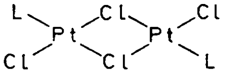
Hydrogen–Deuterium Exchange at a Saturated Carbon Atom in Tertiary Phosphine Complexes of Platinum(II)

By **Albertus A. Kiffen, Christopher Masters,*** and **Laurent Raynand,** Koninklijke/Shell-Laboratorium, Amsterdam (Shell Research B.V.)

Chloro-bridged diplatinum(II) complexes of the type $[Pt_2Cl_4L_2]$ (L = PPr_3, PBu_3, PBu^tPr_2, $PBu^t{}_2Pr$, $PPrPh_2$, PPr_2Ph, or PBu^tPh_2), undergo a regiospecific hydrogen-deuterium exchange in an aqueous (D_2O) acetic acid (CH_3CO_2D) medium to give complexes containing deuterium in the alkyl groups of the tertiary phosphine moiety and, in the case of L = PBu^tPh_2, also in the aryl groups. The steric requirements of the tertiary phosphine have a marked influence on both the rate and the position of deuterium incorporation. The results presented show that, in internal-metallation reactions of platinum, the ease of ring formation decreases in the order five-membered > six-membered > four-membered rings. It is suggested that in such reactions steric rather than electronic factors are dominant.

INTERACTIONS occurring between transition metals and carbon–hydrogen bonds of co-ordinated ligands are currently the subject of much study.[1-11] Such interactions are well established in complexes containing arylphosphine [2-8] or aryl phosphite [9-11] ligands. There are, however, only a few examples known of such interactions in transition-metal complexes containing unidentate tertiary alkylphosphines as ligands. Ring closure of di-t-butylpropylphosphine to platinum(II) *via* the propyl group has been reported [3] and it has been suggested [12] that ring closure of triethylphosphine to platinum(II) occurs when *trans*-$[PtCl_2(PEt_3)_2]$ is treated with lithium derivatives of carbaboranes.

We previously reported [13] that alkenes of the type $RC(CH_3)_2CH{=}CH_2$ (R = Et, Pr, or Bu) undergo platinum-catalysed hydrogen–deuterium exchange in the alkyl moiety, R, exclusively at C-5, indicating the formation of five-membered ring intermediates. We further found that complexes of type (I) where L = $CH_2{=}CHCMe_2R$ (R = Me, Et, or Pr) are formed during the deuteriation reaction. In order to test the generality of this regiospecificity, and to gain a better insight into the mechanism of the exchange, we have investigated the hydrogen–deuterium exchange in complexes of type (I) (L = PEt_3, PPr_3, PBu_3, PBu^tPr_2, $PBu^t{}_2Pr$, $PPhEt_2$, PPh_2Et, PPh_2Pr, $PPhPr_2$, and PBu^tPh_2). This class of compounds was chosen for three main reasons. (*a*) There is a close similarity in structure between the tertiary phosphine–platinum complexes and the alkene–platinum complexes isolated from the platinum-catalysed H–D exchange in alkenes.[13]


(I)

(*b*) Tertiary phosphines are known to form strong bonds with platinum and therefore dissociation of the ligand L, as observed for L = alkene,[14] should not occur. Thus the kinetics of the exchange process should be simplified.

(*c*) Tertiary phosphines are thought to stabilize platinum–hydride complexes [15] and to help in the isolation of complexes containing platinum–carbon bonds. Therefore the presence of tertiary phosphine ligands might facilitate the isolation of some of the intermediates postulated for the H–D exchange process.

A preliminary report of our results has already appeared.[16]

RESULTS

(A) *Initial Experiments.*—As an initial experiment we attempted to exchange H for D in complexes of type (I) (L = PEt_3, PPr_3, or PBu_3), under conditions essentially identical with those adopted for the alkene exchange reactions,[13] *i.e.* 0·02M-complex in D_2O–CH_3CO_2D (1 : 6) containing 0·23M-$HClO_4$ and heated at 100 °C for 2 h. With L = PEt_3 we found no deuterium incorporation; with L = PPr_3 and PBu_3 we observed 31 ± 5 and 25 ± 5% deuteriation, respectively. Apart from the deuteriation the complexes were recovered unchanged.

With L = PPr_3 the 60 MHz ^1H n.m.r. spectrum of complex (I) in CD_2Cl_2 shows two well separated signals, centred at 1·04 and 1·67 p.p.m. The former signal is due to the protons of the terminal methyl group, *i.e.* C-3, and the latter to the protons on C-1 and C-2. Upon deuteriation the intensity of the signal at 1·67 p.p.m. remains unaltered while that of the signal at 1·04 p.p.m. is considerably diminished (see Figure 1). Thus with L = PPr_3 deuterium incorporation occurs specifically at C-3. The i.r. spectrum (KBr disc) of the deuteriated complex is in agreement

---

[1] G. W. Parshall, *Accounts Chem. Res.*, 1970, **3**, 139, and refs. therein.

[2] E. K. Barefield and G. W. Parshall, *Inorg. Chem.*, 1972, **11**, 964.

[3] A. J. Cheney, B. E. Mann, B. L. Shaw, and R. M. Slade, *J. Chem. Soc.* (*A*), 1971, 3833.

[4] D. F. Gill and B. L. Shaw, *J.C.S. Chem. Comm.*, 1972, 65.

[5] B. N. Cockburn, D. V. Howe, T. Keating, B. F. G. Johnson, and J. Lewis, *J.C.S. Dalton*, 1973, 404.

[6] J. M. Duff and B. L. Shaw, *J.C.S. Dalton*, 1972, 2219.

[7] A. J. Cheney and B. L. Shaw, *J.C.S. Dalton*, 1972, 754, 860.

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

[9] M. I. Bruce, G. Shaw, and F. G. A. Stone, *J.C.S. Dalton*, 1973, 1667.

[10] E. W. Ainscough, S. D. Robinson, and J. J. Levison, *J. Chem. Soc.* (*A*), 1971, 3413.

[11] N. Ahmad, E. W. Ainscough, T. A. Jaines, and S. D. Robinson, *J.C.S. Dalton*, 1973, 1151.

[12] S. Bresadola, P. Rigo, and A. Turco, *Chem. Comm.*, 1968, 1205.

[13] P. A. Kramer and C. Masters, preceding paper.

[14] P. A. Kramer and C. Masters, *Rec. Trav. chim.*, 1975, **94**, 25.

[15] M. L. H. Green, 'Organometallic Compounds,' Methuen, London, 1968, vol. II.

[16] C. Masters, *J.C.S. Chem. Comm.*, 1973, 191.

with the n.m.r. findings; the intensities of the bands at 2960s and 2907m cm^{-1}, assigned to the asymmetric and symmetric CH_3 stretching modes of the PPr_3 unit, are considerably reduced and new bands appear at 2210m, 2120m, and 2075m cm^{-1} due to ν(C–D).

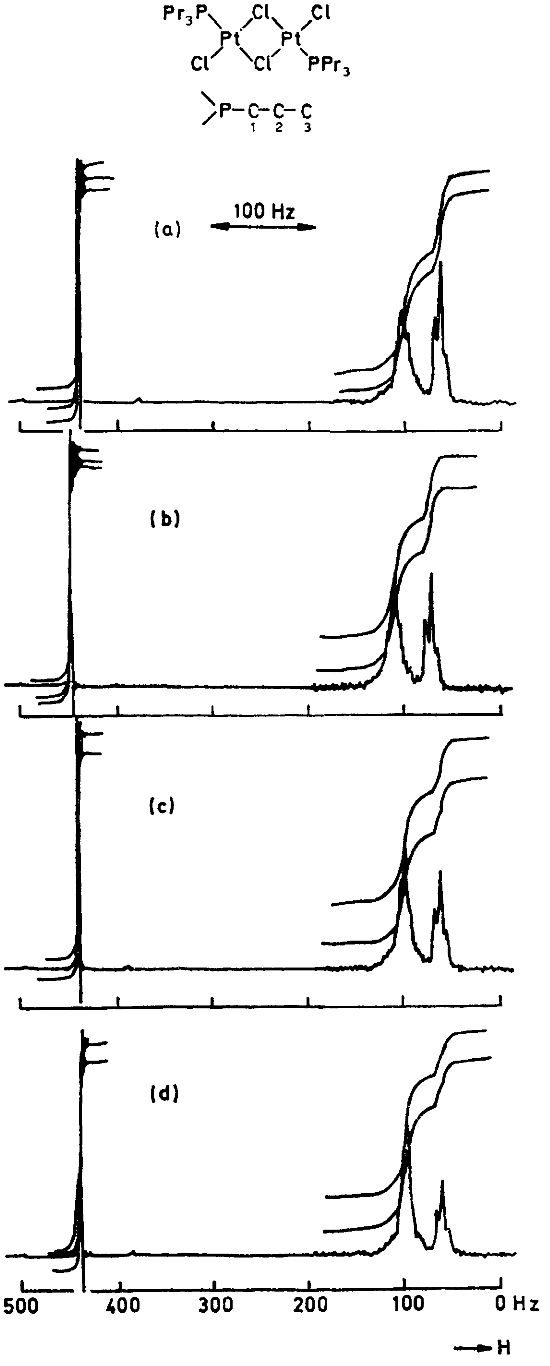
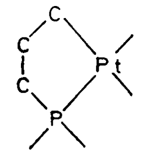


FIGURE 1 60 MHz ^1H N.m.r. spectra of $[Pt_2Cl_4(PPr^n_3)_2]$ in $CDCl_3$ containing C_6H_6 as internal standard: (a) before deuteriation; (b) 24% deuterium incorporation at C-3; (c) 31% deuterium incorporation at C-3; (d) 48% deuterium incorporation at C-3

With L = PBu_3 the ^1H n.m.r. spectrum of (I) is too complex to allow the position of deuterium incorporation to be determined. However, the ^{13}C n.m.r. spectrum (with complete proton decoupling) of the deuteriated complex indicates that the deuterium is situated predominantly (>80%) at C-3 of the butyl group. (The doublet at $\delta_{CS_2} = 168{\cdot}5$ p.p.m., $^3J(P\text{–}C) = 15$ Hz, assigned to C-3 of the undeuteriated butyl group, is absent from the spectrum of the deuteriated complex.) No signal for C-3 of the deuteriated species is observed. This is probably due to ^2H–^{13}C and ^{31}P–^{13}C coupling together with the quadrupole moment of deuterium, rendering the absorption too broad to be detected. The other signals are unaltered.[17]

Thus, as was found for the alkene–platinum hydrogen–deuterium exchange reaction, deuterium incorporation occurs in a regiospecific manner. The observation that incorporation occurs specifically at C-3 in both the tributyl phosphine– and the tripropylphosphine–platinum complexes suggests that the exchange reaction proceeds *via* a five-membered ring intermediate of type (II), analogous to that suggested for the alkene–exchange reaction.[13]



(II)

We have attempted to exchange hydrogen for deuterium in *cis*- and *trans*-$[PtCl_2(PBu_3)_2]$. With these complexes, even after a reaction time of 24 h at 100 °C, less than 5% deuterium incorporation was observed. It therefore appears necessary to use a bridged platinum complex of type (I), where L = a tertiary phosphine ligand.

(B) *Factors Affecting the Exchange.*—(1) *Perchloric acid concentration.* In contrast to what was observed in the platinum-catalysed H–D exchange in alkenes,[13] variations in the perchloric acid concentration (0—0·46M) had virtually no effect on the degree of deuterium incorporation into the tertiary phosphine (see Table 1). Thus perchloric acid is not an essential constituent of the exchange medium.

TABLE 1

Effect of $[HClO_4]$ on the hydrogen–deuterium exchange in $[Pt_2Cl_4(PBu_3)_2]$; solvent CH_3CO_2D (10 ml), D_2O (1·7 ml); $[Pt_2Cl_4(PBu_3)_2]$ 0·02M; reaction time 1 h; temp. 100 °C

$[HClO_4]$/M	D in PBu_3 (% ± 5)
0	23
0·23	27
0·46	26

(2) *Deuterium oxide concentration.* Using a 0·02M-solution of $[Pt_2Cl_4(PBu_3)_2]$ in CH_3CO_2D (10 ml) we varied the amount of D_2O from 0 to 2·00 ml. The results, given in Table 2, show that when the $D_2O : CH_3CO_2D$ ratio is above *ca.* 1 : 10 the percentage of D_2O in the reaction medium has no influence on the amount of deuterium incorporated. The decrease in deuterium incorporation found at lower D_2O concentrations may be due to the acetic acid being present in the form of dimers and to the

---

[17] L. P. Blaauw, A. D. H. Clague, and C. Masters, following paper.

lower dielectric constant of the medium.[18] A similar effect has been reported for the platinum-catalysed hydrogen–deuterium exchange in alkanes.[19]

TABLE 2

Effect of D_2O on the hydrogen–deuterium exchange in $[Pt_2Cl_4(PBu_3)_2]$; solvent CH_3CO_2D (10 ml); $[Pt_2Cl_4(PBu_3)_2]$ 0·223 g; reaction time 1 h; temp. 100 °C

D_2O (ml)	D in PBu_3 (% ± 5)
0	10
0·25	16
0·50	17
0·75	24
1·00	23
1·25	22
1·50	23
1·75	22
2·00	25

(3) *Type of tertiary phosphine.* We synthesized some complexes of type (I; L = PBu^tPr_2 and $PBu^t{}_2Pr$). These tertiary phosphines were chosen since it was thought that the presence of the bulky tertiary butyl group(s) would force the propyl moiety into very close proximity to the platinum and thus possibly stabilize the ring-closed intermediates suggested in the H–D exchange reaction, and allow isolation of these intermediates. Unfortunately, this proved not to be the case. However, we did find the tertiary butyl group to have a marked influence on the rate of the H–D exchange.

Since complexes of this type are only sparingly soluble in aqueous acetic acid we adopted as exchange medium a mixture of deuterioacetic acid, deuterium oxide, and deuteriochloroform in the ratio 5 : 1 : 5. In this medium we compared the rates of H–D exchange in complexes (I; L = PPr_3, PBu^tPr_2, and $PBu^t{}_2Pr$) at 100 °C. The H–D exchange follows first-order kinetics and the observed first-order rate constants for these complexes are given in Table 3. The increase in rate of deuterium incorporation with increasing size of the tertiary phosphine is in agreement with insertion of the platinum into the C–H bond at C-3 being rate determining. Forcing the propyl group closer to the platinum, by increasing the bulkiness of the other alkyl groups on the phosphorus, should encourage the insertion reaction.

TABLE 3

Observed first-order rate constants for hydrogen–deuterium exchange in complexes of $[Pt_2Cl_4L_2]$; solvent CH_3CO_2D–D_2O–$CDCl_3$ (5 : 1 : 5); $[Pt_2Cl_4L_2]$ 0·02M; temp. 100 °C

L	$10^4k_{obs.}$ (for H/D at C-3 of propyl group) s^{-1}
PPr_3	1·8
PPr_2Bu^t	4·3
$PPrBu^t{}_2$	48
PPr_2Ph	2·0
$PPrPh_2$	1·9

With L = PPr_3 or PBu_3 we observed no deuterium incorporation at C-2 even after prolonged (16 h) reaction times. However, with L = $PBu^t{}_2Pr$ we found considerable deuterium incorporation into the tertiary butyl group. The data are presented in Table 4. Initially, deuterium incorporation occurs rapidly at C-3 of the propyl group and is followed by a slower exchange at C-2 and in the methyl groups of the tertiary butyl moiety. After a reaction time of 5 h (deuterium incorporation 78%) the ^{13}C n.m.r. spectrum[17] of the deuteriated complex indicates extensive exchange at C-2 and C-3 of the propyl group and at the tertiary butyl moiety; however, within the accuracy of the ^{13}C n.m.r. method, none of the protons at C-1 have been exchanged for deuterium. Hence, by increasing the steric requirements of the tertiary phosphine ligand we are able to induce formation of four-membered ring intermediates.

TABLE 4

Variation of deuterium incorporation into the $PBu^t{}_2Pr$ ligands of $[Pt_2Cl_4(PBu^t{}_2Pr)_2]$ with time; solvent CH_3CO_2D–D_2O–$CDCl_3$ (5 : 1 : 5); $[Pt_2Cl_4(PBu^t{}_2Pr)_2]$ 0·2M; temp. 100 °C

Time / min	D in $PBu^t{}_2Pr$ (% ± 5)
10	16
20	17
40	30
60	38
90	41
120	59
300	78

With L = PBu^tPr_2, after a reaction time of 15 h at 100 °C, C-3 of the propyl group is completely deuteriated; however, <10% deuterium incorporation has occurred at the other positions in the tertiary phosphine ligand. Thus it appears that two tertiary butyl groups are necessary to induce formation of a four-membered ring intermediate.

When L = PPh_2Pr or $PPhPr_2$ exchange occurs exclusively in the terminal methyl groups. The presence of the phenyl substituents has virtually no effect on the rate of deuterium incorporation (Table 3). With these complexes even after a prolonged reaction time (66 h) no incorporation at other than C-3 of the propyl group was found. With L = PBu^tPh_2 deuterium is incorporated into the *ortho*-positions in the phenyl groups and also into the tertiary butyl unit. The rate of incorporation into the aromatic ring is *ca.* 50 times that of incorporation into the tertiary butyl unit, the observed rate constants being $3{\cdot}1 \times 10^{-4}$ and $6{\cdot}6 \times 10^{-6}$ s^{-1}, respectively.

Although we cannot distinguish between electronic and steric factors our results suggest that in these internal metallation reactions steric rather than electronic factors are dominant. The difference in behaviour between the phenyl-substituted tertiary phosphines and the tertiary butyl-substituted tertiary phosphines reflects the less stringent steric requirements of an aryl unit compared to a tertiary butyl unit. Whereas the presence of two tertiary butyl groups in the tertiary phosphine is sufficient to induce formation of a four-membered ring intermediate, leading to deuterium incorporation in both the tertiary butyl group and at C-2 of the propyl unit, this is not the case for two phenyl substituents. With L = $PPhEt_2$ or PPh_2Et no deuterium incorporation was found even after prolonged (66 h) reaction times.

The importance of steric factors in internal metallation reactions has also been emphasized by Shaw *et al.* in their

---

[18] J. J. Lagowski, ed., 'The Chemistry of Non-aqueous Solvents,' Academic Press, New York, 1970, vol. III, p. 245.

[19] R. J. Hodges, D. E. Webster, and P. B. Wells, *J. Chem. Soc.* (*A*), 1971, 3230.

work on internal metallation reactions of tertiary phosphine ligands with bulky substituents.[3]

(C) *Kinetic Measurements*.—(1) *With* $[Pt_2Cl_4(PPr_3)_2]$. Using a 0·02M-solution of (I; L = PPr_3) in $CDCl_3$–D_2O–CH_3CO_2D (5 : 1 : 5) we measured the percentage exchange as a function of time at 60, 80, 100, and 120 °C. At these temperatures the exchange followed first-order kinetics. The rate constants, k, are given in Table 5.

TABLE 5

Observed first-order rate constants for hydrogen–deuterium exchange in $[Pt_2Cl_4(PPr_3)_2]$ at different temperatures; solvent CH_3CO_2D–D_2O–$CDCl_3$ (5 : 1 : 5); $[Pt_2Cl_4(PPr_3)_2]$ 0·02M

Temp. / °C	10^5k / s^{-1}
60	0·28 ± 0·02
80	2·78 ± 0·14
100	18·3 ± 0·9
120	128 ± 5·0

The Arrhenius plot,[20] ln k *vs.* $1/T$ where T is the absolute temperature, is linear giving a value of 111 ± 2 kJ mol^{-1} for the activation energy and a pre-exponential factor of 6×10^{11} s^{-1}.

The percentage deuterium incorporation under standard conditions is independent of the initial complex concentration, as shown by the data in Table 6. Keeping the acetic acid to water ratio constant at 5 : 1 we lowered the amount of CH_3CO_2D–D_2O in the CH_3CO_2D–D_2O–$CDCl_3$ solvent mixture from 78 to 29%. The results are given in Table 7. As can be seen, when CH_3CO_2D–D_2O constitutes more than *ca.* 50% of the solvent mixture the percentage deuterium incorporation into the propyl moiety of the tertiary phosphine is essentially independent of the acetic acid–water content of the solvent while at lower concentrations there is a decrease in the percentage incorporation.

TABLE 6

Effect of initial dimer concentration on hydrogen–deuterium exchange in $[Pt_2Cl_4(PPr_3)_2]$; solvent CH_3CO_2D–D_2O–$CDCl_3$ (5 : 1 : 5); temp. 100 °C; reaction time 45 min

$[Pt_2Cl_4(PPr_3)_2]$ / M	D at C-3 of PPr_3 (% ± 5)
0·01	34
0·02	38
0·03	36

TABLE 7

Effect of CH_3CO_2D–D_2O concentration on hydrogen–deuterium exchange in $[Pt_2Cl_4(PPr_3)_2]$; solvent CH_3CO_2D–D_2O (5 : 1) in $CHCl_3$; $[Pt_2Cl_4(PPr_3)_2]$ 0·02M; temp. 100 °C; reaction time 1 h

% CH_3CO_2D–D_2O in $CHCl_3$	D at C-3 of PPr_3 (% ± 5)
78	51
55	49
29	37

In an attempt to keep the solvent composition, *i.e.* dielectric constant, *etc.*, approximately constant while changing the acetic acid concentration we used as solvent a large volume of chloroform containing small amounts of acetic acid. The results are given in Table 8. Although the acetic acid concentration clearly affects the percentage exchange observed no simple dependence is apparent from the data. Thus from the Arrhenius plot we are unable to obtain a meaningful value for the entropy of activation.

TABLE 8

Effect of CH_3CO_2D concentration on hydrogen–deuterium exchange in $[Pt_2Cl_4(PPr_3)_2]$; solvent $CHCl_3$ containing CH_3CO_2D; $[Pt_2Cl_4(PPr_3)_2]$ $1{\cdot}8 \times 10^{-3}$M; temp. 100 °C; reaction time 1 h

$[CH_3CO_2D]$ / M	D at C-3 of PPr_3 (% ± 5)
0·43	14
0·86	23
2·59	31
3·45	37

(2) *With* $[Pt_2Cl_4(PBu_3)_2]$. Under conditions identical with those adopted for $[Pt_2Cl_4(PPr_3)_2]$, we followed the percentage deuterium incorporation into the butyl moiety as a function of time during 500 min. The results are shown graphically in Figure 2, from which it can be seen that the rate of deuterium incorporation decreases, by a factor of *ca.* 10, when the butyl group contains more than *ca.* 23% deuterium. ^{13}C N.m.r. spectroscopy shows that during the first 60 min deuterium incorporation occurs almost exclusively (>80%) at C-3 of the butyl group (22% deuteriation corresponds to complete exchange of the hydrogens on C-3). During longer reaction times deuterium incorporation is also found at C-4 as evidenced by the ^{13}C n.m.r. spectrum [17] of a sample containing 48% deuterium. These observations show that in $[Pt_2Cl_4(PBu_3)_2]$ even though the formation of a five-membered ring intermediate is most favourable, formation of intermediate species containing six-membered rings is also possible. With $[Pt_2Cl_4(PPr_3)_2]$ and $[PtCl_4(PBu_3)_2]$ we obtained no evidence for the formation of three- or four-membered rings (*i.e.* exchange at C-1 or C-2) even after prolonged (50 h) reaction times. Using a non-linear regression technique we find, from the data in Figure 2, values for the observed first-order rate constants for H–D exchange at C-3 and C-4 of $2{\cdot}1 \pm 0{\cdot}1 \times 10^{-4}$ and $1{\cdot}9 \pm 0{\cdot}1 \times 10^{-5}$ s^{-1}, respectively. Thus exchange is some 11 times faster at

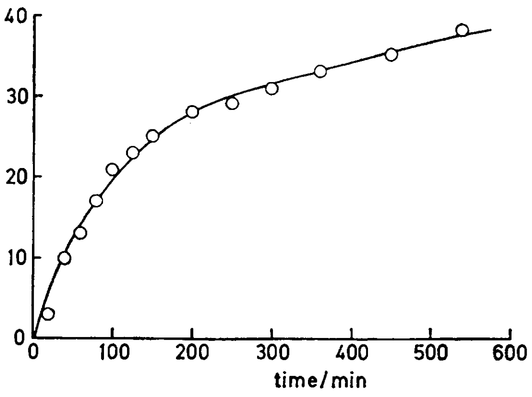


FIGURE 2 Incorporation of deuterium into the butyl groups of the tributylphosphine ligands of $[Pt_2Cl_4(PBu_3)_2]$ as a function of time: solvent $CDCl_3$–D_2O–CH_3CO_2D (5 : 1 : 5); [complex] 0·02M; temp. 100 °C

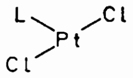
---

[20] K. J. Laidler, 'Chemical Kinetics,' McGraw-Hill, London, 1965.

C-3 than at C-4. Comparison of the rate constant for exchange at C-3 in the butyl moiety ($2{\cdot}1 \times 10^{-4}$ s^{-1}) with that for exchange at C-3 in the propyl group in [$Pt_2Cl_4(PPr_3)_2$] ($1{\cdot}8 \times 10^{-4}$ s^{-1}) shows that replacement of hydrogen by methyl has a small accelerating effect on the rate of deuterium incorporation.

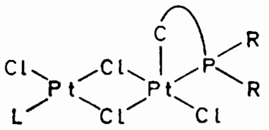
DISCUSSION

Our results indicate that a 'normal' sp^3 carbon–hydrogen bond can be activated towards H–D exchange under relatively mild conditions by bringing the saturated carbon centre into close proximity to the metal (platinum) centre. Moreover, by co-ordinating one end of the molecule to the metal it is possible to activate a specific site in another part of the molecule. In our opinion the exchange occurs *via* oxidative addition of the C–H bond to the platinum to give a ring-closed hydrido-alkyl-platinum species. Our results suggest that the ease of ring formation decreases in the order 5-membered > 6-membered > 4-membered and that in order to induce formation of 4-membered ring intermediates it is necessary to have bulky substituents, *e.g.* t-butyl on the tertiary phosphine ligand. The question arises whether the dimeric species undergoes dedimerization to produce a formally co-ordinatively unsaturated intermediate of type (III) which then undergoes the oxidative-addition reaction to give the alkyl-hydride complex or whether insertion occurs in the dimeric species without complete fission of the bridge.

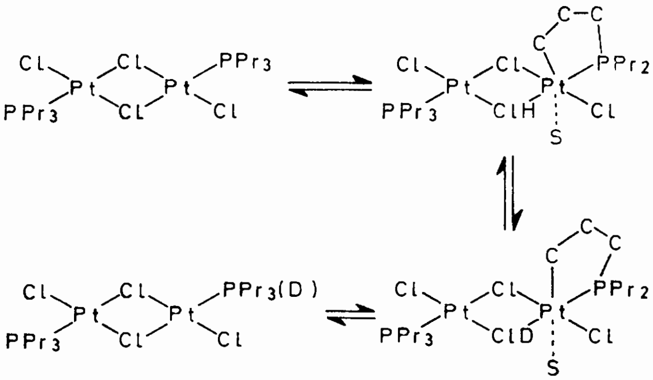


(III)

By analogy with our previous work[13] on the H–D exchange in alkenes we suggest that insertion occurs in the dimeric species to yield an intermediate of type (IV), where the sixth co-ordination site on the inserted platinum is possibly occupied by a solvent molecule (CH_3CO_2D), which assists the exchange of the H for D. The uninserted platinum atom possibly functions as a type of Lewis acid in assisting in the partial rupture of the chloro-bridge with concurrent formation of the inserted intermediate. A possible scheme is given below for L = PPr_3 (S = solvent). We are unable to say conclusively which step is the rate-determining process; however, the observation that increasing the bulkiness of the tertiary phosphine increases the rate of deuterium incorporation suggests that insertion of the platinum into the C–H bond is rate-determining.



(IV)



EXPERIMENTAL

Tertiary phosphines and tertiary phosphine complexes of platinum were prepared by methods reported in the literature.[21-25] Acetic [$^2H_1$]acid was prepared from acetic anhydride (acid-free) by reaction with deuterium oxide.[19] The exchange reactions were carried out in sealed glass ampoules suspended or vibrated in an oil-bath at the required temperature. The ampoules were sealed at atmospheric pressure; no precautions were taken to exclude air. After reaction the ampoule was cooled (0 °C), opened, and the product extracted with chloroform or dichloromethane. The extracts were washed well with water and dried ($MgSO_4$); evaporation of the solvent yielded the complex. In those cases where the complex separated from the reaction mixture on cooling, the precipitated complex was filtered off, washed well with water, and dried *in vacuo*. Apart from the deuteriation the complexes were recovered unchanged after reaction.

^1H N.m.r. spectra were measured either at 60 MHz using a Varian T60 spectrometer or at 100 MHz with a Varian HA 100 spectrometer. The amount of deuterium incorporation was determined from the ^1H n.m.r. spectrum by integration against an internal standard (benzene, toluene, or dibromoethane) in either $CDCl_3$ or CD_2Cl_2. For the complexes of type (I; L = PPh_2Pr and PBu^tPh_2) the solubility of the dimeric species in either $CDCl_3$ or CD_2Cl_2 is too low to allow direct measurement of the ^1H n.m.r. spectrum. For these complexes deuteriated pyridine was added to the dimer in order to split the bridge and obtain the more soluble monomeric species, [$PtCl_2(C_5D_5N)L$]. ^{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 $CHCl_3$; the reference lock was external ^{13}C-enriched CS_2. I.r. spectra were recorded on a Perkin-Elmer 457 spectrometer either from Nujol mulls or KBr discs.

[4/1179 *Received*, 17*th June*, 1974]

---

[21] W. C. Davies, P. L. Pearce, and W. J. Jones, *J. Chem. Soc.*, 1929, 1262; 1930, 463.

[22] W. Voskuil and J. F. Arens, *Rec. Trav. chim.*, 1963, **82**, 302.

[23] K. Issleib, A. Tzscharch, and H. V. Block, *Chem. Ber.*, 1968, **101**, 2931.

[24] K. Issleib, *Pure Appl. Chem.*, 1964, **9**, 205.

[25] F. R. Hartley, *Organometallic Chem. Rev.*, 1970, **6**, 119 and refs. therein.