molecular (over intermolecular) S_N2 reaction of the intermediate $ClCH_2(CH_2SCH_2)_2CH_2S^-$ species that results from the attack of the first thiolate on 1,2-dichloroethane.

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Relative Signs of P-P Coupling Constants in the NMR Spectra of Octahedral Metal Phosphine Complexes

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^{31}P NMR spectroscopy is one of the most important techniques for examining and characterizing diamagnetic metal phosphine complexes. In particular, in six-coordinate complexes, two-bond phosphorus-phosphorus coupling constants $^2J_{PP}$ across the metal center (P-M-P) are characteristic of the relative stereochemistry of the phosphine ligands as well as the nature of metal-ligand bonding in the complex.[1] Generally, the magnitude of $^2J_{PP}$(trans) is greater than $^2J_{PP}$(cis) with $^2J_{PP}$(trans) having a positive sign and $^2J_{PP}$(cis) being negative.[1,2] With the increasing availability of modern NMR facilities and the introduction of new NMR methods[3] sensitive to the relative signs of coupling constants, determination of the signs of coupling constants in metal complexes will become more frequent. The relative (and absolute) signs of interligand coupling constants are potentially important parameters which directly reflect the nature of the metal-phosphorus bonds between the coupled nuclei, and in the future the signs of coupling constants will undoubtedly be invoked to support structural assignments.

Where the specific symmetry of the metal complex leads to spin systems containing chemically but not magnetically equivalent phosphorus nuclei (e.g. AA'XX', AA'BB', AA'XX'Y, etc.) it has been possible to obtain $^2J_{PP}$ coupling constants by analysis of the complex NMR spectra. For simple spin systems, analytical solutions of the NMR spectra exist[4] and iterative computer programs[5] permit routine analysis with a high degree of automation, even for very complex spin systems.

We wish to highlight a common error in spectral analysis, before its occurrence becomes widespread: *in many instances, an NMR spectrum does not have a unique solution.* Even in complex spin systems, e.g. AA'BB' spin systems or spin systems that are second order by virtue of strong coupling between nuclei with similar chemical shifts, the spectra are not necessarily sensitive to the signs or magnitudes of each of the coupling constants in the spin system.

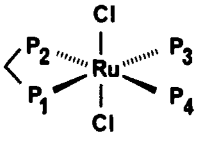
In the particular case of the analysis of an AA'BB' (or AA'XX') spin system, the symmetry of the spin system leads to an *NMR spectrum that does not have a unique solution.* From the NMR spectrum of an AA'BB' spin system, by spectral analysis alone, it is possible to determine the relative signs (i.e. like or opposite) of $J_{AA'}$ and $J_{BB'}$ and the relative signs of J_{AB} and $J_{AB'}$ but the sign relationship between these two sets of coupling constants cannot be established. Moreover, although the magnitudes of the two coupling constants $J_{AA'}$ and $J_{BB'}$ can be determined, by virtue of the symmetry of the spin system it is not possible to distinguish which coupling constant is $J_{AA'}$ and which is $J_{BB'}$. Similarly a distinction between J_{AB} and $J_{AB'}$ is impossible. Given the spectrum of an AA'BB' spin system, without any additional information, there are 16 different combinations of the coupling constants that will give identical NMR spectra. In such spin systems, in order establish the correct solution (or at least to narrow the range of possible solutions) one can rely on precedent from the analysis of the spectra of similar compounds with spin systems where no ambiguity in the analysis exists. Alternatively, additional experiments that are sensitive to either signs or magnitudes of specific coupling constants can be performed.

Table I. $^2J_{PP}$ (Hz) for Complexes **1** and **2**[a]

complex	$J_{P1,P2}$[b]	$J_{P1,P3}$ (=$J_{P2,P4}$)	$J_{P1,P4}$ (=$J_{P2,P3}$)	$J_{P3,P4}$[b]
1a	−31.2 (−37.4)	307.0	−38.4	−37.4 (−31.2)
1b	−28.7 (−35.8)	305.1	−36.4	−35.8 (−28.7)
2a	−35.1 (−17.5)	297.4	−33.2	−17.5 (−35.1)
2b	−33.3 (−16.5)	292.5	−32.8	−16.5 (−33.3)

[a] Magnitudes of $^2J_{PP}$ were taken directly from ref 6. $^2J_{PP}$(trans) is taken to be positive.[1,2] [b] $J_{P1,P2}$ and $J_{P3,P4}$ cannot be distinguished by simple spectral analysis (see text); the alternative assignment is given in parentheses.

In a recent report[6] of the synthesis of a series of octahedral ruthenium complexes, $Ru(DPPM)L_2Cl_2$ [DPPM = bis(diphenylphosphino)methane] (**1**) and $Ru(DPPE)L_2Cl_2$ [DPPE = 1,2-bis(diphenylphosphino)ethane] (**2**) (L = $PPhMe_2$ or PPh_2Me),



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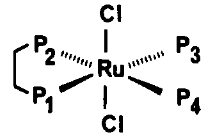

2

a. P_3, P_4 = $PPhMe_2$

b. P_3, P_4 = PPh_2Me

the analysis of the resulting AA'BB' ^{31}P NMR spectra was reported to give the signs of $J_{P1,P2}$, $J_{P3,P4}$ and $J_{P1,P3}$ (=$J_{P2,P4}$) as negative with $J_{P1,P4}$ (=$J_{P2,P3}$) being positive. Although $J_{P1,P3}$ (=$J_{P2,P4}$) cannot, in theory, be distinguished from $J_{P1,P4}$ (=$J_{P2,P3}$), $J_{P1,P3}$ is clearly $^2J_{PP}$(trans) by its magnitude.

The relative signs reported for the coupling constants are clearly unreasonable. There can be no significant difference between the bonding in any pair of cis phosphorus atoms in these complexes and although minor differences between $J_{P1,P2}$, $J_{P2,P3}$ (=$J_{P1,P4}$), and $J_{P3,P4}$ might be anticipated, an inversion of sign would be impossible. Simulation of the reported spectra demonstrates that $J_{P1,P3}$ (=$J_{P2,P4}$) and $J_{P1,P4}$ (=$J_{P2,P3}$) necessarily have opposite sign and that $J_{P1,P2}$ and $J_{P3,P4}$ have the same sign. However, as outlined above, the spectra are insensitive to the relative signs of the set of coupling constants $J_{P1,P2}$ and $J_{P3,P4}$ with respect to the set $J_{P1,P3}$ (=$J_{P2,P4}$) and $J_{P1,P4}$ (=$J_{P2,P3}$). For those complexes of group 8 transition metals where the signs of $^2J_{PP}$ have been determined,[1] $^2J_{PP}$(trans) has a positive sign and the signs of *all* $^2J_{PP}$(cis) in **1** and **2** must therefore be negative to provide solutions to the spectra that are chemically reasonable. Additionally, from the analysis of the AA'BB' spin systems of **1** and **2** it is not possible to distinguish $J_{P1,P2}$ from $J_{P3,P4}$ so the assignment of these coupling constants must remain ambiguous (Table I).

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(1) See, for example: (a) Pregosin, P. S.; Kunz, R. W. *NMR Basic Princ. Prog.* **1979**, *15*, 28-34, 86 and references therein. (b) Verkade, J. G. *Coord. Chem. Rev.* **1972/1973**, *9*, 1-106.

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(4) See, for example: (a) Corio, P. L. *Structure of High-Resolution NMR Spectra*; Academic: New York and London, 1966. (b) Abraham, R. J. *The Analysis of High Resolution NMR Spectra*; Elsevier: Amsterdam, 1971. (c) Günther, H. *NMR Spectroscopy*; Wiley: Chichester, England, New York, Brisbane, Australia, and Toronto, Canada, 1980; pp 171-83.

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The routine analysis of complex NMR spectra is one of the most powerful methods for accurately obtaining spin–spin coupling constants. In many spin systems, particularly simple systems with symmetry, the solution to the analysis is not unique and one must be aware of uncertainties and ambiguities inherent in the analysis before concrete assignments are made.

Registry No. **1a**, 104421-72-9; **1b**, 104421-73-0; **2a**, 104421-74-1; **2b**, 104421-75-2.

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Reactions of Trimethylphosphine–Pentaboranes with Trityl Cation. Formation of Octahydrobis(trimethylphosphine)pentaboron(1+) and Octahydro(trimethylphosphine)pentaboron(1+) Cations

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Earlier, we reported the synthesis of the heptahydrobis(trimethylphosphine)tetraboron(1+) cation, $B_4H_7{\cdot}2P(CH_3)_3^+$.[1] This cation was prepared by abstracting a hydride ion from $B_4H_8{\cdot}2P(CH_3)_3$ with the use of triphenylcarbenium (trityl) cation.

$$B_4H_8{\cdot}2P(CH_3)_3 + C(C_6H_5)_3^+ \rightarrow B_4H_7{\cdot}2P(CH_3)_3^+ + C(C_6H_5)_3H$$

This method of hydride abstraction should be applicable to the preparation of other polyboron complex cations. However, the ease of hydride abstraction must be dependent upon the hydridic nature of the borane hydrogens on the substrate borane compound. As the borane structure becomes larger, the borane hydrogen atoms are expected to become less hydridic.[2] Furthermore, the hydridic character of borane hydrogen atoms should be influenced by the number of the trimethylphosphines that are attached to the borane framework. It was, therefore, of interest to test the reaction on other higher borane compounds containing different numbers of trimethylphosphines. Synthesizing new polyboron cations was of interest by itself. In particular, the structures of these cations were of interest. The above tetraboron cation is isoelectronic and isostructural with $B_4H_8{\cdot}P(CH_3)_3$ and $B_4H_9^-$ as $B_3H_6{\cdot}2P(CH_3)_3^+$, $B_3H_7{\cdot}P(CH_3)_3$, and $B_3H_8^-$ are isoelectronic and isostructural with each other.[3] The generality of this isoelectronic–isostructural feature had yet to be tested. This paper describes the results of these tests, which were performed on trimethylphosphine adducts of pentaborane(9).

Results and Discussion

A. Reaction of Bis(trimethylphosphine)–Pentaborane(9) with Trityl Cation. The adduct $B_5H_9{\cdot}2P(CH_3)_3$ reacted with trityl tetrafluoroborate or hexafluorophosphate in dichloromethane at −80 °C to give the $B_5H_8{\cdot}2P(CH_3)_3^+$ cation. The BF_4^- salt of this cation was reasonably stable at room temperature, but the PF_6^- salt decomposed rapidly above 0 °C.

NMR Spectra. The NMR data for the $B_5H_8{\cdot}2P(CH_3)_3^+$ cation are listed in Table I. The ^{11}B spectra shown in Figure 1 immediately indicate that the molecule is of C_1 symmetry and that the −49.4 ppm signal is due to the apex boron atom[4] to which one of the phosphines is attached. The triplet feature of the −14.3 ppm signal (due to the other phosphine-attached boron atom) and the two doublet signals at 0.3 and 6.9 ppm suggest the structure of the cation to be that shown in Figure 1. The assignments were based on the ^1H spectra obtained by the selective decoupling of boron spins.

Table I. NMR Shift Data for the $B_5H_8{\cdot}2P(CH_3)_3^+$ Cation

	temp, °C	shift in ppm, assignt (J in Hz, J_{XY}) [rel intens]
^{11}B	+20	−49.4, B_1 (143, J_{BP}) [1]; −14.3, B_2 (103, J_{BP}) [1]; −9.7, B_5 [1]; +0.3, B_3 (125, J_{BH}) [1]; 6.9, B_4 (128, J_{BH}) [1]
^1H	−10	−1.84, $H_{\mu(3,4)}$ [1]; −1.21, $H_{\mu(4,5)}$ [1]; −0.75, $H_{\mu(2,3)}$ [1]; 1.87, H_2 [1]; 1.93, H_5 [1]; 2.44, H_5 [1]; 3.21, H_3 [1]; 3.46, H_4 [1]; 1.36, $H_{C(1)}$ (11.9, $^2J_{HP}$) [9]; 1.56, $H_{C(2)}$ (12.8, $^2J_{HP}$) [9]
^{31}P	+20	−2.3, P_1 (146, J_{PB}) [1]; −5.3, P_2 [1]

Table II. NMR Shift Data for the $B_5H_8{\cdot}P(CH_3)_3^+$ Cation

	temp, °C	shift in ppm, assignt (J in Hz, J_{XY})[rel intens]
^{11}B	−20	−48.6, B_1 (220, J_{BP}) [1]; −11.2, $B_{2,3,4,5}$ (172, J_{BH}) [4]
^1H	−10	−1.54, H_μ [4]; 2.86, H_t (168, J_{HB}) [4]; 1.74, H_C (13, $^2J_{HP}$; 3, $^3J_{PB}$) [9]
^{31}P	−10	−9.5 (215, J_{PB})

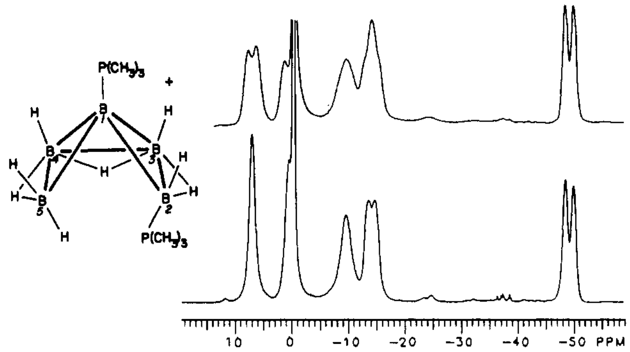

Figure 1. Left: Structure proposed for $B_5H_8{\cdot}2P(CH_3)_3^+$. Position of the basal phosphine (endo or exo) is uncertain. Right: 96.2-MHz ^{11}B NMR spectra of the cation (BF_4^- salt, +20 °C, CD_2Cl_2 solvent). The upper spectrum is normal; the lower spectrum is proton spin decoupled. The truncated tall peak at −0.4 ppm is due to BF_4^-.

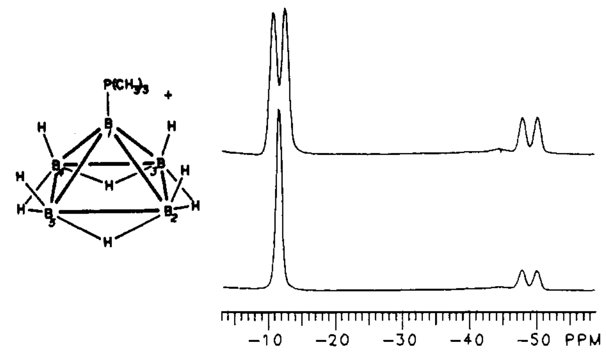

Figure 2. Left: Structure proposed for $B_5H_8{\cdot}P(CH_3)_3^+$. Right: 96.2-MHz ^{11}B NMR spectra of the cation (BF_4^- salt, −20 °C, CD_2Cl_2 solvent). The upper spectrum is normal; the lower spectrum is proton-spin decoupled.

B. Reaction of Trimethylphosphine–Pentaborane(9) with Trityl Cation. A 1:1 mixture of $B_5H_9{\cdot}P(CH_3)_3$ and trityl tetrafluoroborate in dichloromethane remained unchanged at −80 °C. At −30 °C, however, a rapid reaction occurred and the $B_5H_8{\cdot}P(CH_3)_3^+$ cation was produced. The BF_4^- salt of this cation was fairly stable at room temperature. When trityl hexafluorophosphate was used, the pentaboron cation could not be obtained. Apparently, the PF_6^- ion was involved in the reaction. Thus, even at −80 °C $B_5H_9{\cdot}P(CH_3)_3$ was consumed and various boron compounds were produced. These compounds included BF_4^-, $BF_3{\cdot}P(CH_3)_3$, B_5H_9, $BH_3{\cdot}P(CH_3)_3$, and other unidentified species.

NMR Spectra. The data are listed in Table II. The ^{11}B spectra shown in Figure 2 suggest that the molecule is of C_4 symmetry. The spectral data are consistent with the structure illustrated in

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