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Proton n.m.r. Spectrum of a Novel "Triple Mixed Hydride"

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THE formation of 'triple metal mixed hydrides' containing lithium, aluminium, and boron as the non-hydrogen species has been questioned by Ashby and Foster.[1] They found that these hydrides were best described in an ionic form with lithium cations and aluminium–boron hydride anions. Whilst investigating the reaction of mixed hydrides with boron Lewis acids, we found that a 2:1 adduct can be formed between monosilylphosphine and diborane.

The proton n.m.r. spectrum of this liquid adduct shows that it has the structure $SiH_3PH_2BH_3$ rather than an ionic form containing the borohydride ion or the form $2SiH_3PH_2{\cdot}B_2H_6$. Thus we not only have a 'triple mixed hydride' with all three different non-hydrogen species directly connected, but there is the added novelty that at least one isotope of each element has a nuclear spin. The spectrum was run in a sealed n.m.r. tube on a Varian A60 with tetramethylsilane (TMS) as an internal standard. A spectrum (run at 0° to minimise effects due to the slow decomposition of the adduct) is shown in the Figure.

The spectrum is readily analysed in terms of first-order coupling. Three distinct groups of hydrogen signals can be seen which arise from the three different environments of the hydrogen atoms in $SiH_3P\dot{H}_2B\ddot{H}_3$.

The $-SiH_3$ resonance is seen as the doublet of 1:2:1 triplets centred at 4·0 p.p.m. downfield of TMS. The triplet pattern results from the spin–spin coupling of the hydrogen atoms on silicon with the two equivalent phosphorus protons ($J_{H\dot{H}} = 4$ c./sec.). The coupling of phosphorus ($I = \frac{1}{2}$) with the hydrogen atoms on silicon gives the main doublet ($J_{PH} = 13{\cdot}5$ c./sec.). In addition to the above coupling, the interaction between the ^{29}Si nucleus (5% abundant, $I = \frac{1}{2}$) and its protons results in a further doublet splitting. Although the high-field side of this doublet is partly coincident with a $-B\ddot{H}_3$ resonance, the 'satellites' can be seen clearly at 5·9 and 2·1 p.p.m. downfield of TMS ($J_{SiH} = 228$ c./sec.).

The $-P\dot{H}_2$ resonance is seen as the widely separated doublet of ten-line multiplets centred at 3·9 p.p.m. resulting from the coupling between phosphorus and its protons. The large value of the coupling constant ($J_{P\dot{H}} = 358$ c./sec.) is common in four-co-ordinated phosphorus compounds. The multiplet pattern arises from the coupling of the hydrogen atoms on phosphorus with both the three equivalent silicon protons, and the three equivalent boron protons. Both these spin–spin interactions should give rise to 1:3:3:1 quartets. However, if it is assumed that the value of the $J_{\dot{H}\ddot{H}}$ coupling constant is of the order of twice that of $J_{H\dot{H}}$, then a multiplet of ten lines would be predicted with the approximate intensity ratio 1:3:6:10:12:12:10:6:3:1. Confirmation of this assignment is given by the integration of the low-field multiplet (centred at 6·9 p.p.m.) which gives the ratio 1:2·8:5·4:9·6:

11·9 : 12·2 : 10·2 : 6·4 : 3·4 : 1·6. Thus the value of the $J_{\dot{H}\ddot{H}}$ coupling constant must be close to 8 c./sec., which is the value found for the corresponding coupling in PH_3BH_3.[2] As was the case with the spectrum of monosilylphosphine, we were unable to detect coupling between the ^{29}Si nucleus and the phosphorus protons.[3]

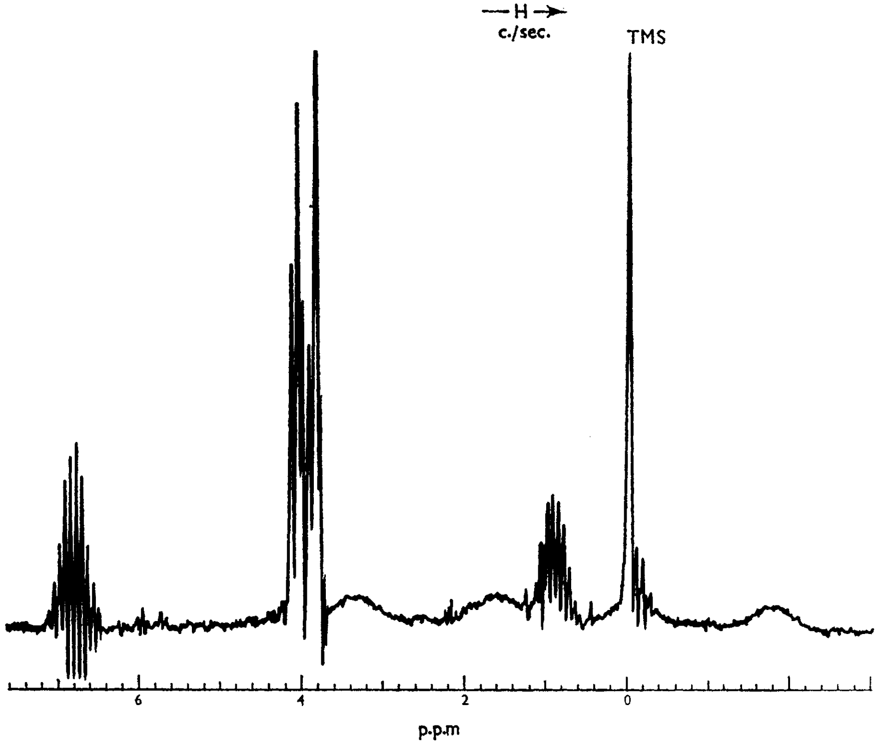

FIGURE. *The proton n.m.r. spectrum of* $SiH_3P\dot{H}_2BH_3$, *with tetramethylsilane* (TMS) *as an internal standard.*

The $-B\ddot{H}_3$ resonance is seen as the 1 : 1 : 1 : 1 quartet of unresolved multiplets centred at 0·75 p.p.m. The spin–spin coupling of the hydrogen atoms on boron with the ^{11}B nucleus (80% abundant, $I = \frac{3}{2}$) gives the quartet. The multiplet pattern arises from the overlap of the coupling of the hydrogen atoms on boron with the phosphorus protons and with the phosphorus nucleus. It is not sufficiently resolved to allow us to obtain a value for $J_{P\ddot{H}}$ but the width of each multiplet indicates that it is probably close to the value of 16 c./sec. found in PH_3BH_3.

Finally, our experimental value for the ratio of the peak intensities for $-SiH_3$, $-P\dot{H}_2$, and $B\ddot{H}_3$ is of the order of the theoretical ratio 3 : 2 : 2·4. The analysis of the spectrum is therefore entirely consistent with the structure $SiH_3PH_2BH_3$.

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[3] J. E. Drake and W. L. Jolly, *J. Chem. Phys.*, 1963, **38**, 1033.