Use of Carbon-13 Nuclear Magnetic Resonance Spectroscopy for determining the Position of Deuterium Incorporation into Simple Alkenes and into Tertiary Phosphine Complexes of Platinum(II)

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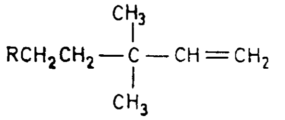
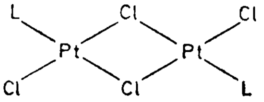
Carbon-13 n.m.r. spectroscopy is shown to be a valuable analytical tool—offering considerable advantages over other physical methods—for investigating the site, and in some cases the degree, of deuterium incorporation in several simple alkenes and also in various tertiary phosphine complexes of platinum(II). ^{13}C N.m.r. data are presented for the alkenes, $CH_2{=}CHC(CH_3)_2R$ (R = Et, Pr, and Bu) together with their partially deuteriated analogues and also for the complexes $[M_2Cl_4L_2]$ (M = Pd or Pt; and L = PEt_3, PPr_3, PBu_3, or $PBu^t{}_2Pr$) together with the partially deuteriated analogues [M = Pt and L = $PPr_3(D)$, $PBu_3(D)$, or $PBu^t{}_2Pr(D)$].

THE application of ^{13}C n.m.r. spectroscopy to problems arising in organometallic chemistry is a rapidly expanding area of study.[1-7] ^{13}C N.m.r. spectroscopy has been shown to be useful in studying the stereochemistry of tertiary phosphine- or tertiary arsine–transition-metal complexes [1] and also in determining, to some extent, the nature of bonding in transition metal–olefin,[2,4-6] -allyl,[3,5] -acetylene,[4] and -carbene [7] complexes. We here report on the application of ^{13}C n.m.r. spectroscopy to the problem of locating the site of deuteriation in several alkenes and also in some alkyl-tertiary phosphine complexes of platinum(II).


(I)


(II)

We have recently reported [8,9] that alkenes of type (I; R = H, CH_3, or Et) undergo H–D exchange in the presence of a homogeneous platinum catalyst and further that complexes of type (II; L = PPr_3, PBu_3, or $PBu^t{}_2Pr$) give rise to complexes containing deuteriated tertiary phosphine ligands on treatment with aqueous (D_2O) acetic acid (CH_3CO_2D) at 100 °C.[10,11]

In any discussion of the mechanism of these exchange reactions it is clearly of considerable importance to know the position of deuterium incorporation into the alkyl moiety. The ^{1}H n.m.r. spectra of deuteriated samples of either (I) or (II) show that deuterium has entered the compound [integration of the signals due to the protons of either (I) or (II) against an internal standard]. However, owing to the extensive overlap of the proton signals of alkyl groups with three or more carbon atoms it is difficult and sometimes impossible to determine which of the protons have exchanged with deuterium. Similarly, i.r. and mass-spectral techniques, while showing the presence of deuterium in the sample, do not easily allow the position of deuterium incorporation to be determined.

^{13}C N.m.r. spectroscopy, however, appears to be a very convenient analytical tool for determining the position of deuterium incorporation into an alkyl chain since each carbon atom in an alkyl group of six or less carbon units generally gives rise to a distinct ^{13}C n.m.r. signal. Thus, by observing changes in the intensity—and in some cases in the multiplicity—of these signals after deuteriation of the molecule, it is possible to locate the position of deuterium incorporation.

TABLE 1

^{13}C Shifts of 3,3-dimethylpent-1-ene, 3,3-dimethylhex-1-ene, and 3,3-dimethylhept-1-ene and their 5-deuterio-analogues [a]

	C_1	C_2	C_3	C_4	C_5	C_6	C_7	CH_3
$H_2C{=}CHC(CH_3)_2CH_2CH_3$	82·9	45·1	156·6	158·0	184·4			166·7
$H_2C{=}CHC(CH_3)_2CH_2CD_3$	82·9 [b]	45·1 [b]	156·5	158·0	[c]			
$H_2C{=}CHC(CH_3)_2CH_2CH_2CH_3$	82·9	44·7	156·4	147·4	175·2	178·0		166·0
$H_2C{=}CHC(CH_3)_2CH_2CHDCH_3$	82·3 83·2 [d] 84·1	44·1 44·9 [d] 45·7	156·4	147·4	174·8 175·5 176·3	178·0		166·0
$H_2C{=}CHC(CH_3)_2CH_2CH_2CH_2CH_3$	82·9	44·7	156·5	150·1	166·0	169·5	179·0	166·0
$H_2C{=}CHC(CH_3)_2CH_2CHDCH_2CH_3$	83·0 [e]	44·7 [e]	156·5	150·1	165·8 [d] 166·5 [d] 167·2	169·5	179·0	166·0

[a] Obtained using solvent CH_3CO_2D (50 mol %) in D_2O. [alkene] = 0·2M, [$HClO_4$] = 0·2M, [K_2PtCl_4] = 0·02M; temp. = 100 °C; reaction time = 3 h. [b] Very little deuterium exchange at these sites. [c] No signal observed for deuteriated methyl group. [d] Signal masked by residual protonated-carbon signal. [e] Broad ill-defined signal.

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[9] P. A. Kramer and C. Masters, *J.C.S. Dalton* 1975, 849.

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RESULTS AND DISCUSSION

(A) *Position of Deuterium Incorporation into Alkenes of Type* $RCH_2CH_2C(CH_3)_2CH=CH_2$ (R = H, Me, or Et).—The ^{13}C n.m.r. spectra were recorded for 3,3-dimethylpent-1-ene, 3,3-dimethylhex-1-ene, and 3,3-dimethylhept-1-ene both before and after deuteriation. The data are listed in Table 1. We shall only discuss our results for 3,3-dimethylhex-1-ene in detail since the data for the other two alkenes may be interpreted in an analogous manner.

The ^{13}C n.m.r. spectrum of undeuteriated 3,3-dimethylhex-1-ene, with complete decoupling of the protons, shows seven distinct signals arising from the seven different carbon nuclei present in the alkene. The procedure for assigning the signals to the different carbon atoms is relatively simple. In addition to the fully proton-decoupled spectrum, a spectrum is recorded with only partial proton decoupling. In the latter spectrum some of the proton–carbon spin decoupling is restored and from the signal pattern thus generated the type of carbon can be identified (*i.e.* a CH_3 group gives rise to a quartet, a CH_2 group to a triplet, *etc.*). When a number of CH_2 groups are present in an alkyl chain then the assignments are made with the aid of empirical shift formulae.[12] Complete assignments are given in Table 1.

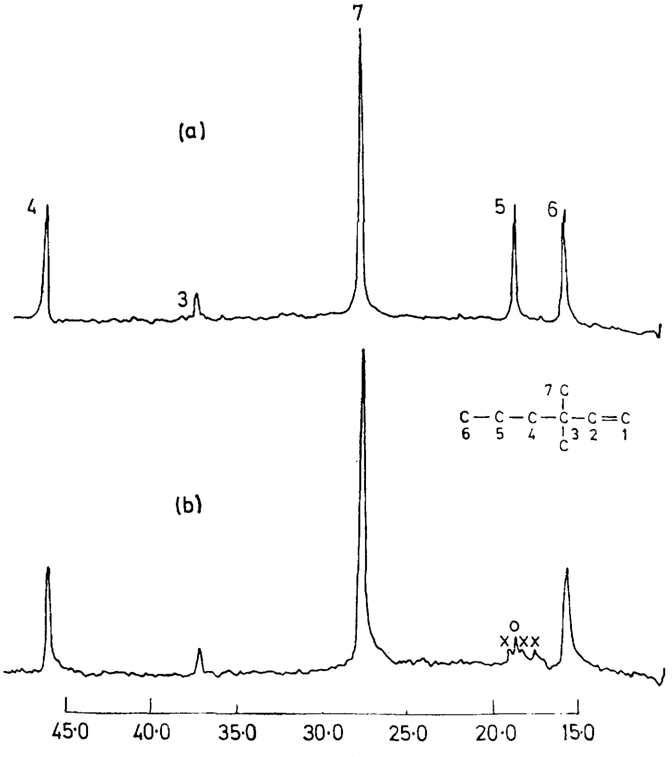
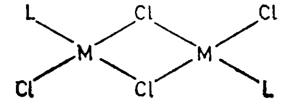


FIGURE 1 ^{13}C N.m.r. spectra of the alkyl carbons of 3,3-dimethylhex-1-ene in chloroform: (a) undeuteriated and (b) partially deuteriated

For the deuteration studies the signals arising from the alkyl carbons are of most interest. The alkyl part of the ^{13}C n.m.r. spectrum of 3,3-dimethylhex-1-ene (with full decoupling of all the protons) is shown in Figure 1(a) together with the assignments. Figure 1(b) depicts the corresponding region for a deuteriated sample of the alkene which is known to contain 8 $\pm$ 5% deuterium in the alkyl moiety. A comparison of the two spectra reveals that in the spectrum of the deuteriated sample the signal due to C-5 is considerably reduced in intensity and further that a triplet (indicated by x) is present. Apart from this the spectrum is essentially unaltered. These observations show that (i) deuterium incorporation has occurred specifically in the alkyl moiety at C-5, since the signals due to the other carbon nuclei are unchanged, (ii) the predominant deuteriated species is –CHD– since we observe a triplet resulting from coupling of C-5 with one deuterium nucleus (spin = 1), and (iii) the degree of deuteriation at C-5 is *ca.* 45% {from a comparison of the relative intensity of the signal due to undeuteriated C-5, indicated by o [Figure 1(b)] in the deuteriated sample to that present in the undeuteriated sample}.

The change in position of the signal from the deuteriated C-5 compared to that of undeuteriated C-5 (0·3 p.p.m. to high field) is due to the isotope effect of deuterium. Such isotope shifts of 0·2—0·5 p.p.m. to higher field in ^{13}C chemical shifts induced by directly bonded deuterium have been observed [13] in other deuteriated systems.*

(B) *Position of Deuterium Incorporation into Tertiary Phosphine Complexes of Platinum*(II) *of Type* $[Pt_2Cl_4L_2]$ (L = PPr_3 *or* PBu_3).—We have recorded the ^{13}C n.m.r. spectra of a series of platinum and palladium complexes of type (III; M = Pd or Pt and L = PEt_3, PPr_3, or PBu_3; and M = Pt, L = PBu^t_2Pr) together with deuteriated samples of di-μ-chloro-dichlorobis(tri-n-propylphosphine)diplatinum(II), di-μ-chloro-dichlorobis(tri-n-butylphosphine)diplatinum(II), and di-μ-chloro-dichlorobis(di-t-butylpropylphosphine)diplatinum(II).



(III)

The data are listed in Tables 2 and 3 together with the spectral assignments. The assignments for the platinum complexes are somewhat complicated by the effect of ^{31}P–^{13}C coupling and by the fact that the usual alkane shifts are modified by the proximity of both phosphorus and platinum nuclei. The CH_3 carbon of the tertiary phosphine ligand is easily identified by partial decoupling. The remaining assignments given in Table 2 were obtained mainly by identifying the ^{195}Pt–$^{13}C(1)$ and ^{195}Pt–$^{13}C(2)$ coupling constants. These coupling constants were found by comparing the ^{13}C n.m.r. spectra of

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* While this work was in progress, others [13] reported on the use of ^{13}C n.m.r. spectroscopy in determining the position of deuterium incorporation into benzonitriles.

[12] L. P. Lindeman and J. Q. Adams, *Analyt. Chem.*, 1971, **43**, 1245.

[13] G. L. Lebel, J. D. Laposa, B. G. Sayer, and R. A. Bell, *Analyt. Chem.*, 1971, **43**, 1500.

TABLE 2

^{13}C Chemical shifts and ^{31}P–^{13}C and ^{195}Pt–^{13}C coupling constants (J/Hz) for three tertiary phosphine complexes of platinum and their deuteriated analogues plus three analogous complexes of palladium

Metal and ligand	C_1	C_2	C_3	C_4	J_{PC_1}	J_{PC_2} †	J_{PC_3}	J_{PC_4}	J_{PtC_1}	J_{PtC_2}
$[PtP(CH_2CH_3)_3]$	15·3	8·1			41	4			38	22
$[PdP(CH_2CH_3)_3]$	17·5	8·6			32	<5				
$[PtP(CH_2CH_2CH_3)_3]$	25·3	17·2	16·1		39	<5	14		34	20
$[PtP(CH_2CH_2CD_3)_3]$	25·3	16·9			41	<5			36	24
$[PdP(CH_2CH_2CH_3)_3]$	27·2	18·4	16·3		32	<5	14			
$[PtP(CH_2CH_2CH_2CH_3)_3]$	22·8	26·2	24·6	14·2	39	<5	15	0	39	20 *
$[PtP(CH_2CH_2CD_2CH_3)_3]$	22·8	26·2		14·2	39	<5		0	34	20
$[PtP(CH_2CH_2CD_2CD_3)_3]$	22·8	26·2		13·3	39	<5			38	20
$[PdP(CH_2CH_2CH_2CH_3)_3]$	24·5	26·6	24·6	14·1	32	<5	15	0		

* Not fully resolved shoulders. † Slight signal broadening observed.

the platinum complexes with the spectra of the analogous palladium complexes. Palladium has no spin whereas platinum-195 (natural abundance 33·7%) has a spin of $\frac{1}{2}$. Similar chemical shifts are expected for complexes of the two metals. Thus by comparing the ^{13}C n.m.r. spectrum of $[Pt_2Cl_4(PEt_3)_2]$ with that of $[Pd_2Cl_4(PEt_3)_2]$ having identified the $-CH_3$ signal by partial decoupling, we were able to show that $J_{^{195}Pt-^{13}C(1)} = 36 \pm 3$ Hz and that $J_{^{195}Pt-^{13}C(2)} = 22 \pm 2$ Hz. Identification of these couplings in the spectra of $[Pt_2Cl_4(PPr_3)_2]$ and $[Pt_2Cl_4(PBu_3)_2]$ together with the CH_3 signal assignment allows a complete assignment of the spectrum to be made. One unusual feature of the spectra is the fact that $J_{^{31}P-^{13}C(3)}$ is greater than $J_{^{31}P-^{13}C(2)}$, (*ca.* 14 compared to *ca.* 5 Hz); we are not able to offer any satisfactory explanation for this observation at the present time. No such trend is observed in the free phosphines:

PPr_3 $\delta C(1) = 30{\cdot}1$; $\delta C(2) = 19{\cdot}6$; $\delta C(3) = 15{\cdot}5$
$J_{PC(1)} = 14{\cdot}5$; $J_{PC(2)} = 14{\cdot}5$; $J_{PC(3)} = 11{\cdot}5$
PBu_3 $\delta C(1) = 27{\cdot}9$; $\delta C(2) = 27{\cdot}1$; $\delta C(3) = 24{\cdot}0$; $\delta C(4) = 13{\cdot}0$
$J_{PC(1)} = 14{\cdot}0$; $J_{PC(2)} = 14{\cdot}5$; $J_{PC(3)} = 10{\cdot}5$; $J_{PC(4)} \leqslant 1$

We have used ^{13}C n.m.r. spectroscopy to determine the position of deuterium incorporation into deuteriated samples of the three platinum complexes, di-μ-chloro-dichlorobis(tri-n-propylphosphine)diplatinum(II), di-μ-chloro-dichlorobis(tri-n-butylphosphine)diplatinum(II), and di-μ-chloro-dichlorobis(di-t-butylpropylphosphine)-diplatinum(II). Figure 2(a) shows the ^{13}C n.m.r. spectrum of the undeuteriated tri-n-butylphosphine complex together with the spectral assignments. Figure 2(b) is the spectrum of the sample complex containing 20 ± 5% deuterium in the butyl moiety. It can be seen that the signal assigned to C-3 is absent from the spectrum while the other signals are essentially unaltered. This shows that the deuterium is situated predominantly (>80%) at C-3 (the absence of a signal from the deuteriated C-3 is probably due to carbon–deuterium coupling together with deuterium quadrupole broadening, rendering it too weak to be observed).

In Figure 2(c) we show the spectrum of the sample containing 48 ± 5% deuterium. In this spectrum both the signals due to C-3 and C-4 are absent, indicating that in this case the deuterium is situated both at C-3 and C-4. In the case of the deuteriated tri-n-propyl complex we found that deuterium incorporation occurred specifically at C-3 (see Table 2).

The ^{13}C data of the deuteriated di-t-butylpropylphosphine complex presented in Table 3 show that deuterium incorporation occurs initially at C-3 of the propyl group followed by a slower exchange at C-2 of the propyl group and at the methyl groups of the t-butyl units.

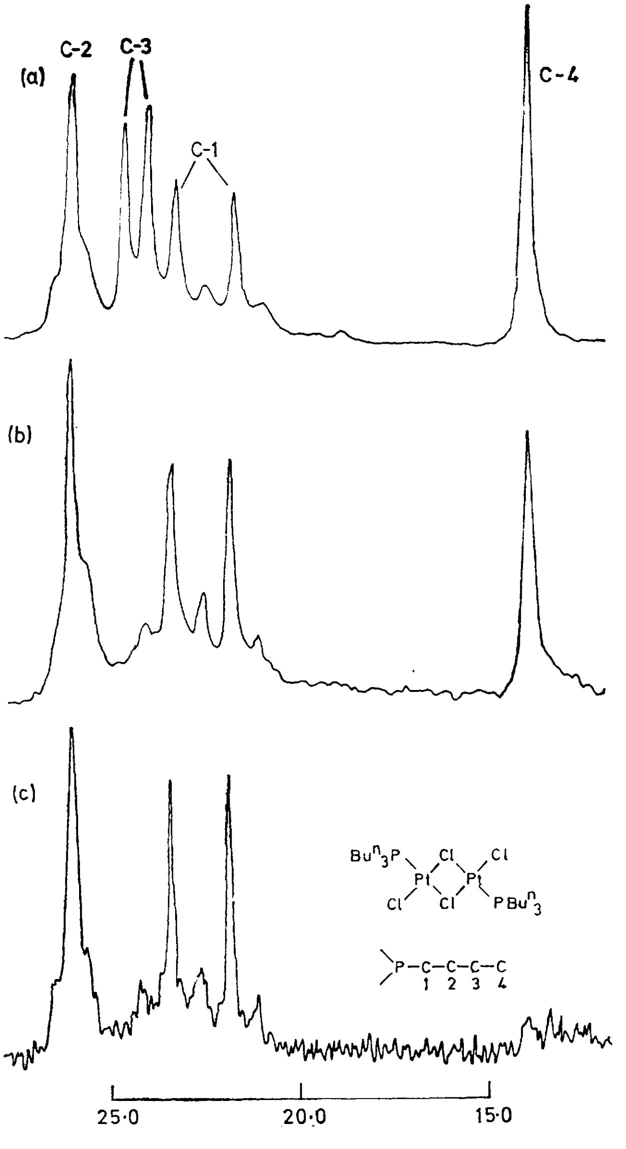
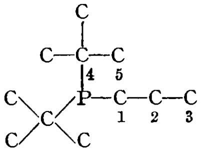


FIGURE 2 ^{13}C N.m.r. spectra of $[Pt_2Cl_4(PBu^n_3)_2]$ in chloroform: (a) undeuteriated, (b) deuteriated at C-3, and (c) deuteriated at C-3 and C-4

TABLE 3

^{13}C N.m.r. data of [$Pt_2Cl_4(PBu^t{}_2Pr)_2$] and deuteriated analogues



D in PBu$^t{}_2$Pr	Chemical shifts, δ(CS_2) (±0·3 p.p.m.)					Coupling constants (J/Hz; ±3 Hz)									
% ± 5	C_1	C_2	C_3	C_4	C_5	J(P-C_1)	J(P-C_2)	J(P-C_3)	J(P-C_4)	J(P-C_5)	J(Pt-C_1)	J(Pt-C_2)	J(Pt-C_3)	J(Pt-C_4)	J(Pt-C_5)
0	171·3	173·4	176·9	156·3	162·4	32	$\leqslant 5$	14	28	3	27	11	*e*	38	16
16	170·7	173·5	177·3 [a]	156·0	163·0	29	*e*	*e*	*e*	*e*	*e*	*e*	*e*	*e*	*e*
38	171·3	173·5	*b*	156·6	162·8 [d] 163·1 164·1	32	*e*	*b*	29	*e*	27	*e*	*b*	*e*	*e*
59	171·4	173·8	*b*	156·9	163·4 [d] 163·8 164·1 164·8	34	*e*	*b*	27	*e*	*e*	*e*	*b*	*e*	*e*
78	171·0	173·5	*c*	156·2	162·4 [d] 163·3 164·0 164·8	32	*e*	*e*	*e*	*e*	*e*	*e*	*e*	*e*	*e*

[a] Very weak signal. [b] No signal for C-3 observed. [c] Complex signal centred at 178 p.p.m. assigned to completely deuteriated C-3. [d] Complex signal due to partially deuteriated C-5 methyl groups. [e] No coupling detected.

EXPERIMENTAL

The preparation of the various complexes has been described elsewhere.[9,11,14] ^{13}C N.m.r. spectra were recorded on a Varian HA 100 spectrometer in the pulse Fourier-transform mode at 25·1 MHz. Solutions were *ca.* 0·1M in either chloroform or carbon tetrachloride; the reference lock was external ^{13}C-enriched CS_2. Proton-decoupled spectra were obtained with the aid of random noise decoupling. The partially decoupled spectra were recorded by offsetting the proton-decoupling frequency.

Spectral resolution was in general of the order of 5 Hz.

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