Hydrogen-1 Nuclear Magnetic Resonance Studies of Exchange Reactions between Complexes $MR_3{\cdot}M'R'_3$ and their Components. Part III.[1] The Systems Dimethylphenylphosphine–, Dimethyl(dimethylamino)phosphine–, and Dimethyl-t-butylphosphine–Trimethylborane, and Trimethylphosphine–Dimethylphenylborane †

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Dimethylphenylborane has been prepared from BMe_2Cl and $HgPh_2$, and its vapour pressure measured over a range of temperature. The ^1H n.m.r. band-shape method has been used to determine exchange parameters for the systems $PMe_2Ph{\cdot}BMe_3$, $PMe_2(NMe_2){\cdot}BMe_3$, $PMe_3{\cdot}BMe_2Ph$, and $PMe_2Bu^t{\cdot}BMe_3$. Reactions between complex and an excess of either donor or acceptor proceed by a dissociative mechanism. In dichloromethane at 27 °C, basicities towards BMe_3 decrease in the order $NMe_3 \sim PMe_3 > PMe_2Bu^t \sim PMe_2(NMe_2) > PMe_2Ph \gg P(CH_2Ph)_3 > PMe_2(CF_3) \sim PMe_3O \sim PMePh_2$.

IN previous parts of this series we described the derivation of kinetic parameters for exchange reactions between donor–acceptor complexes $MR_3{\cdot}M'R'_3$(DA) and an excess of donor MR_3(D)[2] and between the complexes and an excess of acceptor $M'R'_3$(A).[1] The method was illustrated with data for the system $PMe_3{\cdot}BMe_3$. In this paper, we give data for several other boron–phosphorus systems.

EXPERIMENTAL

Starting Materials.—Trimethylborane, trimethylphosphine, dimethylphenylphosphine, and methyldiphenylphosphine were made by well known methods. Dimethyl(trifluoromethyl)phosphine[3] was also prepared without difficulty, but tribenzylphosphine could not be purified as described.[4] It was readily isolated (m.p. 90—92 °C) by recrystallisation from hexane. (Dimethylamino)dimethylphosphine was obtained from dichloro(dimethylamino)phosphine and trimethylaluminium.[5] The small amount of PMe_3 formed by P–N bond cleavage was easily separated by trap-to-trap distillation: the $PMe_2(NMe_2)$ was then distilled, b.p. 49—50 °C at 120 mmHg, and stored at −78 °C before use.‡ Dimethyl-t-butylphosphine[6] was distilled into a suspension of silver(I) iodide in a saturated solution of potassium iodide, and pure samples were obtained by heating the dry silver(I) iodide complex.

Dimethylphenylborane.—Chlorodimethylborane was made in 92% yield from trimethylborane–trichloroborane (2 : 1) in an ampoule heated at 170 °C for 14 h.[7] A lower yield (*ca.* 70%) was obtained from the reaction at 200 °C. Chlorodimethylborane (0.9 g, 11.8 mmol) and diphenylmercury (12.1 g, 5.9 mmol) were sealed in an ampoule for several days and the volatile products separated by fractional condensation to give BMe_2Cl (2.6 mmol) and *dimethylphenylborane* (0.4 g, 3.4 mmol; 37% based on BMe_2Cl used) [Found: C, 81.2; H, 9.7%; *M*(cryoscopy in benzene) 117. $C_8H_{11}B$ requires C, 81.5; H, 9.3%; *M* 118]. Details of the i.r. and mass spectra are given in Supplementary Publication No. SUP 21726 (6 pp.).§

The vapour pressure of BMe_2Ph, measured between 20 and 50 °C, defined the equation $\log(p/\text{mmHg}) = -(2\,270/T) + 8.250$, from which the calculated latent heat of evaporation is 43.5 kJ mol^{-1}, the extrapolated b.p. 150 °C, and Trouton's constant 102.7 J K^{-1} mol^{-1}. As with other boranes, the volatility is similar to that of the hydrocarbon in which B is replaced by CH ($CHMe_2Ph$, b.p. 152 °C). No disproportionation,[8] giving BMe_3, was detected during the vapour-pressure measurements below 50 °C, or by n.m.r. measurements on toluene solutions.

There were two peaks in the spectrum of BMe_2Ph–BMe_3 (1 : 1), showing that exchange of methyl groups between the molecules BMe_3 and BMe_2Ph was slow on the n.m.r. time scale. In contrast, exchange of methyl groups between Al_2Me_6 and $Al_2Me_4Ph_2$ is fast at 20 °C.[9] However, when BMe_2Ph (0.95 mmol) was heated in a sealed tube for 12 h at 75 °C, the volatile materials recovered were BMe_3 (0.18 mmol) and BMe_2Ph (0.21 mmol), so that 42% of the original BMe_2Ph had decomposed [equation (1)]. Pure

$$2BMe_2Ph \longrightarrow BMe_3 + BMePh_2 \qquad (1)$$

methyldiphenylborane was not isolated and no triphenylborane was detected.

Preparation of Samples for N.m.r. Measurements.—Techniques for volatile compounds have been described.[1,2] Less volatile phosphines and boranes were distilled into weighed fragile glass ampoules which were sealed, reweighed, and subsequently broken into a known volume of solvent inside an evacuated glass vessel which was connected to a vacuum line through a No. 1 glass frit and a Rotaflo tap. Solutions from this vessel were run directly into n.m.r. tubes, which were sealed after condensing in any volatile materials. Concentrations determined by this method agreed with those found by integration of the n.m.r. spectra. Because of the low temperatures needed for kinetic measurements, no allowance for gaseous BMe_3 was required.[1]

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† No reprints avilable.

‡ 1 mmHg ≈ 13.6 × 9.8 Pa.

§ For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1975, Index issue (items less than 10 pp. are supplied as full-size copies).

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The complexes $PMe_3{\cdot}BCl_3$, $PMe_3{\cdot}BPh_3$, and $PMe_3{\cdot}BMe_2Cl$ were all insufficiently soluble in toluene or dichloromethane to give satisfactory spectra.

RESULTS

In all cases studied there were methyl or methylene groups bound to phosphorus in donor D and to boron in acceptor A, each spin-coupled to phosphorus in complex DA. Band-shape analyses of exchange-broadened 100-MHz spectra could therefore be carried out as described previously.[1,2]

TABLE 1

Chemical shifts and coupling constants of methyl protons in donor and acceptor in complexes DA

DA	Solvent	θ_c/°C	δ_D	δ_D'	δ_A	δ_A'	${}^2J$(PCH)/Hz	${}^2J$(PCH)′/Hz	${}^3J$(PBCH)′/Hz
$PMe_2Ph{\cdot}BMe_3$	C_6H_5Me [a]	−60	1.25	1.35	1.40	1.81	+3.6	−9.0	±18.5
$PMe_2(NMe_2){\cdot}BMe_3$	$C_6D_5CD_3$ [b]	−45	3.38	3.59	1.40	4.11	+5.5	−8.0	±18.0
			1.92 [c]	2.19			±10.0	±10.1	
$PMe_3{\cdot}BMe_2Ph$	CH_2Cl_2 [d]	−30	4.29	4.20	4.11	5.25	+2.5	−9.5	±19.2
$PMe_2Bu^t{\cdot}BMe_3$	C_6H_5Me [a]	−70	1.38	1.42	1.40	1.80	+3.2	−8.3	±16.8
			1.21 [e]	1.68			±11.5	±12.5	
$PMe_2(CF_3){\cdot}BMe_3$	C_6H_5Me [a]	−60	1.46	1.70	1.40	1.81	3.2	−13.5	
$P(CH_2Ph)_3{\cdot}BMe_3$	CH_2Cl_2 [d]	−60	2.56	2.45	1.40	5.33	*ca.* 1	−9.0	

[a] δ In p.p.m. upfield from *Me*Ph. [b] δ Upfield from CH_2Cl_2 as internal reference. [c] For *N*–Me protons. [d] δ Upfield from solvent peak. [e] For protons of Bu^t group.

TABLE 2

Mean life-times of complex

DA	Solvent	θ_c/°C	Excess of	Range of [D] or [A]/mol dm^{-3}	No. of samples	τ_{DA}^{-1}/s^{-1}
$PMe_2Ph{\cdot}BMe_3$	C_6H_5Me	−30	D	0.011—0.645	7	115 ± 5 *
	C_6H_5Me	−30	A	0.132—0.154	3	109 ± 2
$PMe_2(NMe_2){\cdot}BMe_3$	C_6H_5Me	−24	D	0.270—0.691	5	93 ± 7
$PMe_3{\cdot}BMe_2Ph$	CH_2Cl_2	24	D	0.078—0.173	5	47 ± 3
	CH_2Cl_2	16	A	0.077—0.218	5	18 ± 1.4

* Standard deviations of the mean.

When exchange between DA and an excess of D is fast on the n.m.r. time scale, the observed δ(PC*H*) and ${}^2J$(PCH) are weighted mean averages, as is δ(BC*H*) with an excess of A. For the systems $PMe_2Ph{\cdot}BMe_3$, $PMe_2(NMe_2){\cdot}BMe_3$, and $PMe_3{\cdot}BMe_2Ph$, plots of all three parameters against the mole ratio total D : total A showed sharp discontinuities at 1 : 1, indicating that complex formation was complete within the limits of detection. Chemical shifts and coupling constants for the individual species were measured under slow-exchange conditions (Table 1).

Signs of coupling constants were assumed by analogy with the system $PMe_3{\cdot}BMe_3$.[2] The value of ${}^3J$(PBCH) for the complex $PMe_2(NMe_2){\cdot}BMe_3$ suggested that, as in the BH_3 adduct,[10] the donor atom was phosphorus rather than nitrogen. Values for T_2, similar to those used previously, were taken from linewidths at −60 °C. Activation energies $E^‡$ were found from plots of log (τ_{DA}^{-1}) or log (τ^{-1}) against $1/T$ ($\tau^{-1} = \tau_{DA}^{-1} + \tau_D^{-1}$), and thermodynamic activation parameters from the equations $\Delta H^‡ = E^‡ - RT$ and $\log(\tau_{DA}^{-1}) = \log(\boldsymbol{k}T/\boldsymbol{h}) + (\Delta S^‡/2.3R) - (\Delta H^‡/2.3RT)$. Spectra of the complex $PMe_2Bu^t{\cdot}BMe_3$ with an excess of PMe_2Bu^t showed five doublets (Table 1) at −70 °C, coalescing to two doublets and a singlet at 20 °C. The P-methyl doublets overlapped at −40 °C, and an attempt to compute the band envelope using five sets of two-site exchanges was not successful. The activation energy was found, however, by band-shape analysis of the B-methyl resonance alone. The mean life-times are summarised in Table 2, and activation parameters from variable-temperature experiments are given in Table 3 (see SUP 21726 for the full results).

For the systems $PMe_2(CF_3){\cdot}BMe_3$, $P(CH_2Ph)_3{\cdot}BMe_3$, and $PMe_3O{\cdot}BMe_3$, chemical shifts and coupling constants for mixtures of the two components did not differ significantly from those of the separate species. Although it is possible that the free and complexed components have the same n.m.r. parameters, it is more likely that complex formation was not appreciable. Significant differences between chemical shifts and coupling constants of free and complexed

TABLE 3

Activation parameters [a]

DA	Solvent	Excess of	$E^‡$	$\Delta H^‡$	$\Delta S^‡$
$PMe_3{\cdot}BMe_3$	C_6H_5Me	D [b]	65	63	36
		A [c]	67 ± 6	65 ± 6	39
	CH_2Cl_2	D [b]	73	71	55
		A [c]	66 ± 5	64 ± 6	27
$PMe_2Ph{\cdot}BMe_3$	C_6H_5Me	D	49	47	−1
		A	54	52	20
	CH_2Cl_2	D	62	60	42
		A	67	65	65
$PMe_2(NMe_2){\cdot}BMe_3$	C_6H_5Me	D	65 [d]	63	49
			61 [e]	59	37
		A	59	57	36
$PMe_3{\cdot}BMe_2Ph$	CH_2Cl_2	D	106	104	142
		A	93	90	92
$PMe_2Bu^t{\cdot}BMe_3$	C_6H_5Me	D	75	73	100

[a] Except where indicated, estimated errors for $E^‡$ and $\Delta H^‡$ are ±3 kJ mol^{-1}; for $\Delta S^‡$, ±20 J K^{-1} mol^{-1}. [b] Ref. 2. [c] Ref. 1. [d] From *N*–Me region. [e] From *P*–Me and *B*–Me regions.

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components were found in spectra of samples at lower temperatures, and the parameters δ_D' and $^2J_D'$ for the complexed species were found from samples with a large excess of acceptor. For the system $P(CH_2Ph)_3{\cdot}BMe_3$, equilibrium constants K_1 (Table 4) for equilibrium (2) were estimated

$$D + A \rightleftharpoons DA \qquad (2)$$

both from observed donor shifts and coupling constants. In view of the assumptions made, the agreement is probably to some extent fortuitous. From the temperature variation of K_1, the dissociation energy for the complex is probably between 20 and 30 kJ mol^{-1}.

TABLE 4

Equilibrium constants for tribenzylphosphine–trimethylborane [a]

θ_c / °C	$^2J(PCH)_{obs.}$ / Hz	K_1 / dm^3 mol^{-1}	
25	−1.0	1.0 [b]	1.9 [c]
20	−2.0	2.1	
10.5	−3.0	3.9	3.4
−10.5	−4.5	10.4	8.3
−30	−5.0	15.2	
−40	-5.2_5	18.3	20.6

[a] In dichloromethane: $P(CH_2Ph)_3$, 0.346; BMe_3, 0.307 mol dm^{-3}. [b] From coupling constants. [c] From acceptor shifts.

The n.m.r. technique does not allow the determination of equilibrium constants K_1 for systems suitable for kinetic study. Relative equilibrium constants, K_2, referring to equilibrium (3), were obtained from the observed coupling

$$PMe_3{\cdot}BMe_3 + L \rightleftharpoons L{\cdot}BMe_3 + PMe_3 \qquad (3)$$

constants: L = NMe_3, 1.62; PMe_2Ph, 0.035; $PMe_2(NMe_2)$, 0.11; PMe_2Bu^t, 0.12. Thus in dichloromethane at 37 °C, the basicities of NMe_3 and PMe_3 towards BMe_3 were similar, as in the gas phase.[11] If equilibrium constants in the gas phase and in solution are comparable, the values of K_1 for NMe_3 or PMe_3 are likely to be *ca.* 5×10^4 dm^3 mol^{-1}.

DISCUSSION

The order of basicities towards trimethylborane in dichloromethane is $NMe_3 \sim PMe_3 > PMe_2Ph > PMe_2(NMe_2) \sim PMe_2Bu^t \gg P(CH_2Ph)_3 > PMe_2(CF_3) \sim PMe_3O \sim PMePh_2$. A similar order was found from i.r. stretching frequencies in the compounds $[Ni(CO)_3D]$.[12] For the last four bases, exchange between free and complexed donor and between free and complexed acceptor was fast on the ^1H n.m.r. time scale at all observable temperatures and so kinetic data could not be obtained. For the first five bases it was possible to measure the rates of exchange between free and complexed species. In all cases where data over a range of concentrations [D], [A], or [DA] could be obtained, the life-times of the complex, τ_{DA}, varied only slightly and so the rate-determining step appeared to be dissociation of the complex DA, as found previously for the systems $NMe_3{\cdot}BMe_3$[13] and $PMe_3{\cdot}BMe_3$.[1,2] As expected, the rates of

$$DA \xrightarrow[\text{slow}]{k_1} D + A;$$

$$\tau_{DA}^{-1} = (-d[DA]/dt)/[DA] = k_1 \qquad (4)$$

exchange are in the same order as the basicities of the donors D. Rate study by exchange between components within a spin multiplet has a major advantage over that by exchange between chemically shifted sites, since the site separation is usually independent of temperature in the former case but may vary considerably in the latter when it is best treated as an extra variable. This makes higher demands on the quality of the spectrum, so that parameters given here for systems with excess of donor [obtained wholly or in part through collapse of the $^3J(PBCH)'$ doublet] are probably more reliable than those for systems with excess of acceptor. Undoubtedly, the biggest constraint in extending this method to a wide range of compounds is the low solubility of many complexes, particularly at low temperatures.

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