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Intermolecular Exchange in a Triarylborane-Phosphine Complex: A Multinuclear Magnetic Resonance Study

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Intermolecular exchange in a triarylborane–phosphine complex: a multinuclear magnetic resonance study

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It has been shown using ^{1}H, ^{19}F, and ^{31}P NMR spectroscopy that the *tris*-(pentafluorophenyl)borane–phosphine adduct undergoes intermolecular exchange in toluene solution involving transfer of the phosphine group. The rate coefficient (k) for the exchange process was measured using the ^{31}P NMR selective inversion experiment on a series of samples containing excess phosphine. At 254 K, k is 3.60 ± 0.15 s^{-1} and is independent of the excess phosphine concentration. The mechanism for the exchange process is proposed to be two step, a slow initial dissociation of the adduct followed by a rapid recombination step. The rate coefficient is strongly temperature dependent in the range 243–263 K and a value of 126 kJ mol^{-1} is obtained for the activation energy of the dissociation step. The appearance of the ^{1}H two-dimensional exchange spectrum (NOESY) is described in terms of the competing effects of nuclear spin relaxation and chemical exchange.

1. Introduction

We have recently demonstrated (Bradley *et al.* 1991) the reversible complexation between *tris*-(pentafluorophenyl)borane and phosphine. Our interest in this system is that large quantities of very pure phosphine gas are used in the vapour phase deposition of indium phosphide films for semiconductor devices. This borane-phosphine adduct provides a relatively safe method for the fixation and storage of the highly toxic phosphine, which can be released from the adduct by heating to moderate temperatures. To gain insight into the behaviour of the adduct we have conducted a multinuclear (^{1}H, ^{11}B, ^{19}F, ^{31}P) magnetic resonance investigation and used ^{1}H NMR to quantify the rates of exchange of phosphine between free and complexed states in solution.

2. Results and discussion

(a) *One-dimensional NMR spectra*

The ^{1}H spectrum of a solution of the adduct containing excess phosphine shows two phosphine doublets at 1.55 δ (^{1}J, 188 Hz; free phosphine) and 3.0 δ (^{1}J, 412 Hz; adduct phosphine). The increase in $^{1}J(^{1}H–^{31}P)$ on complexation of the phosphine implies an increase in *s*-character in the P–H bonds (cf. ^{1}J 547 Hz for PH_4^+; Mavel

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Table 1. NMR *Data for* tris-(*pentafluorophenyl*)*borane and its phosphine adduct*

(Chemical shifts are reported on the high frequency positive δ scale and are referenced for ^{1}H spectra to external TMS, for ^{11}B spectra to external $BF_3{\cdot}Et_2O$, for ^{19}F spectra to external $CFCl_3$ and for ^{31}P spectra to external 85% H_3PO_4.)

	^{1}H[a]	^{11}B[b]	^{19}F[c]	^{31}P[d]
$(C_6F_5)_3B$		60.7 δ	−164.8 δ(*m*) −145.4 δ(*p*) −133.7 δ(*o*)	
PH_3	1.55 δ $^{1}J(^{1}H–^{31}P) = 188$ Hz			−235 δ
$(C_6F_5)_3BPH_3$	3.0 δ $^{1}J(^{1}H–^{31}P) = 412$ Hz	−17.0 δ	−162.3 δ(*m*) −154.6 δ(*p*) −131.7 δ(*o*)	−94 δ

[a] These data were from a sample containing an equimolar mixture of adduct and phosphine in toluene-$[^{2}H]_8$ solution at 243 K.
[b] As [a], except that the temperature of the measurement was 293 K.
[c] These data were from samples in toluene-$[^{2}H]_8$ solution at 223 K.
[d] As [a], except that the temperature of the measurement was 253 K.

1973). Similarly the ^{31}P and ^{11}B chemical shifts (table 1) show large changes on complexation. The ^{1}H spectrum of a solution of the adduct alone at 303 K consists of a sharp doublet with $^{1}J(^{1}H–^{31}P) = 412$ Hz; on lowering the temperature the components of this doublet show a maximum width at *ca.* 268 K and at 253 K each half of the doublet shows septet fine structure (J = 5.3 Hz) due to coupling to ^{19}F. To explain these observations we propose that the phosphine group is undergoing intermolecular exchange between adduct molecules and that at 303 K the rate of exchange is sufficiently fast to collapse the long range $^{1}H–^{19}F$ coupling. It was to further investigate this phenomenon that excess phosphine was added to the adduct sample so that two chemically shifted sites could be observed in the exchange process.

For the study of the exchange kinetics a series of samples in toluene-$[^{2}H]_8$ solution (see §3) was prepared containing a constant adduct concentration and varying concentrations of excess phosphine. The ^{1}H and ^{31}P spectra of these samples at ambient temperature showed two chemical shifts but with significant broadening of the resonances indicative of an exchange process. As the temperature was lowered from 263 to 203 K these resonances sharpened, as expected for slower exchange at the lower temperature. The exchanging system is summarized as

$$(C_6F_5)_3BPH_3 + {}^{*}PH_3 \rightleftharpoons (C_6F_5)_3B{}^{*}PH_3 + PH_3. \qquad (I)$$

The resonances in the ^{19}F spectrum of the adduct alone in toluene-$[^{2}H]_8$ solution showed improved resolution at lower temperature (223 K) with no evidence of dissociation because of the absence of free borane resonances. The broadening in the ^{19}F spectrum of the adduct alone at ambient temperature is ascribed to scalar coupling interactions with ^{11}B, which are thermally decoupled at the lower temperature. The sample of adduct and excess phosphine has a $^{31}P–\{^{1}H\}$ spectrum consisting of two singlet resonances, one at −235 δ due to free phosphine and the other at −94 δ due to phosphine in the adduct, this latter resonance being considerably broadened ($\Delta\nu_{\frac{1}{2}} \approx 100$ Hz) by unresolved long range coupling to fluorine and/or boron. All the NMR data are summarized in table 1.

(b) Selective inversion experiments

To obtain quantitative rate information on the exchange process it was decided to use the relatively simple and economical (in terms of spectrometer time) selective inversion experiment (see Campbell *et al.* 1978) on the ^{1}H-decoupled ^{31}P spectrum. Three samples were studied, each containing the same concentration of adduct but with different levels of excess phosphine, and one of these was studied over a limited temperature range. The selective inversion experiments yield ^{31}P signal intensities ($M_i(t)$, $i = 1, 2$) at times t after the initial perturbation and, in keeping with our previous notation (Beringhelli *et al.* 1988) the time dependence of these intensities is described by

$$\boldsymbol{D} = [\exp(\boldsymbol{L}t)] \cdot \boldsymbol{D}(0), \tag{1}$$

where $\boldsymbol{D}$ is the 2×1 column matrix with elements of the deviations of the two site intensities from equilibrium, i.e. $M_i(t) - M_i(\infty)$. $\boldsymbol{D}(0)$ is $\boldsymbol{D}$ at time zero, and different columns $\boldsymbol{D}$ having the same column $\boldsymbol{D}(0)$ describe the time evolution of the intensities. The 2×2 matrix $\boldsymbol{L}$ is the sum of the kinetic ($\boldsymbol{K}$) and relaxation ($\boldsymbol{R}$) matrices

$$\boldsymbol{L} = \boldsymbol{K} + \boldsymbol{R}. \tag{2}$$

To derive the kinetic matrix consider that the phosphine is exchanging between free (site 1) and bound (adduct site 2) states:

$$1 \leftrightharpoons 2.$$

At equilibrium $p_1 k_{12} = p_2 k_{21}$, where k_{ij} is the rate coefficient for exchange from site i to site j and p_i is the concentration at site i. The off-diagonal elements, K_{ij}, of $\boldsymbol{K}$ are k_{ji} and the diagonal elements, K_{ii}, are $-k_{ij}$.

$$\boldsymbol{K} = \begin{bmatrix} -k_{12} & k_{21} \\ k_{12} & -k_{21} \end{bmatrix} = \begin{bmatrix} -k_{21}\, p_2/p_1 & k_{21} \\ k_{21}\, p_2/p_1 & -k_{21} \end{bmatrix}.$$

The relaxation matrix $\boldsymbol{R}$ is simply given by:

$$\boldsymbol{R} = \begin{bmatrix} -R_1 & 0 \\ 0 & -R_2 \end{bmatrix},$$

where R_i is the spin-lattice relaxation rate for site i. Off-diagonal elements of $\boldsymbol{R}$ are cross relaxation terms and are reasonably set to zero for the present case. The experimental data were analysed using the iterative method described previously (Beringhelli *et al.* 1988), care being taken because $\boldsymbol{L}$ is not a symmetrical matrix owing to the unequal populations of the two sites. The results are collected in table 2; the meaning of k will be discussed below.

(c) Relaxation rates

The quality of the fit between calculated and experimental intensities in the selective inversion experiments is defined by the goodness of fit parameter Γ. This is quite insensitive to the values of the relaxation rates R_1 and R_2, but is sensitive to k. For example the relaxation rates for free phosphine and adduct in sample 1 (3.23 and 1.74 s^{-1}) are clearly out of line with values from the other samples. When these

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Table 2. *Kinetic and relaxation data from analysis of selective inversion experiments*

sample no.	$[PH_3]^a$	T/K	$R_1{}^b/s^{-1}$	$R_2{}^b/s^{-1}$	k/s^{-1}	$\Gamma^c/10^{-2}$
1	2.36	253	3.23	1.74	3.75	3.25
			[1.30]	[2.50]	3.94	3.27
2	8.01	253	1.36	2.74	3.56	1.89
3	13.9	243	1.46	1.94	0.27	5.87
			1.43	[2.65]	0.30	5.90
3	13.9	253	1.22	3.05	3.48	1.82
3	13.9	263	0.73	3.45	31.4	2.67

[a] Concentrations are 10^2 mol dm^{-3}; the concentration of adduct in all three samples was 11.4×10^{-2} mol dm^{-3}.

[b] The spin lattice relaxation rates are for ^{31}P in phosphine and the adduct (R_1 and R_2 respectively). Values in square brackets are the values locked in the iterative analysis.

[c] The goodness of fit parameter $\Gamma = S^{-1}[\Sigma r^2/m]^{\frac{1}{2}}$, where S is a scaling factor between experimental and calculated signal intensities, m is the number of data points, and Σr^2 is the sum of the squares of the differences between the experimental and the calculated intensities.

rates were 'locked' in the iterative analysis to more consistent values (1.30 and 2.50 s^{-1}) both k and Γ were little different. Similarly the best fit value for R_2 from sample 3 at 243 K (1.94 s^{-1}) is low, and when this parameter was locked to a more reasonable value (2.65 s^{-1}), R_1, k and Γ only changed a little.

(*d*) *Interpretation of the kinetic data*

For the exchanging system shown in (I) it is possible to consider two mechanisms. The first is a concerted bimolecular process where a new phosphorus–boron bond is formed simultaneously with the breaking of the old, and the reaction might conceivably proceed via a symmetric transition state (cf. the S_{N2} mechanism of reaction of substituted alkanes). For such a mechanism to hold the rate of reaction should depend upon the concentration of excess phosphine and the k in our analysis (table 2) would refer to a pseudo first-order reaction; it should therefore be different for the samples with different concentrations of free phosphine. In addition, if the reaction is first order in the concentration of excess phosphine then we would expect the second-order rate coefficient, calculated as $k_2 = k/[PH_3]$ to be constant for the different samples. This is clearly not the case since $k_2 = 1.59 \times 10^2$, 0.44×10^2 and 0.25×10^2 mol^{-1} dm^3 s^{-1} respectively for samples 1, 2 and 3 at 253 K. Instead, the rate coefficient is constant (3.60 ± 0.15 s^{-1}) for the three samples and is therefore taken to be a true first-order rate coefficient. A mechanism which is consistent with this assumption is given in (II) in which the initial step, dissociation of the adduct, is slow and rate determining and the second step is much faster. This mechanism requires that there is a negligible concentration of free borane in a sample of either adduct alone or with excess phosphine, a factor confirmed by ^{19}F spectroscopy.

$$\left.\begin{aligned} (C_6F_5)_3BPH_3 &\rightarrow (C_6F_5)_3B + PH_3 \quad \text{slow step,} \\ (C_6F_5)_3B + {}^*PH_3 &\rightarrow (C_6F_5)_3B{}^*PH_3 \quad \text{fast step.} \end{aligned}\right\} \qquad \text{(II)}$$

For sample number 3 (table 2) the first order rate coefficient was found to be strongly temperature dependent and a plot of $\ln k$ against T^{-1} is linear (figure 1), the slope giving a value of *ca.* 126 kJ mol^{-1} for the activation energy of the proposed dissociation of the adduct.

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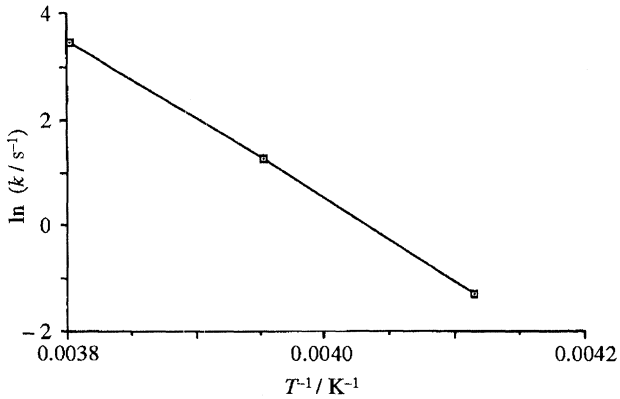

Figure 1. Arrhenius plot of the temperature dependence of the rate coefficient obtained from the ^{31}P selective inversion data.

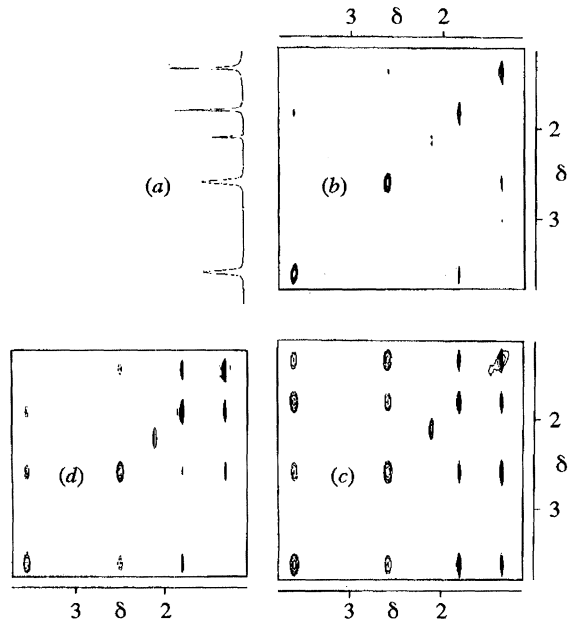

Figure 2. 400 MHz ^{1}H NMR spectra of sample 3; (*a*) one-dimensional spectrum at 253 K; (*b*) and (*c*) two-dimensional NOESY spectra at 253 K with $\tau_m = 50$ ms and 0.6 s respectively; (*d*) two-dimensional NOESY spectrum at 243 K with $\tau_m = 0.6$ s.

(*e*) *Two-dimensional NMR spectra*

Because of our experience (Beringhelli *et al.* 1988) in the analysis of kinetics of *intra*molecular rearrangements in organometallic complexes we first sought to analyse the kinetics of slow *inter*molecular phosphine exchange in a sample of adduct containing excess phosphine using the two-dimensional (2D) NOESY experiment (reviewed by Orrell *et al.* 1990). Representative ^{1}H and ^{31}P 2D NOESY spectra are shown in figures 2 and 3. The off-diagonal multiplets arise from the intermolecular exchange process alone, since the other possible mechanism contributing to these multiplets (homonuclear dipole–dipole cross relaxation) is likely to be negligible in the present case. An unusual feature of the ^{1}H spectra at 253 K (figure 2*b*) is the

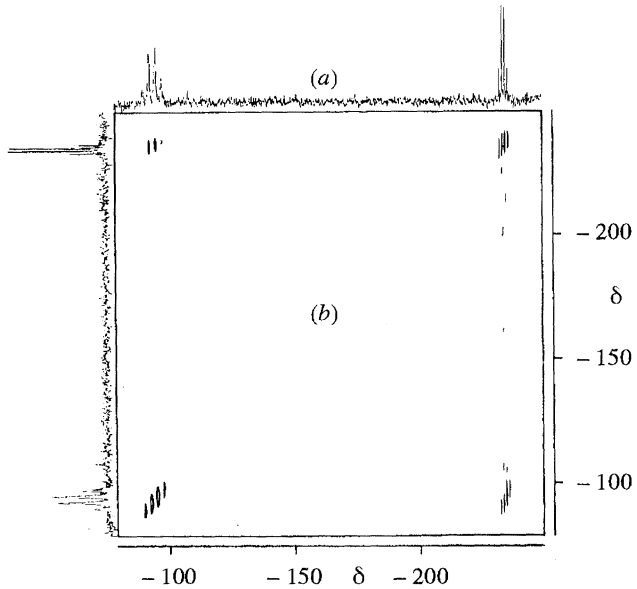

Figure 3. 162 MHz ^{31}P NMR spectra of sample 3 at 253 K; (*a*) one-dimensional spectrum; (*b*) two-dimensional NOESY spectrum with $\tau_m = 50$ ms.

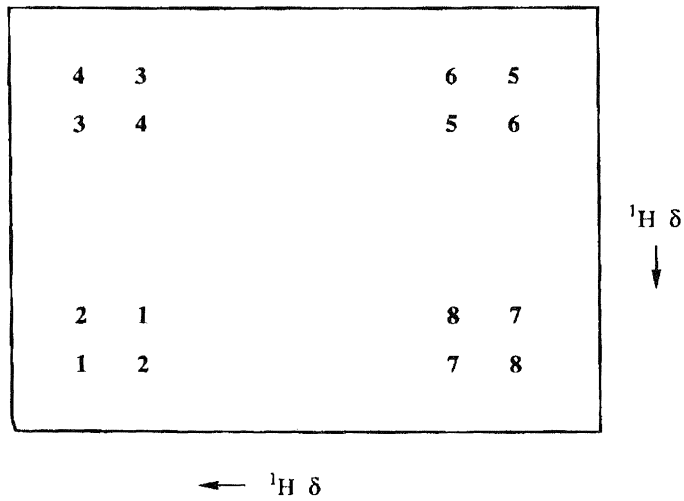

Figure 4. Schematic 2D contour plot of a NOESY spectrum illustrating slow exchange between two doublet resonances.

absence of certain peaks at short mixing times ($\tau_m = 0.05$ s in the acquisition pulse sequence; see §3): the peaks on the upper left to lower right diagonals of each multiplet are absent, i.e. peaks 2, 4, 6 and 8 in the schematic 2D plot (figure 4). For the longer mixing time (0.6 s) all possible correlation peaks are present (figure 2*c*). At the lower temperature of 243 K and with $\tau_m = 0.6$ s only peaks 4 and 8 are absent (figure 2*d*). In a purely qualitative manner we can ascribe this behaviour to the occurrence of relatively little ^{31}P spin-lattice relaxation during the elapsed mixing time. In fact the relaxation times (R_i^{-1}, table 2) are all significantly longer than the mixing time in question (50 ms). Those peaks which internally correlate the lines of

the ^{1}H multiplets (peaks 2 and 6 in figure 4) will only occur if there is sufficient mixing time for transitions to occur between the ^{31}P α and β spin states. The same argument applies for the missing peaks in the off-diagonal multiplets (peaks 4 and 8 in figure 4) providing that the ^{31}P–^{1}H coupling constant has the *same sign* in free phosphine and the adduct. This explanation is related to the discussion by Huang *et al.* (1981) of the ^{1}H-coupled ^{13}C spectrum of imidazole where the ^{13}C spectrum acts as a 'spy' on the ^{1}H relaxation. However in this way we cannot differentiate between the behaviour at 243 K for peaks 2 and 6 on the one hand and peaks 4 and 8 on the other hand. A full quantitative analysis of these 2D spectra would involve consideration of two exchanging 4-spin systems (PH_3) in the presence of scalar coupling. Such an analysis is beyond the scope of this study. It would be difficult because the $\boldsymbol{L}$ matrix would have dimensions of 32×32 (2^4 basis functions for each site) and involve many (unknown) relaxation parameters. Even the analysis for PH (instead of PH_3) involves an 8×8 matrix. However, in this case, if simplifying assumptions are made (K. D. Sales, unpublished work) then the observed behaviour can be rationalized. These assumptions are that $W_2 = W_0 = 0$ (where W_2 and W_0 are the double and zero quantum transition probabilities) and that $\exp(\boldsymbol{L}t)$ can be expanded up to second-order terms in t. The spin lattice relaxation rates are then directly related to the single quantum transition probabilities W_1. With the above assumptions the expressions for the intensities of peaks 4 and 8 consist entirely of terms of the form $\tau_m^2 k W_1$, where W_1 is an average of the single quantum transition probabilities for the two sites. On the other hand, the expressions for peaks 3 and 7 contain terms of the form $\tau_m k$, whereas the intensity of peaks 2 and 6 have terms of the form $\tau_m W_1$. For the situation at 253 K, where the relaxation rate and the exchange rate have similar values (see table 2) and for small values of τ_m, peaks 4 and 8 will have the lowest intensity. In the spectrum at 253 K (figure 2*b*) the 'exchange' peaks 3 and 7 are clearly more intense than the 'relaxation' peaks 2 and 6. In the spectrum at 243 K (figure 2*d*) these are of comparable intensity because of the significantly smaller value for k at the lower temperature.

3. Experimental

The *tris*-(pentafluorophenyl)borane : phosphine adduct was prepared as previously described (Bradley *et al.* 1991). The samples for NMR spectroscopy were prepared by making a stock solution of the adduct in toluene-$[^2H]_8$, transferring a portion to a 5 mm o.d. NMR tube and introducing phosphine gas. The samples were sealed under vacuum. The concentrations of the adduct and excess phosphine were determined by ^{31}P NMR spectroscopy: the sample in the 5 mm tube was positioned concentrically inside a 10 mm tube containing a standard solution of triphenylphosphine in toluene-$[^2H]_8$ (0.154 mol dm^{-3}). Relative concentrations of the three species were then determined from integration of the ^{31}P–{^{1}H} spectra measured with inverse gated decoupling to suppress the ^{31}P–{^{1}H} nuclear Overhauser enhancement and consideration of the relative volumes of sample and reference.

^{1}H and ^{31}P NMR spectra were obtained at 400 MHz and 162 MHz respectively using a Bruker WH-400 instrument. 2D NOESY spectra were obtained in the phase sensitive mode using the $\frac{1}{2}\pi - t_1 - \frac{1}{2}\pi - \tau_m - \frac{1}{2}\pi$ – Acquire sequence (Jeener *et al.* 1979). Selective inversion of the free phosphine resonance was achieved using the DANTE sequence (Morris & Freeman 1978) in the manner previously described (Hawkes *et al.* 1984) and for each selective inversion run 30 spectra were recorded with different values of

the delay after the initial perturbation. ^{11}B and ^{19}F NMR spectra were measured at 80.2 MHz and 235 MHz respectively using Bruker AM-250 and WM-250 spectrometers.

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