Transition Metal–Carbon Bonds. Part XXXIV.[1] ^{1}H and ^{13}C Nuclear Magnetic Resonance Studies on π-Allylic–Palladium Complexes †

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Under high resolution the ^{1}H n.m.r. spectra of π-allylic–palladium compounds are more complex than previously reported: *e.g.*, the resonance of the central allylic hydrogen of $[Pd_2I_2(C_3H_5)_2]$ consists of 15 ' lines '. The spectra are thus interpretable as AA'BB'C patterns. Some relative signs of coupling constants in π-allylic complexes are reported for the first time. ^{13}C N.m.r. spectral shifts and $J(^{13}C^1H)$ values are reported and discussed. [Pd(acac)-(1,2,3,7-cyclo-octa-2,4-dienylpalladium] is shown not to be fluxional at 25° by ^{13}C n.m.r. spectroscopy.

HYDROGEN-1 n.m.r. spectroscopy is very important in the chemistry of allylic complexes, having been used to determine structure and stereochemistry and also to study rapid rate phenomena in solution.[2-4] We have now determined the ^{1}H n.m.r. spectra of some allylic–palladium complexes in more detail than previously and also measured ^{13}C n.m.r. spectra. The specific aims of the work were as follows. (i) The ^{1}H n.m.r. spectrum of the π-allyl group (1) in allyl-palladium complexes is often described as arising from an AM_2X_2 spin system.[5-9] However, if coupling between the *syn*- and *anti*-protons is significant then it must be at least AA'MM'X, if not AA'BB'C. Such second order spectra have been previously reported for $[Mn(\pi\text{-}C_3H_5)(CO)_4]$ [10] where the *syn*- and *anti*-proton resonances are doublets of triplets and for $[Co(\pi\text{-}C_3H_5)(CO)_3]$,[11] where the central proton resonance consists of 11 lines rather than the 9 lines predicted by treatment as A_2M_2X. (ii) To measure some relative signs of coupling constants. The assignments of stereochemistry and *syn*- and *anti*-proton resonances of π-allylic groupings have been made assuming that the

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† No reprints.

[1] Part XXXIII, D. F. Gill, B. E. Mann, and B. L. Shaw, *J.C.S. Dalton*, 1973, 270.

[2] S. D. Robinson and B. L. Shaw, *J. Chem. Soc.*, 1963, 4806.

[3] K. Vrieze, H. C. Volger, and P. W. N. M. Van Leeuwen, *Inorg. Chim. Acta, Rev.*, 1969, **3**, 109.

[4] H. C. Volger, *Ind. and Eng. Chem.* (*Product Res. and Development*), 1970, **9**, 311.

[5] G. E. Coates, M. L. H. Green, and K. Wade, ' Organometallic Compounds,' Methuen, Third Edn., 1968, p. 46.

[6] L. A. Fedorov, *Russ. Chem. Rev.*, 1970, **39**, 655.

[7] K. C. Ramsey, D. C. Lini, and W. B. Wise, *J. Amer. Chem. Soc.*, 1968, **90**, 4275.

[8] A. N. Nesmeyanov, Yu. A. Ustynyuk, I. I. Kritskaya, and G. A. Schembelov, *J. Organometallic Chem.*, 1968, **14**, 395.

[9] J. K. Becconsall, and S. O'Brien, *Chem. Comm.*, 1966, 303.

[10] F. A. Cotton, J. W. Faller, and A. Musco, *Inorg. Chem.*, 1967, **6**, 179.

[11] W. R. McClellen, H. H. Hoehn, H. N. Cripps, E. L. Muetterties, and B. W. Howk, *J. Amer. Chem. Soc.*, 1961, **83**, 1601.

relative magnitudes of their couplings with the central proton; *i.e.*, $^3J(H_1H_2)$ and $^3J(H_1H_3)$ in (I) are the same as that found for alkenes; *i.e.*, $^3J(HH)$*trans* > $^3J(HH)$*cis*.[12] For alkenes, both these couplings are positive, but not even the relative signs of $^3J(H_1H_2)$ and $^3J(H_1H_3)$ are known for allylic complexes. (iii) To measure $^1J(^{13}C^1H)$: we hoped that this would give information on the hybridization of the allylic carbon atoms. (iv) To determine some ^{13}C n.m.r. spectra of allylic complexes.

RESULTS

A detailed examination of the ^1H n.m.r. spectra of $[Pd_2X_2(C_3H_5)_2]$ (X = Cl or I) and of $[PdY(C_3H_5)]$ (Y = acac, or C_5H_5) shows the spectra to be more complex than one would expect from the description as A_2M_2X patterns. Thus we observed eleven lines for the central proton {H_1} with X = Cl, or Y = acac or C_5H_5 and fifteen lines when X = I, see Figure 1 and Table 1. Also for X = Cl or I, or for Y = acac the *syn* (H_2 and H_4) and *anti* (H_3 and H_5) proton resonances form badly resolved triplets, see Figure 2. Using LAOCOON 3 [13] and typical values for chemical shifts and coupling constants in π-allylic ligands determined as described below we could readily account for the fifteen lines (H_1) and the doublet of triplet patterns (H_2 and H_3). We were therefore interested in measuring the various coupling constants between H_2, H_3, H_4, and H_5 in symmetrical π-allylic–palladium compounds. Some of these couplings have been reported previously for asymmetric π-allylic ligands. For example, in chloro(1,1,2-trimethylallyl)(triphenylphosphine)palladium(II) there is a coupling of 2·9 Hz between the *syn*- and *anti*-protons.[14] Similarly in chloro(2-methylallyl)(triphenylphosphine)palladium(II) there is a coupling of 2·9 Hz between the two *syn*-protons.[3,14]

TABLE 1

^1H N.m.r. data for allylic palladium(II) complexes [a]

	τ_1	τ_2	τ_3	$J_{1,3}$	$J_{1,2}$	$J_{2,3} + J_{3,4}$
$[Pd_2Cl_2(allyl)_2]$	4·61(11)	5·89	6·94	12·1	6·8	1·0
$[Pd_2I_2(allyl)_2]$	5·02(15)	5·62	6·92	12·3	6·8	*ca.* 1
[Pd(acac)(allyl)]	4·43(11)	6·03	7·44	12·0	6·7	*ca.* 1
$[Pd(C_5H_5)(allyl)]$	5·06(11)	6·34	7·72	10·8	6·1	0·7
[Pd(acac)(2-chloroallyl)]		5·93	6·89			2·6
$[Pd(C_5H_5)(2\text{-methylallyl})]$	8·07 [b]	6·47	7·82			
	8·20 [c]	6·55	7·84			

[a] In deuteriochloroform (unless stated otherwise) relative to $SiMe_4$ as internal standard. τ Values ±0·01; *J* values ±0·1 Hz. The multiplicity of the resonance due to H_1 is given in parentheses. [b] $\tau(C_5H_5)$ 4·29. [c] In C_6H_6; $\tau(C_5H_5)$ 4·20.

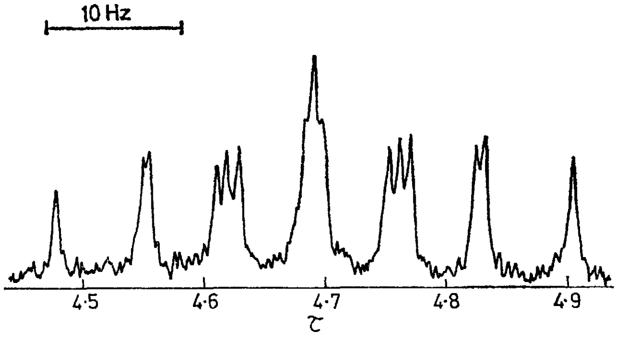

FIGURE 1 ^1H N.m.r. pattern for the central allylic hydrogen (H_1) of $[Pd_2I_2(C_3H_5)_2]$ showing the fifteen 'lines'

We have now measured these small couplings in two symmetrical π-allyl ligands. It has been previously reported that the ^1H n.m.r. 2-chloroallyl pattern of [Pd(2-chloroallyl)(acac)] consists of two doublets.[15,16] Under high resolution we now observe eight 'lines' for each type of hydrogen (*syn* or *anti*) and analysis of the spectrum as an AA′XX′ spin system yields *J*(2—3) 2·8 Hz, *J*(2—4) 2·7 Hz, *J*(2—5) 0·2 Hz, and *J*(3—5) 0·5 Hz; error ± 0·2 Hz. We have also determined H–H coupling constants, not observable in the main resonance by examining ^{13}C satellite patterns. Thus the *syn*-hydrogen satellite pattern for [Pd(2-methylallyl)(cyclopentadienyl)] in C_6H_6 {$J(^{13}CH)$ 157·3 Hz} showed *J*(2—4) to be 2·8 Hz and for the *anti*-hydrogen $J(^{13}CH)$ 159·3 Hz and *J*(3—5) 0·9 Hz. Coupling of H_3 to H_2 or H_4 must be small (<0·4 Hz). In addition we find that for the methyl group $^1J(^{13}CH)$ 127·6 Hz and that the cyclopentadienyl group has a ^{13}C satellite pattern similar to that already reported for ferrocene and related

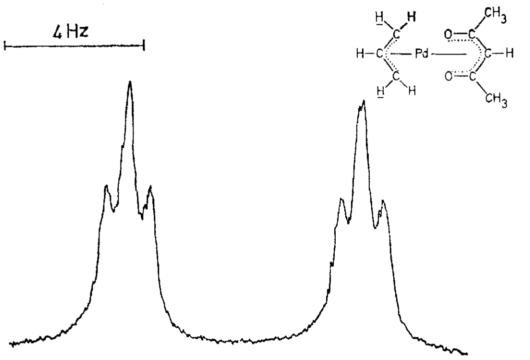

FIGURE 2 ^1H N.m.r. pattern of the *anti*-protons (H_3 and H_5) of $[Pd(acac)(C_3H_5)]$

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[12] J. W. Emsley, J. Feeney, and L. H. Sutcliffe, 'High Resolution N.M.R. Spectroscopy,' Pergamon, London, 1966.

[13] C. W. Haigh in 'Annual Reports of N.M.R. Spectroscopy 1971, **4**, p. 311; 'LAOCOON 3,' by A. A. Bothner-By and S. Castellano in 'Computer Programmes for Chemistry,' ed. D. F. De Tar, Benjamin, New York, vol. 1, 1968.

[14] K. Vrieze, A. P. Praat, and P. Cossee, *J. Organometallic Chem.*, 1968, **12**, 533.

[15] M. S. Lupin and B. L. Shaw, *Tetrahedron Letters*, 1964, 883.

[16] M. S. Lupin, J. Powell, and B. L. Shaw, *J. Chem. Soc.* (*A*), 1966, 1687.

compounds[17] with $^1J(^{13}CH)$ 170·96 ± 0·17 Hz, $^3J(HH)$ 2·490 ± 0·084, and $^4J(HH)$ 1·945 ± 0·063 Hz.

We have examined in detail including the determination of *relative signs* by double resonance, the ^1H n.m.r. spectra of $[Pd_2Cl_2(1,1\text{-dimethylallyl})_2]$ and [Pd(acac)(1-phenylallyl)] in deuteriochloroform. With the numbering of the protons shown in (2) the data are τ_1 4·91, τ_2 6·16, τ_3 6·99, τ_6 8·56, τ_7 8·75, $J(1—2)$ ±7·3, $J(1—3)$ ±12·7, $J(1—6)$ 0·45, $J(2—3)$ ±1·3, $J(2—6)$ 0·2, $J(2—7)$ $\leqslant$0·1, $J(3—6)$ *ca.* 0·1, $J(3—7)$ *ca.* 0·1 Hz. For the *syn*-1-phenylallyl ligand (3) of [Pd(acac)(1-phenylallyl)] the data are τ_1 4·15, τ_2 6·17, τ_3 8·05, τ_5 5·55, $J(1—2)$ ±6·9, $J(1—3)$ ±11·9, $J(1—5)$ ±11·2, $J(2—3)$ ∓1·0, $J(3—5)$ ∓1·0, $J(2—5)$ ∓0·4 Hz. At room temperature, two rather broad methyl resonances due to the acetylacetonate of [Pd(acac)(1-phenylallyl)] were found. The resonances sharpened when the solution was cooled to −10° and coalesced on warming, but attempts to determine activation parameters were foiled due to decomposition. The coalescence temperature depended on the extent of decomposition.

^{13}C *N.m.r. Data*.—Some of the ^{13}C n.m.r. data have previously been reported by us.[18] We give in Table 2 the complete data. For $[PdCl(allyl)(PPh_3)]$ only broad ^{13}C n.m.r. signals were observed at room temperature, probably due to chemical exchange, but at 0° the signals were sharp. We have also examined the ^{13}C n.m.r. spectra of 1—3-η-cyclo-octa-2,4-dienyl-palladium complexes $[PdY(C_8H_{11})]$ (Y = acac or C_5H_5).

DISCUSSION

Our spectra, Figures 1 and 2, multiplicity and coupling constant data (see above and Table 1), show that the spin system of symmetrical π-allylpalladium complexes should be described as AA′BB′C. Previously assignments of stereochemistry in allylic-palladium complexes have been made on the assumption that *trans*-(HH) and *cis*-(HH) couplings parallel those found in olefins;[2-9] *i.e.*, *trans* > *cis*. Our results for $[Pd_2Cl_2(1,1\text{-dimethylallyl})_2]$ and [Pd(acac)(1-phenylallyl)] lend support to this assumption since we show that $^3J(H_1H_2)$ and $^3J(H_1H_3)$ are of the same sign; couplings between *cis*- and *trans*-vicinal hydrogens in olefins are also of the same sign.

The ^{13}C n.m.r. data of several allylic palladium complexes have been reported previously in a brief note.[18] Recently, data have been published for $[Ni_2X_2(1\text{-methylallyl})_2]$ where X = Cl, Br, I.[19] There are several features of note. Firstly, as the ligand(s) in *trans*-position to the allylic group are changed the chemical shift of the terminal allylic carbons moves to high field in the order, I < Br < Cl < acac < C_5H_5. This order is similar to that found for the methyl group *trans* to X in compounds $[PtMe_3X(AsMe_2Ph)_2]$, configuration (4). Here for Me_A the order of increasing chemical shift is I < Br < Cl < Me, whereas for Me_B (*trans* to arsenic) the order is Cl < Br < I ∼ Me.[20] When the π-allyl

TABLE 2

^{13}C N.m.r. chemical shift data for allylic palladium complexes

	C-1	C-2	C-3	Me	acac			Others
					CO	Me	CH	
$[(\pi\text{-}C_3H_5)PdCl]_2$	63·2	111·9	63·2					
$[(\pi\text{-}C_3H_5)PdBr]_2$	65·2	111·3	65·2					
$[(\pi\text{-}C_3H_5)PdI]_2$	68·0	110·2	68·0					
$[(\pi\text{-}C_3H_5)Pd(acac)]$	55·8	113·5	55·8		187·7	27·9	99·0	
$[(\pi\text{-}C_3H_5)Pd(C_5H_5)]$	45·8	95·0	45·8					94·7 (C_5H_5)
$[(\pi\text{-}C_3H_5)PdCl(PPh_3)]$	62·0	118·7	79·4					
$[(\pi\text{-}2\text{-}MeC_3H_4)PdCl]_2$	61·7	127·9	61·7	23·1				
$[(\pi\text{-}2\text{-}MeC_3H_4)PdBr]_2$	64·4	127·2	64·4	23·3				
$[(\pi\text{-}2\text{-}MeC_3H_4)PdI]_2$	67·6	125·6	67·6	23·5				
$[(\pi\text{-}2\text{-}MeC_3H_4)Pd(acac)]$	54·8	129·2	54·8	23·4	187·9	27·9	99·7	
$[(\pi\text{-}2\text{-}MeC_3H_4)Pd(C_5H_5)]$	47·0	112·2	47·0	23·6				94·7 (C_5H_5)
$[(\pi\text{-}1\text{-}MeC_3H_4)Pd(acac)]$	73·6	113·3	51·6	17·0	188·7	28·2	100·0	
$[(\pi\text{-}1\text{-}MeC_3H_4)Pd(acac)]$	75·0	108·8	*a*		188·8	28·2	97·8	C_6H_5: π-C_3H_4-C< 139·6; *o*-CH 129·7; *m*-CH 128·7; *p*-CH 128·4
$[(\pi\text{-}1\text{-}PhCH_2C_3H_4)Pd(acac)]$	77·6	112·0	52·6		188·9	28·3	100·1	$CH_2C_6H_5$: CH_2 38·0; CH_2–C< 145·4; *o*-CH 130·1; *m*-CH 129·5; *p*-CH 127·3
$[(\pi\text{-}1\text{-}Me\text{-}3\text{-}PhC_3H_3)Pd(acac)]$	70·6 [b]	109·5	71·4 [b]	17·0	*c*	28·3	100·1	C_6H_5: –C< 140·1; *o*-CH 129·6; *m*-CH 128·2; *p*-CH 128·1
$[(C_8H_{11})Pd(acac)]$	68·0	103·6	73·6		188·7	28·3	99·9	=CH 126·0; 133·6 >CH_2 25·2; 26·7; 29·2
$[(C_8H_{11})Pd(C_5H_5)]$	62·2	91·1	67·1					=CH 124·6; 136·2 >CH_2 26·1; 30·4; 32·2 C_5H_5 95·2

[a] Not found. Possibly obscured by CH_2Cl_2 solvent resonance. [b] Relative assignment unknown. [c] Not found.

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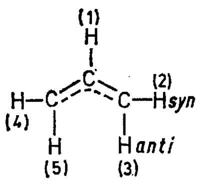
[17] R. W. Crecely, K. M. Crecely and J. H. Goldstein, *Inorg. Chem.*, 1969, **8**, 252.

[18] B. E. Mann, R. Pietropaulo, and B. L. Shaw, *Chem. Comm.*, 1971, 790.

[19] L. A. Churlyaeva, M. I. Lobach, G. P. Kondratenkov, and V. A. Korner, *J. Organometallic Chem.*, 1972, **39**, C23.

[20] A. J. Cheney, B. E. Mann, and B. L. Shaw, unpublished results.

group is substituted with a methyl, phenyl, or benzyl group, the signal due to the carbon atom at which the substitution occurs moves between 15 and 22 p.p.m. to



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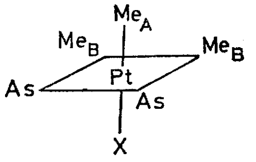

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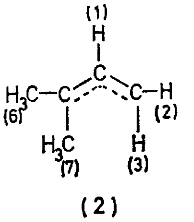

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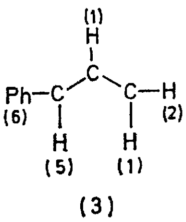

(3)

low field (Table 2). This can be compared with the average shift of *ca.* 9 p.p.m. found for alkanes or arenes [21] on substitution of a proton by a methyl group. Thus the ^{13}C chemical shifts of π-allylic groups appear to be more sensitive to substitution than alkanes or arenes. A similar larger shift on substitution has been found for ferrocenes,[22] where the methyl group in (MeC$_5$H$_4$)Fe(C$_5$H$_5$) produces a shift of 15·5 p.p.m. to low field in the substituted carbon atom and for [Cr(CO)$_3$(mesitylene)] compared to [Cr(CO)$_3$C$_6$H$_6$] where substitution produces a low-field shift of 17·8 p.p.m.[23,24]

Secondly, in all cases where data are available, the formation of a π-complex produces a shift in the ^{13}C resonance to high field. In our preliminary communication, we explained these observations on allylic palladium compounds by a valence bond treatment of the bonding between the allyl ligand and the metal. We now discuss this explanation in more detail. There are six contributing canonical forms (a)—(f) (Figure 3) that we shall consider. On the basis that forms (a), (b), (d), and (e) are important contributions to the structure one would reasonably expect terminal π-allylic carbons to have a ^{13}C chemical shift half way between that of an olefinic CH$_2$ and a CH$_2$ group attached to a metal. In agreement with this, our range of terminal ^{13}C shifts 47·0—67·6 p.p.m. spans the average (59·3 p.p.m.) of the shifts for [IrCl$_2$(*C*H$_2$CMe:CH$_2$)(CO)(AsMe$_2$Ph)$_2$], δ 10·6 p.p.m. and [IrCl$_2$(CH$_2$CMe:*C*H$_2$)(CO)(AsMe$_2$Ph)$_2$], δ 107·9 p.p.m.[25] However, the ^{13}C shifts for the central carbon atoms of [PdX(2-methylallyl)]$_2$ (*ca.* 127 p.p.m.) are not close to the shift of the central carbon atom of [IrCl$_2$(CH$_2$CMe:CH$_2$)(CO)(AsMe$_2$Ph)$_2$] (δ 145·2 p.p.m.), possibly because canonical forms (c) and (f) contribute significantly to the structure. Further information on the bonding comes from the magnitude of $^1J(^{13}C^1H)$ for the terminal CH$_2$ groups of the allyl ligand, being 157·3 Hz for the *syn*-hydrogens and 159·3 Hz for the *anti*-hydrogens of [Pd(2-methylallyl)(C$_5$H$_5$)]. Similar results have been reported for [NiX(1-methylallyl)]$_2$.[19] Thus the terminal allylic carbons are approximately sp^2 in character, consistent with either the Chatt–Dewar model for π-complexes or with the valence bond treatment described above if it is postulated that the terminal carbon atoms bond to the metal using $2p$-orbitals.

We have also examined briefly the ^{13}C n.m.r. spectra of 1—3-η-cyclo-octa-2,4-dienyl-palladium complexes [PdY(C$_8$H$_{11}$)] (Y = acac or C$_5$H$_5$). The *X*-ray structure of the acac-compound shows that only three carbons are bonded to the palladium,[26] but from ^{1}H n.m.r. spectroscopy we could not decide whether the molecules were fluxional at 34°.[27] Our observations of all eight ^{13}C resonances for the cyclo-octadienyl ligand (Table 2) show that they are not fluxional.

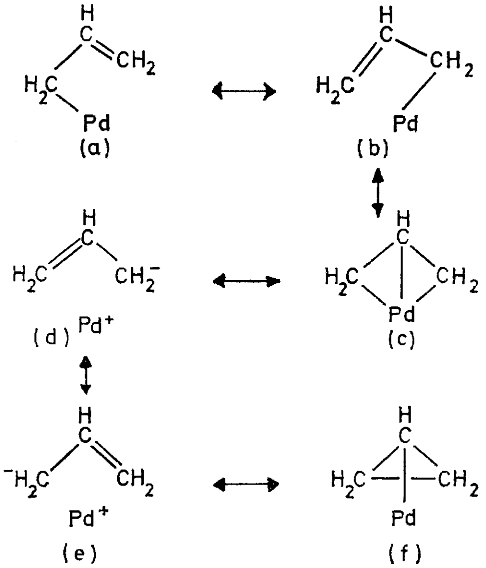

FIGURE 3 Canonical forms of the allyl–palladium system

EXPERIMENTAL

The allylic palladium complexes have all been described previously. The ^{1}H and ^{13}C n.m.r. spectra were measured using a Bruker HFX-90 n.m.r. spectrometer. For the ^{13}C n.m.r. spectra *ca.* 10% C$_6$F$_6$ was added to the CH$_2$Cl$_2$ solution to provide a field-frequency lock and white noise ^{1}H decoupling was used. The ^{13}C chemical shifts are with respect to internal ^{13}CH$_3$SiMe$_3$ and are in the sense that increasing frequency is positive.

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[21] D. M. Grant, and E. G. Paul, *J. Amer. Chem. Soc.*, 1964, **86**, 2984.

[22] B. E. Mann, B. L. Shaw, and M. M. Truelock, unpublished results.

[23] E. Farnell, E. W. Randall, and E. Rosenberg, *Chem. Comm.*, 1971.

[24] B. E. Mann, *Chem. Comm.*, 1971, 976.

[25] B. E. Mann, B. L. Shaw, and R. E. Stainbank, unpublished results.

[26] M. R. Churchill, *Chem. Comm.*, 1965, 625.

[27] S. D. Robinson and B. L. Shaw, *J. Chem. Soc.*, 1964, 5002.