Competition between Different Nucleophilic Sites belonging to the Same Lewis Bases. Part 3.[1] The Basicity of Arsenic and Phosphorus Sites relative to Borane

By **Marcel Durand, Claude Jouany,** and **Gérard Jugie,*** Laboratoire de Chimie de Coordination du CNRS, BP 4142, 31030 Toulouse Cedex, France
Lucien Elegant and **Jean-François Gal,** Laboratoire de Chimie Physique Organique, Université de Nice, Parc Valrose, 06034 Nice, France

After establishing some structural characteristics of a few simple $AsR_3{\cdot}BH_3$ adducts (R = Me, Et, or Ph) by n.m.r. spectroscopy, the reaction of BH_3 with a ligand (L) containing both phosphorus and arsenic donor sites ($Ph_2PCH_2CH_2AsPh_2$) has been studied. The superior basicity of phosphorus as compared to arsenic in these adducts is shown by displacement reactions and a calorimetric study. Enthalpic data (in kJ mol^{-1}) obtained for the gas–liquid reactions (i) and (ii) are $\Delta H_1 = -160.4$ and $\Delta H_2 = -153.4$ for M = P, and $\Delta H_1 = -76.1$ and $\Delta H_2 = -111.3$

$$2MPh_3(sol) + B_2H_6\,(g) \xrightarrow{\Delta H_1} 2MPh_3{\cdot}BH_3(sol) \qquad (i)$$

$$MPh_3(sol) + BH_3\,(g) \xrightarrow{\Delta H_2} MPh_3{\cdot}BH_3(sol) \qquad (ii)$$

for M = As. In the case of L, two stages of complexation may be separated and the corresponding enthalpies (kJ mol^{-1}) are $\Delta H_1 = -165.3$ ($2L + B_2H_6$) and $\Delta H_2 = -155.6$ ($L + BH_3$) corresponding to complexation of the phosphorus site, and $\Delta H_1 = -60.7$ ($2L{\cdot}BH_3 + B_2H_6$) and $\Delta H_2 = -103.3$ ($L{\cdot}BH_3 + BH_3$) corresponding to complexation of the arsenic site.

THE co-ordinating powers of simple boranes with respect to Group 5A donors containing nitrogen or phosphorus have been extensively investigated during the last two decades,[2] but relatively little is known about arsenic–boron adducts.[3-7] We therefore report the characterization of several $AsR_3{\cdot}BH_3$ compounds (R = Me, Et, or Ph) using n.m.r. spectroscopy as the main analytical tool; moreover, following our previous investigation [1] of the competition between two different donor sites within the same molecule, we have studied the behaviour of phosphorus and arsenic atoms when they occur in chemically similar environments, as in 1-diphenylarsino-2-diphenylphosphinoethane, $Ph_2PCH_2CH_2AsPh_2$ (L). Then, with the aid of calorimetric results, the order of basicity of phosphorus and arsenic towards BH_3 is compared.

EXPERIMENTAL

Owing to the sensitivity of the ligands and adducts to air, the experiments were made in a dry inert atmosphere. Trimethylarsine and triethylarsine were prepared by the action of arsenic trichloride on Grignard reagents and were purified by standard procedures.[8,9] Triphenylphosphine, triphenylarsine, and 1-diphenylarsino-2-diphenylphosphinoethane (L) were obtained commercially. Microanalytical data were within acceptable limits and the purity was checked by n.m.r. tests, which in this case can detect *ca.* 1% of impurity.

Preparation of Diborane.—(*a*) When a large excess was necessary, B_2H_6 was prepared by Schlesinger's method [10] using diethylether–boron trifluoride and sodium tetrahydroborate in glyme [bis(2-methoxyethyl) ether]. The resulting B_2H_6 was introduced into a benzene solution of the free ligand by means of a capillary or a tube having a small sintered-glass tip.

(*b*) When known amounts of BH_3 had to be mixed with the ligands, we used Reetz's method.[11] In a typical experiment, a mixture of equimolar amounts of $Na[BH_4]$ and base in an excess of tetrahydrofuran (thf) was treated

---

[1] Part 2, F. Grasnier, C. Jouany, G. Jugie, J. F. Labarte, and J. M. Savariault, *J. Chim. phys.*, 1976, **73**, in the press; part 1, C. Jouany, J.-P. Larent, and G. Jugie, *J.C.S. Dalton*, 1974, 1510.

[2] See, for example, T. D. Coyle and F. G. A. Stone, *Progr. Boron Chem.*, 1964, **1**, 83; G. W. Parshall, 'The Chemistry of Boron and its Compounds,' Wiley, New York, 1967, p. 615; K. Niedenzu and J. W. Dawson, *ibid.*, p. 377; H. Nöth, *Progr. Boron Chem.*, 1970, **3**, 212.

[3] F. Hewitt and A. K. Holliday, *J. Chem. Soc.*, 1953, 530.

[4] F. G. A. Stone and A. B. Burg, *J. Amer. Chem. Soc.*, 1954, **76**, 386.

[5] A. B. Burg and L. R. Grant, *J. Amer. Chem. Soc.*, 1959, **81**, 1.

[6] J. R. Durig, B. A. Hudgens, and J. M. Odom, *Inorg. Chem.*, 1974, **13**, 2306.

[7] R. Goetze and H. Nöth, *Z. Naturforsch.*, 1975, **B30**, 343.

[8] E. G. Claeys, *J. Organometallic Chem.*, 1966, **5**, 446.

[9] W. J. C. Dyke and W. J. Jones, *J. Chem. Soc.*, 1930, 2426; J. Seifter, *J. Amer. Chem. Soc.*, 1939, **61**, 530.

[10] H. C. Brown and P. A. Tierney, *J. Amer. Chem. Soc.*, 1958, **80**, 1552.

[11] T. Reetz and B. Katlafsky, *J. Amer. Chem. Soc.*, 1960, **82**, 5036; T. Reetz, *ibid.*, p. 5039.

with carbon dioxide at room temperature, with vigorous stirring, until the exothermic reaction was complete and the absorption of CO_2 had ceased. The reaction product was filtered off and the filtrate was evaporated. Fractional crystallization of the residue yielded the adduct. The stoicheiometry of these adducts was determined from microanalytical data; calorimetric titrations confirmed the formation of 1 : 1 adducts between BH_3 and PR_3 or AsR_3 ligands.

TABLE 1

Hydrogen-1, ^{31}P, and ^{11}B n.m.r. data

Compound	Chemical shift (p.p.m.) [a]						Coupling constant (Hz)	
	$\delta(CH_3)$	$\delta(CH_2)$	$\delta(C_6H_5)$	$\delta(BH_3)$	$\delta(^{31}P)$	$\delta(^{11}B)$	$^1J(BP)$	$^1J(BH)$
$AsMe_3$	0.9_4							
$AsMe_3 \cdot BH_3$	1.2_6			1.0_8		-34.5 [b] -32.5 [b]		105 100 [b]
$AsEt_3$	1.1_1	1.3_6						
$AsEt_3 \cdot BH_3$	1.1_8	1.6_6		1.1		-40.5		102
$AsPh_3$			7.3_2					
$AsPh_3 \cdot BH_3$			7.4_6	*ca.* 1.3_5		-35 [c] -34 [c]		95
PPh_3			7.2_7		-118.5			
$PPh_3 \cdot BH_3$			7.4_7	*ca.* 1.7	-92	-37.5	60	95
L					-127			
$L \cdot BH_3$					-94.5	-39	60	95
$L \cdot 2BH_3$					-94.5	-39 [d]	60	95

[a] The following standards were used: ^1H, $SiMe_4$ (internal); ^{31}P, P_4O_6 (external); and ^{11}B, $OEt_2 \cdot BF_3$ (external). High-field shifts are shown as negative values. [b] See ref. 6. [c] See ref. 7. [d] For this compound the resonances of the two different boron nuclei (P·B and As·B) were so close that the pattern was not resolved. Nevertheless, the As·B resonance appeared as a shoulder on the low-field area of the P·B resonance.

Proton and ^{31}P magnetic resonance measurements were made on Perkin-Elmer R 10 and R 12 spectrometers operated at 60.00 and 24.29 MHz; ^{11}B and some ^1H n.m.r. spectra were recorded on a Brücker WH 90 spectrometer operating at 28.88 and 90.00 MHz. For the displacement reactions, a weighed amount of the adduct was dissolved in benzene and the equimolar amount of a base was added. The solution was then transferred to the n.m.r. tube and the spectrum recorded (at 33 °C in the Perkin-Elmer spectrometer, and at room temperature in the Brücker spectrometer).

Calorimetric titrations were made with a Calvet calorimeter [12a] fitted with a vacuum line.[12b] Diborane was prepared under low pressure by the reaction of $K[BH_4]$ with 85% phosphoric acid.[13] The gas was purified by passage through traps at -76 °C (solid carbon dioxide–acetone), and at -111 °C (CS_2 slush) and condensed at -196 °C (liquid nitrogen). After completion of the reaction, the condensed B_2H_6 was evaporated, passed through another trap at -111 °C, and condensed in a calibrated glass bulb. The titrations were carried out by adding successive small quantities of B_2H_6 (*ca.* 10^{-4} mol precisely measured by pressure differences) to a 0.5 mol dm^{-3} solution (0.2 mol dm^{-3} in the case of L) of base (3 cm^3, 1.5×10^{-3} or 0.6×10^{-3} mol). Quantities of heat were measured by electronic integration of the voltage delivered by the calorimeter sensor, which is proportional to the heat flow. The calorimeter and the integrator were calibrated by the Joule effect. A plot of the sum of all the measurements of the heat evolved against the number of moles of B_2H_6 added gave a line of gradient $-\Delta H_1$ with a sharp change in gradient when 0.5 mol of B_2H_6 had been added to 1 mol of PPh_3 or $AsPh_3$. In the case of L the titration curves showed two changes in gradient at mol ratios of 1 : 2 and 1 : 1 between B_2H_6 and L. In the latter case the gradients gave $-\Delta H_1(P)$ and $-\Delta H_1(As)$ for the complexation of the phosphorus and arsenic site respectively (see Discussion and Figure). No correction for the heat of solution of B_2H_6 was made since the Lewis acid is almost insoluble in C_6H_6, and therefore no significant heat effect appears when B_2H_6 is passed through the pure solvent.

RESULTS

Reaction of Free Bases with Diborane.—The direct introduction or *in-situ* generation of B_2H_6 in ligand solutions gave rise to adduct formation according to the general scheme: Base + $\frac{1}{2}$ $B_2H_6 \longrightarrow$ Base·BH_3. The bases $AsMe_3$, $AsEt_3$, and $AsPh_3$ consumed one equivalent of BH_3 as shown by the microanalytical data, the calorimetric titrations, and the n.m.r. data. In these three cases the reactions were quantitative and did not lead to any secondary products, as was verified by ^{11}B and ^1H n.m.r. On the other hand, the reaction of L ($Ph_2PCH_2CH_2AsPh_2$) with B_2H_6 occurred in two stages: first, the base combined with one equivalent of BH_3, producing a white crystalline compound which is readily soluble in benzene; secondly, the $L \cdot BH_3$ adduct reacted with another equivalent of BH_3 to produce an adduct which is slighly soluble in benzene. Thus, the two adducts ($L \cdot BH_3$ and $L \cdot 2BH_3$) may be isolated by fractional crystallization. This two-step addition provides chemical evidence that both sites (P,As) of L are active towards borane fragments.

N.M.R. Spectra.—In contrast to phosphine–borane adducts, very few complete investigations are described in the literature [6,7] for the arsine–borane analogues. Nevertheless the ^{11}B and ^1H n.m.r. spectra clearly demonstrate the structure of the molecules: in each case, the ^{11}B spectra consisted of a 1 : 3 : 3 : 1 quartet (poorly resolved for $AsPh_3 \cdot BH_3$), displaced upfield from the standard $OEt_2 \cdot BF_3$, in a position typical of a four-co-ordinate boron;[14] the ^1H spectra gave at least two other pieces of evidence for the

---

[12] (*a*) H. D. Brown, 'Biochemical Microcalorimetry,' Academic Press, New York, 1969, chs. 1 and 14; (*b*) L. Elegant, J. Cassan, and M. Azzaro, *Bull. Soc. chim. France*, 1968, 2675.

[13] A. D. Norman, *Inorg. Synth.*, 1968, **11**, 15.

[14] W. Phillips, H. Miller, and E. Muetterties, *J. Amer. Chem. Soc.*, 1959, **81**, 4496; H. Nöth and H. Vahrenkamp, *Chem. Ber.*, 1966, **89**, 1049.

formation of the As·B bond since we simultaneously observed a quartet * of broad peaks attributable to the BH_3 resonances, a shift to low field of the CH_3 (in $AsMe_3\cdot BH_3$) and C_6H_5 resonances, and a large increase in the internal shift, Δ_{int}, of the ethyl group (CH_3CH_2As) (0.48 p.p.m. for the $AsEt_3\cdot BH_3$ adduct compared to 0.25 p.p.m. in the parent arsine).

Concerning the L adducts ($L\cdot BH_3$ and $L\cdot 2BH_3$), the ^{11}B and ^1H spectra were complex because of the overlapping of the resonance patterns attributable to the phosphorus and arsenic environments. Fortunately the interpretation of the ^{31}P spectra is more straightforward and clear indications are obtained from them; in fact, when the first BH_3 group was added ($L\cdot BH_3$) a large shift was observed relative to the free-ligand (L) resonance, but further addition of BH_3 (leading to $L\cdot 2BH_3$) gave no appreciable change in the ^{31}P resonance pattern. In view of the sensitivity of the $\delta(^{31}P)$ parameter to the co-ordination environment in this kind of compound, this affords strong evidence for the initial attack of BH_3 on the phosphorus atom of the L molecule.

Calorimetric Results.—The calorimetric determinations give values for the enthalpies of reaction (1). Knowing the

$$2MR_3(sol) + B_2H_6\ (g) \xrightarrow[\Delta H_1]{C_6H_6} 2MR_3\cdot BH_3(sol) \qquad (1)$$

value for the enthalpy of dissociation of diborane,[16] we obtain ΔH_2 corresponding to reaction (2). The ΔH_1 and

$$MR_3(sol) + BH_3\ (g) \xrightarrow{\Delta H_2} MR_3\cdot BH_3(sol) \qquad (2)$$

ΔH_2 values are given in Table 2, from which it can be seen that there is a marked difference of *ca.* 40 kJ mol^{-1} between the two phenyl analogues of phosphorus and arsenic; this difference is significant and shows that the donor–acceptor bond strength is very much stronger in $PPh_3\cdot BH_3$ than in $AsPh_3\cdot BH_3$. These results are still more striking when we look at a plot of the calorimetric titration of the two-donor-site base (L) with BH_3: this clearly shows two different gradients with a sharp inflexion corresponding exactly to one equivalent of BH_3 added to L. The two gradients of the plot (see Figure) give two different heats of complexation (ΔH_2) which correspond almost exactly with the individual phosphine–borane and arsine–borane values.

DISCUSSION

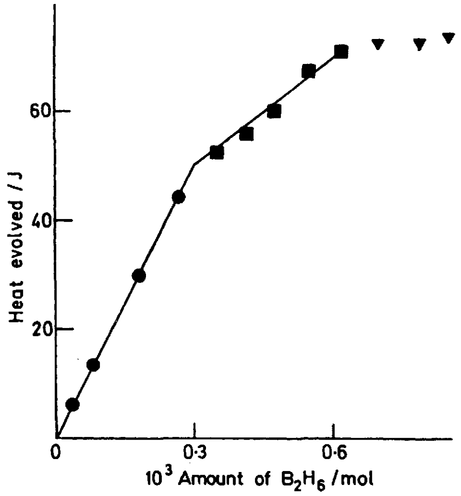
Although the general trend of co-ordination P > As towards BH_3 has already been established by various methods,[17] we wanted to test this sequence in such a way that there would be no ambiguity arising from experimental factors. The chemical and n.m.r. data cited above confirm the structure given for $AsR_3\cdot BH_3$, $L\cdot BH_3$, and $L\cdot 2BH_3$; moreover, the analysis of the ^{31}P n.m.r. spectra demonstrates the difference in basicity between the phosphorus and the arsenic atoms with reference to the Lewis acid BH_3. The calorimetric determinations confirm the validity of the sequence P > As. We note that the basicity of the arsenic site in L is not greatly affected by the complexation of phosphorus with BH_3 since the observed ΔH_2 value (−103.3 kJ mol^{-1}) appears to be very close to that obtained for $AsPh_3$ (*cf.* Table 2). We emphasize this feature, which indicates that in L we are not confronted with steric-hindrance effects as we were during the study of the BH_3 adducts of $P(CH_2NEt_2)_3$;[1] we recently obtained [18] calorimetric data which thoroughly confirm the previous n.m.r. results.[1] In fact, the calorimetric-titration curve of $P(CH_2NEt_2)_3$ does not show any inflexion before three BH_3 groups are co-ordinated with the free ligand; moreover, the ΔH_2 value (−161.7 kJ mol^{-1}), which corresponds to the bonding of borane to the nitrogen's lone pair of electrons (*cf.* ΔH_2 *ca.* 168 kJ mol^{-1} in $NEt_3\cdot BH_3$), is in perfect agreement with the conclusion of the n.m.r. study which shows that in the particular case of $P(CH_2NEt_2)_3$ the formation of the P·B bond is extremely unfavourable when compared to that of the N·B bond.

TABLE 2

Enthalpies (kJ mol^{-1}) of reaction of the Lewis bases and diborane

Compound	$-\Delta H_1$ [a]	$-\Delta H_2$
PPh_3 [b]	160.4 ± 2.5	153.4
$AsPh_3$	76.1 ± 3.3	111.3
$Ph_2PCH_2CH_2AsPh_2$ (L)	165.3 ± 3.8	155.6
	60.7 ± 4.2	103.3

[a] The quoted errors are the 95% confidence levels. [b] These results are in good agreement with the values of 37.5 kcal mol^{-1}, *i.e.* 156.9 ± 1.3 kJ mol^{-1}, obtained by T. McAllister and H. Mackle, *Trans. Faraday Soc.*, 1969, **65**, 1734.



Plot of the heat evolved against quantity of B_2H_6 added to 0.2 mol dm^{-3} solution of L (3 cm^3, 6 × 10^{-4} mol): (●), complexation of the phosphorus site; (■), complexation of the arsenic site; (▼), no further reaction

As a final test of the conclusion given above for

---

* In fact, the observed splitting does not rigorously consist of four 1 : 1 : 1 : 1 equidistant peaks owing to the well known 'thermal-decoupling' effect.[15] However, since the BH_3 quartet only slightly collapsed at the recording temperature (33 °C), a first-order analysis was possible and $^1J(BH)$ was measured as the separation of the central peaks.

[15] See, for example, J. Bacon, R. J. Gillespie, and J. W. Quail, *Canad. J. Chem.*, 1963, **41**, 3063; R. V. Ammon, B. Kanellakopulos, G. Schmid, and R. D. Fischer, *J. Organometallic Chem.*, 1970, **25**, C1; D. W. Lowman, P. D. Ellis, and J. D. Odom, *J. Magnetic Resonance*, 1972, **8**, 289.

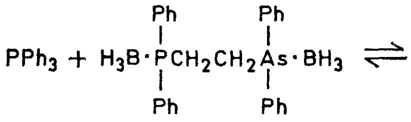
[16] T. P. Fehlner and G. W. Mappes, *J. Phys. Chem.*, 1969, **73**, 873; G. W. Mappes, S. A. Fridmann, and T. P. Fehlner, *ibid.*, 1970, **74**, 3307.

[17] D. C. Mente, J. L. Mills, and R. E. Mitchell, *Inorg. Chem.*, 1975, **14**, 123; D. C. Mente and J. L. Mills, *ibid.*, p. 1862.

[18] L. Elegant, J. F. Gal, C. Jouany, and G. Jugie, unpublished work.

PPh_3, $AsPh_3$, and L, some homogeneous displacement reactions were studied which involved equimolar amounts of an adduct Base-1$\cdot BH_3$ and another ligand Base-2. Using ^{31}P n.m.r. spectra, we took advantage of the well known large shift in the phosphorus signal towards low fields (50—70 p.p.m.) when PR_3 is complexed by boron Lewis acids [19] in order to determine the position of the equilibria (3) and (4). In both cases equilibrium was reached rapidly and in (3) we observed the complete disappearance of the signal attributable to the free phosphine; this was replaced by the $PPh_3\cdot BH_3$ pattern, which is displaced 26 p.p.m. downfield from PPh_3. In (4) a very similar behaviour was found, that is the free PPh_3 signal vanished, and an unchanged pattern for the signal attributable to $Ph_2P(\cdot BH_3)CH_2CH_2AsPh_2$ was observed. It is of interest to note that, in the system $PPh_3\cdot BH_3 + AsPh_3$, borane is not displaced by the arsine from the triphenylphosphine adduct. The results of these investigations of the equilibria provide new evidence that the As$\cdot$B bond is less favoured than the P$\cdot$B bond in systems such as alkyl derivatives of phosphorus and arsenic not involving steric hindrance.

$$PPh_3 + AsPh_3\cdot BH_3 \rightleftharpoons \quad (3)$$



$$PPh_3 + H_3B\cdot \underset{Ph}{\overset{Ph}{P}}CH_2CH_2\underset{Ph}{\overset{Ph}{As}}\cdot BH_3 \rightleftharpoons \quad (4)$$

[6/244 *Received, 5th February*, 1976]

---

[19] J. F. Nixon and A. Pidcock, *Ann. Rev. N.M.R. Spectroscopy*, 1969, **2**, 346.