
Pt J(C–H)^b	145	157	154	146		
J(Pt–C)^b	730	255	260			

(VI)



	C_1	C_8	C_9	C_6	C_2	C_3
δ^a	32.8	87.9*	85.4*	78.4	40.5**	55.2
Pt J(C–H)^b	150	170	168	158	144	144
J(Pt–C)^b	782	250	259	28	25	71

(VII)



	C_1	C_9	C_{10}	C_2	C_3	C_4
δ^a	64.3	108.1	76.1	47.0	42.5	28.8*
Pd J(C–H)^b		156	159			
δ^a	37.4	87.0	56.2	45.4	42.2	29.0*
Pt J(C–H)^b		157	159			
J(Pt–C)^b	758	277	305			

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[a] Ppm relative to internal TMS. [b] J values in Hz (quoted to nearest integral value). [c] Unequivocal assignment impossible. Note: * and ** indicate peak assignments may possibly be reversed.

C_7	C_8	C_9	Hfacac		
			CH	C=O	CF_3
53.2	169.3	20.8	89.2	175.5	117.9
134		129	164	J(C–C–F)34	J(C–F)286
53.8	170.0	21.1	92.2		117.9
134			165		J(C–F)286
179			54		

C_6,	$C_7)^c$	C_9	C_{10}	Hfacac		
				CH	C=O	CF_3
27.1,	26.3)	164.5	20.7	89.1	175.5	117.9
			129	164	J(C–C–F)34	J(C–F)287
27.6,	27.6)	170.0	21.0	92.3		117.9
			129	165		J(C–F)266
				54		

C_4	C_5	C_7	C_{10}	C_{11}	C_{12}	Hfacac		
						CH	C=O	CF_3
55.8	42.7**	36.0	30.4	170.0	21.3	92.4		117.9
137	145	134	143		129	166		J(C–F)286
		56	29			55		

C_5	C_6	C_7	C_8
28.2*	40.0	34.2	36.8
28.8*	38.7**	34.4	38.5**

values of $J(^{195}Pt-^{13}C)$ for these carbons (255, 260 Hz) are consistent with this assignment. The approximately equal values of $J(^{195}Pt-^{13}C)$ for C(4) and C(5) imply a symmetrical bonding interaction between Pt and each olefinic carbon in (Vb).

The values of $J(^{13}C-H)$ for C(1) in both (Va) and (Vb) are higher than the value observed for an sp^3 C–H bond in a hydrocarbon. However an X-ray structural study of chloro(2-methoxycycloocta-5-en-1-yl)pyridineplatinum(II) has shown the stereochemistry of the C(1) bonds to be very close to that expected of an sp^3 C-atom[15]. By analogy with the effect of halogens (X) on $J(^{13}C-H)$ in CH_3X and $XHC{=}CH_2$ relative to $J(^{13}C-H)$ in CH_4 and C_2H_4 respectively, the higher value of $J(^{13}C-H)$ for C(1) in (Va) and (Vb) may be considered due to a substituent effect associated with the effective nuclear charge on the metal and the metal–carbon bond length rather than an increase in the *s*-character of the C(1)-orbital used in C–H bonding[28]. In agreement with this the value of $J(^{13}C-H)$ for C(8) which contains the electronegative OAc substituent (146 Hz) is very similar to $J(^{13}C-H)$ of C(1) (145 Hz) (*e.g.* see Vb). As anticipated the values of $J(^{13}C-H)$ for C(4) and C(5) are greater than for C(1). This is consistent with the greater *s*-character of the C-orbital anticipated for the olefinic C–H bonds.

Assignment of C(1), C(8), and C(9) in the NMR spectrum of (VI) is made on the basis of chemical shift and $J(^{195}Pt-^{13}C)$ values. Other carbon resonances have been assigned on the basis of known chemical shifts of norbornane systems[29,30]. The internal C–C bonds in norbornanes have been shown to have more *p*-character than those in unstrained hydrocarbon systems. The C–H bonds in these systems therefore exhibit more *s*-character. It is thus not surprising that J(Pt–C(1)) in complex (VI) is somewhat larger than J (Pt–C(1)) in complex (Vb) (758 relative to 730 Hz) since the carbon hybrid orbital involved in the Pt–C bond in the former complex is expected to be richer in *s*-character. This conclusion is also supported by the value of $J(^{13}C-H)$ for C(1) in (VI) being larger than (Vb).

Similarly the value for J(Pt–C(1)) in complex (VIIb) is greater than that for J(Pt–C(1)) in comples (Vb). It is clearly established therefore that a representative value of J(Pt–C(1)) for a system involving a formal σ-bond from Pt to a norbornane-type carbon *trans* to Hfacac lies between 750–790 Hz.

The ^{13}C *NMR spectra of (IVb) and (IVc)*

The ^{13}C NMR spectra of (IVb) and (IVc) (Fig. 5 and Table 2) exhibit a number of unusual features, relative to those of (V)–(VII) which provide an insight into the nature of bonding in these systems. Carbon resonances C(1), C(3) and C(4) are assigned again on the basis of chemical shift similarity with complexes (V)–(VI), and C(7) can be unambiguously assigned since it is the only triplet resonance observed in the ^1H-coupled spectra. The remaining two resonances thus comprise the bridgehead carbons C(2) and C(5).

The first notable feature is that J(Pt–C) for C(1) in (IVc) is considerably less than those observed for enyl Pt complexes [470 Hz relative to 750–790 Hz in (Vb) (VI) and (VIIb)]. This value implies a significant reduction in *s*-character in the carbon–metal bonding orbital in the norbornenyl complex (IVb) (*i.e.* the carbon–Pt bond has more C *p*-orbital character than a typical norbornyl–Pt σ-bond.) This is substantiated by an increase in the value of $J(^{13}C-H)$ for C(1) compared to those values found in (V), (VI), and (VII), [*i.e.* the C–H carbon orbital has more *s*-character than is observed in a typical *endo*-norbornyl–Pt σ-bond, *e.g.* (VI)].

This is the same conclusion as that reached from analysis of the ^1H NMR data of (IVb) and (IVc) and further substantiates the "π-homoallylic" bonding scheme (Fig. 1b).

The second notable feature is the dramatic difference in the values of J(Pt–C) for C(3) and C(4) in (IVc) implying a significant difference in the metal interaction with these two carbon atoms. A consequence of the rigid bicyclic system in complexes (IV) is that the C(3)–C(4) axis must tilt away from the perpendicular with the result that the coordination plane of the metal must intersect the C(3)–C(4) axis at a point much closer to C(4) than C(3). This feature has previously been proposed by Haszeldine *et al.*[12] and may be compared with known distortion of the metal olefin bond in complexes (VII)[31] and the significant difference in the values of J(Pt–C) to the olefinic carbons in complex (VIIb) (see Table 2).

The third significant feature of the ^{13}C NMR spectra of (IVa) and (IVb) concerns the chemical shifts of the carbon atoms directly involved in metal–ligand bonding*. Compared to the chemical shift values of analogous carbon atoms in the "enyl" complexes (V)–(VII), C(1) and C(3) in (IV) undergo a large shift [ca. 25–30 ppm] to high field (*i.e.* more shielded) while the value for the chemical shift of C(4) is of a similar magnitude in all the complexes (for a given metal). A possible rationale for this effect may be found by considering the π-homoallylic bonding model. The π-homoallylic interaction shown in Fig. 1b requires significant delocalization of electron density between C(1) and C(3) with the result that compression of the C(1)–C(2)–C(3) angle at the bridgehead is expected such that $\theta' < \theta$ (see Fig. 1). This is an analogous feature to that proposed by Winstein[32] to explain the stability of the 5-norbornenyl cation. This compression effect of course introduces an increase in the strain energy of the system and as such a balance of the two opposing effects would be expected in order to obtain the optimum conditions of energy gain for the system[32]. A significant contribution from the π-homoallylic model would have two observable effects in the ^{13}C spectrum of the norbornenyl ligand [excluding the effects upon J(Pt–C(1)) and J(C(1)–H) already discussed above]. Firstly carbon atoms C(1) and C(3) might be expected to acquire some cyclopropanoid character as observed for these carbon atoms in nortricyclene[29]. This would result in a substantial shift of these carbon atom resonances to high field compared to the values expected for the π–σ enyl model, thereby accounting for the observed large upfield shifts of C(1) and C(3) relative to C(4). Secondly, compression of the C(1)–C(2)–C(3) angle must result in an increase in *p*-character in the C–C bonds of the C(2) carbon atom with a concomitant increase in *s*-character in the C–H bond of the C(2) carbon. That this is indeed the case is reflected in larger values of $J(^{13}C–H)$ for the bridgehead carbons C(2) and C(5) in (IV) [*e.g.* 153 and 153 Hz in (IVc)] compared to those observed for the bridgehead carbons in (VI) (144 and 145 Hz) and organic norbornenes (ca. 142 Hz)[25].

A final unusual feature of the ^{13}C NMR spectrum of complex (IVc) is the extremely large value of $J(^{195}Pt–^{13}C)$ observed for C(7) (179Hz). This value is significantly larger than the values of $J(^{195}Pt–^{13}C)$ observed for either of the bridgehead carbons C(2) or C(5) in the same complex, or the value observed for $J(^{195}Pt–^{13}C)$ of C(7) in complex (VI). Although the expression for a one-bond coupling constant

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* For a discussion of some of the factors affecting the ^{13}C chemical shift of carbon atoms bound to transition metals see ref. 34.

$^1J(^{195}\mathrm{Pt}-^{13}\mathrm{C})$ is expected to be dominated by the Fermi contact term[27,28a], little is known concerning factors affecting coupling constants over three or more bonds and we are unable to present a satisfactory explanation of this observation at the present. However it is noteworthy that C(7) lies very close to the Pt coordination plane suggesting the possibility of a directional through space coupling effect.

CONCLUSION

The above analysis of the ^{1}H and ^{13}C magnetic resonance spectra of complexes (IV) and related "enyl" complexes provides clear evidence that the π-homoallylic description of bonding (Fig. 1b) provides a significant contribution to the overall hydrocarbon–metal bonding in complexes containing a coordinated norbornenyl ligand.

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