rectly coordinated to the solutes. A referee has correctly observed that limiting shifts depend upon the geometry of the complexes and that the generalization, while possibly true for sulfoxides, is not necessarily true for all other substrates.
(12) The synthesis, resolution, and assignment of absolute configuration for this alcohol is being reported elsewhere.
(13) D. M. Fiegl, Ph.D. Thesis, Stanford University, 1966. See also J. D. Morrison and H. S. Mosher, "Asymmetric Organic Reactions", Prentice-Hall, Englewood Cliffs, N.J., 1971, p 192.
(14) The position of the minimum should reflect the enantiomeric purity of the solute provided types C and D nonequivalence make negligible contributions.
(15) The Ajisaka–Kainosho mechanism[7] cannot be operative for racemic solutes. Hence, the observation of nonequivalence for racemic **4**, racemic methyl *p*-nitrophenyl sulfoxide, and unlabeled Me_2SO must have a different origin.
(16) G. R. Sullivan, D. Ciavarella, and H. S. Mosher, *J. Org. Chem.*, **39**, 2411 (1974).
(17) K. Ajisaka, M. Kamisaku, and M. Kainosho, *Chem. Lett.*, 857 (1972).
(18) O. Červinka, P. Malon, and P. Trška, *Collect. Czech. Chem. Commun.*, **38**, 3299 (1973).
(19) C. J. Reich, G. R. Sullivan, and H. S. Mosher, *Tetrahedron Lett.*, 1505 (1973).
(20) K. K. Andersen, *Tetrahedron Lett.* 93 (1962).
(21) W. H. Pirkle and S. D. Beare, *J. Am. Chem. Soc.*, **90**, 6250 (1968).
(22) R. S. Cooke and G. S. Hammond, *J. Am. Chem. Soc.*, **92**, 2739 (1970).
(23) A. Cernians and G. Modena, *Gazz. Chim. Ital.*, **89**, 843 (1959).
(24) J. F. Carson and F. F. Wong, *J. Org. Chem.*, **26**, 3028 (1961).

Carbon-13 Nuclear Magnetic Resonance Studies of Organoboranes
The Relative Importance of Mesomeric B–C π-Bonding Forms in Alkenyl- and Alkynylboranes[1]

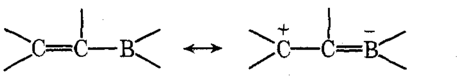
Yoshinori Yamamoto* and Ichiro Moritani[2]

Department of Chemistry, Faculty of Engineering Science, Osaka University, Toyonaka, Osaka 560, Japan

Received July 21, 1975

The ^{13}C NMR spectra have been obtained for trialkylboranes, dialkylborinates, alkylboronates, dialkylchloroboranes, alkenylboranes, and alkynylboron derivatives. In the alkenyl- and alkynylboranes, it is concluded on the basis of the ^{13}C NMR chemical shifts that π interaction between the π-electron system and the vacant p orbital of the boron atom exists to a certain extent, and that the mesomeric B–C π-bonding forms contribute to the ground state of these α,β-unsaturated compounds.

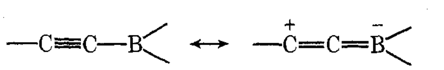
The question of B–C π bonding in alkenylboranes has presented chemists with an intriguing problem (eq 1).[3]



(1)

Though a substantial body of evidence now exists supporting π interaction between the π-electron system and the vacant p orbital of boron in an alkenylborane,[3] objection against such π bonding has also been raised.[3a] The large volume of experimental data gathered so far has been obtained by infrared,[4-10] Raman,[10] ultraviolet,[7,8,11] ^1H NMR,[8] ^{11}B NMR,[7,8] ^{19}F NMR,[7,12,13] and photoelectron[14] spectroscopic techniques, data which seem to provide mainly indirect evidence. The question has also been the subject of LCAO-MO-SCF,[11] CNDO,[15,16] and INDO[17] calculations. However, ^{13}C NMR spectra have not as yet been obtained, despite the superior advantage that their chemical shifts can more directly provide insight into the bonding situations.[18,19]

Alkynylboranes may also exist in the mesomeric allenyl form (eq 2),[3a] though to our knowledge there is no literature evidence for such B–C π bonding. In this paper, we report in full on the ^{13}C NMR spectra and the bonding situation of alkenyl- and alkynylboranes.



(2)

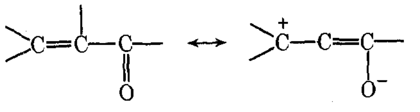
Experimental Section

All boranes were prepared as previously described.[20] ^{13}C NMR spectra were measured on a Varian XL-100-15 spectrometer operating in the Fourier transform mode at 25.2 MHz. All spectra were determined with noise-modulated proton decoupling. Single-frequency off-resonance decoupled spectra were used to assign the resonances in questionable cases. The spectra were taken in benzene-d_6 (ca. 50% concentration), except where otherwise indicated, in 12-mm sample tubes, and were calibrated using the solvent resonances as secondary standards.

Results and Discussion

The chemical shifts obtained from the ^{13}C NMR spectra of alkenyl- (**1–5**), alkynyl- (**6** and **7**), and alkylboron derivatives (**8–14**), and those of the corresponding alkenes, alkynes, and alkanes are listed in Tables I–III. Assignments of ^{13}C signals were made on the basis of (1) off-resonance decoupling spectra, (2) consistency with other shift data,[18,19] and (3) broadening and weakening of the peak corresponding to the ^{13}C nuclei directly attached to boron. The last phenomenon was generally observed for the alkyl- and alkenylboranes, and is presumably due to large carbon–boron couplings which are incompletely relaxed by the quadrupole mechanism.[21,22] In the case of the alkynylboranes, the absorption of the α carbon had completely disappeared.

As is apparent from Table I, the chemical shifts at C_1 and C_2 of **1** are similar to those of acrylic acid (δ C_1 128.0, δ C_2 131.9).[18] Also, the shifts in the other alkenylboranes show an analogous trend to those in α,β-unsaturated carbonyl compounds, where the contribution of enolate form is important (eq 3).[18,19]

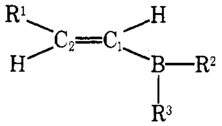


(3)

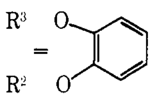
This phenomenon is highly interesting in connection with the relationship between the ^{13}C shielding and the chemical reactivity of boron derivatives, since the suggestion that many reactions of aldehydes and ketones have counterparts in the reactions of trialkylboranes has already been presented.[23]

The $^{13}C_2$–H coupling constants of di-*n*-butylvinylboronate (**1**) were 158 and 164 Hz, indicating that the C_2 has a normal sp^2 hybridization. The coupling constant of di-*n*-butylacetyleneboronate (**6**) was 240 Hz, demonstrating that the C_2 has a normal sp hybridization. The $^{13}C_2$–H coupling constant of *n*-butylboronate (**9**) was 124 Hz, indicating here also that the C_2 has a normal sp^3 hybridization.

Table I
^{13}C Chemical Shifts for Alkenylboranes (1-5)[a]



1, $R^1 = H$; $R^2 = R^3 = O$-*n*-Bu
2, $R^1 =$ *n*-Bu; $R^2 = CH{=}CH$-*n*-Bu; $R^3 = Cl$
3, $R^1 =$ *n*-Bu; $R^2 = CH{=}CH$-*n*-Bu; $R^3 = OCH_3$
4, $R^1 =$ *n*-Bu; $R^2 = R^3 = CH(CH_3)CH(CH_3)_2$
5, $R^1 =$ *n*-Bu;



Borane	Alkenyl δ C_1	δ C_2	δ C_3	δ C_4	δ C_5	δ C_6	Other
1	*b*	135.5					δ OCH_2 64.4, δ C_2 35.3, δ C_3 20.7, δ CH_3 15.1
1[c]	127.8	134.1					δ OCH_2 63.3 δ C_2 34.0 δ C_3 19.2, δ CH_3 13.9
2	133.0	160.9	37.1	31.8	23.8	15.2	
3	129.1	153.8	37.3	32.4	23.8	15.3	δ OCH_3 52.3
4	134.6	155.2	37.6	32.3	23.9	15.4	δ CH_3 14.9, 14.9, 14.5, δ CH 32.5, δ B–CH 38.5
5	114.3	158.2	37.0	31.8	23.7	15.1	δ C_1 149.6, δ C_2 113.3, δ C_3 123.4
Ethene[d]	122.8	122.8					
1-Hexene	113.4	137.8	33.6	31.3	22.1	13.4	

[a] In parts per million (±0.1) (downfield positive) from Me_4Si, converted using δ_C (C_6D_6) 128.7. [b] The absorption is not obvious, owing to overlap with that of C_6D_6. [c] Using $CDCl_3$ as a solvent with an internal standard of Me_4Si. [d] References 18 and 19.

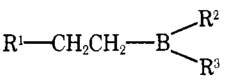
Table II
^{13}C Chemical Shifts for Alkynylboranes (6 and 7)[a]

$R^1{-}C{\equiv}C{-}B(O\text{-}n\text{-}Bu)_2$ 6, $R^1 = H$; 7, $R^1 =$ *n*-Bu

Borane	Alkynyl δ C_1	δ C_2	δ C_3	δ C_4	δ C_5	δ C_6	Other
6	*b*	91.4					δ OCH_2 64.2, δ C_2 35.1, δ C_3 20.4 δ C_4 15.0
7	*b*	104.9	20.5	32.0	23.2	14.7	δ OCH_2 64.1, δ C_2 35.2, δ C_3 20.5 δ C_4 15.0
Acetylene[c]	70	70					
1-Hexyne[c]	68.6	84.0	18.6	31.1	22.4	14.1	

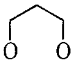
[a] See footnotes to Table I. [b] The absorption is not obvious, owing to the neighboring boron. [c] Reference 18.

Table III
^{13}C Chemical Shifts for Alkylboranes (8–14)[a]

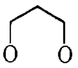


$R^1{-}CH_2CH_2{-}B(R^2)(R^3)$

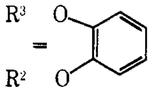
8, $R^1 = H$; $R^2R^3 =$



9, $R^1 = Et$; $R^2R^3 =$



10, $R^1 =$ *n*-Bu; $R^2 =$ *n*-hexyl; $R^3 = Cl$
11, $R^1 =$ *n*-Bu; $R^2 =$ *n*-hexyl; $R^3 = OCH_3$
12, $R^1 = H$; $R^2 = R^3 = Et$
13, $R^1 = Et$; $R^2 = R^3 =$ *n*-Bu
14, $R^1 =$ *n*-Bu;

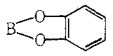


Borane	δ C_1	δ C_2	δ C_3	δ C_4	δ C_5	δ C_6	Other
8	8.6	8.6					δ OCH_2 62.4, δ CH_2 29.0
9	16.4	27.8	26.8	15.1			δ OCH_2 62.5, δ CH_2 29.1
10	30.4	26.0	33.4	33.4	24.1	15.4	
11	21.3	25.5	34.0[b]	33.4[b]	24.1	15.3	δ OCH_3 53.8
12	20.8	9.3					
13	29.8	28.4	27.5	15.3			
14	12.2	25.2	33.4[b]	33.2[b]	24.0	15.3	δ C_1 149.6, δ C_2 113.2, δ C_3 123.3
Ethane[c]	5.9	5.9					
Butane[c]	13.2	25.0	25.0	13.2			
Hexane[c]	13.9	22.9	32.0	32.0	22.9	13.9	

[a] See footnotes to Table I. [b] There is a possibility that the assignments should be interchanged. [c] Reference 18.

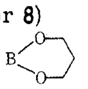
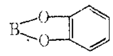
The data presented in Table IV demonstrate the effects of substituent groups on the boron in the alkenyl- and alkynylboron derivatives. The substituent effect (Δδ C_1) at C_1 in the alkynylboranes are unknown, because of disappearance of the α carbon in 6 and 7 (Table II). However, from the data for the alkenyl (5.0 or 0.9 ppm from Table IV) and alkyl (2.7, 3.2, or −1.7 ppm from Table V) derivatives, it appears that the α effect of the boronate group on the triple bond is estimated to be at most ca. 5 ppm, since the α effect of the boronate group is generally slight, as shown in

Table IV
Substituent Effects on ^{13}C Chemical Shifts of Boron-Substituted Alkenes and Alkynes[a]

Substituent	$\Delta\delta C_1$	$\Delta\delta C_2$	$\Delta\delta C_3$
Boron-substituted alkene			
$B(O\text{-}n\text{-}Bu)_2$	5.0	11.3	
$BR'Cl$[b]	19.6	23.1	3.5
$BR'OCH_3$[b]	15.7	16.0	3.7
$B(Sia)_2$[c]	21.2	17.4	4.0
	0.9	20.4	3.4
Boron-substituted alkyne			
$B(O\text{-}n\text{-}Bu)_2$[d]		21.4	
$B(O\text{-}n\text{-}Bu)_2$[e]		20.9	1.9

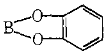
[a] In parts per million with respect to the corresponding hydrocarbons (ethene, 1-hexene, acetylene, and 1-hexyne). Higher values correspond to lower shielding. [b] R′ = 1-hexenyl. [c] Sia = $CH(CH_3)CH(CH_3)_2$. [d] Substituent effect for **6**. [e] Substituent effect for **7**.

Table V
Substituent Effects on ^{13}C Chemical Shifts of Boron-Substituted Alkanes[a]

Substituent	$\Delta\delta C_1$	$\Delta\delta C_2$	$\Delta\delta C_3$
$B(OR)_2$ (for **8**)	2.7	2.7	
$B(OR)_2$ = 			
$B(OR)_2$ (for **9**)	3.2	2.8	1.8
$BR'Cl$[b]	16.5	3.1	1.4
$BR'OCH_3$[b]	7.4	2.6	2.0
BR_2; R = Et	14.9	3.4	
BR_2; R = *n*-Bu	16.6	3.4	2.5
	−1.7	2.3	1.4

[a] In parts per million with respect to the corresponding hydrocarbons (ethane, butane, and hexane). Higher values correspond to lower shielding. [b] R′ = *n*-hexyl.

Table VI
Difference in Substituent Effect between Unsaturated and Saturated Boranes[a]

Substituent	$\Delta\Delta\delta C_1$	$\Delta\Delta\delta C_2$	$\Delta\Delta\delta C_3$
Alkene			
$B(OR)_2$	2.3	8.6	
$BR'Cl$	3.1	20.0	2.1
$BR'OCH_3$	8.3	13.4	1.7
BR_2	4.6	14.0	1.5
	2.6	18.1	2.0
Acetylene			
$B(OR)_2$		19.7(18.1)[b]	0.1[b]

[a] $\Delta\Delta\delta C_n = \Delta\delta C_n$ (alkenyl or alkynylboranes) − $\Delta\delta C_n$ (alkylboranes), where n = 1, 2, and 3, R = alkyl, and R′ = 1-hexenyl and *n*-hexyl, on the assumption 1, 2, 3. [b] The value for **7**.

Tables IV and V, and the difference in α effect between alkenes and alkynes may be not great.[24]

Table V contains data on substituent effects in the alkylboranes, where the effect of BR_2 (R = Et or *n*-Bu) is determined from the shift data (Table III) of triethyl- (**12**) and tributyl- (**13**) boranes. That these data are somewhat, but not essentially, different from the reported values[22] must be due to the differences in experimental conditions.[25]

Comparison of the data in Tables IV and V leads to a conclusion that the α effect ($\Delta\delta C_1$) in unsaturated boranes show ranges comparable to those in saturated boranes. However, for the β carbons, the substituent effects ($\Delta\delta C_2$) exhibit a much wider range of shifts than those observed in saturated boranes. The comparisons are summarized in Table VI, being made on the assumption that the following pairs of groups are equivalent: (1) $B(O\text{-}n\text{-}Bu)_2$ and $B(OR)_2$ (see Table V), (2) 1-hexenyl and *n*-hexyl in $BR'Cl$ and $BR'OCH_3$,[26] and (3) $B(Sia)_2$ and $B(n\text{-}Bu)_2$. The difference at C_1 ($\Delta\Delta\delta C_1$) for acetylene is estimated to be of the same order of magnitude as that for alkene.

Evidently, the substituent effect is more strongly felt at the β positions than at the point of substitution. This clearly indicates that in all cases (**1**–**7**) there is some contribution of the mesomeric B–C π-bonding forms shown in eq 1 or 2.[18,19,24]

To roughly estimate the relative contribution of the mesomeric B–C π-bonding form in **2**, we have chosen the isopropyl cation[27] as a model for the C_β carbon in the mesomeric form, where the chemical shift of the central carbon is 319.6 ppm from Me_4Si,[18] and have chosen 2-hexene as a model for the C_β carbon without such π interaction, where the chemical shift of C_3 carbon is 129.8 ppm from Me_4Si.[18] Experimentally the C_β of **2** is deshielded by 160.9 ppm relative to Me_4Si, the relative contribution of the B–C π-bonding form consequently being about 16%.

Conclusion

There is much circumstantial evidence for the B–C π bonding, but there is also an argument that most if not all such data, taken individually, are inconclusive.[3a] The present results clearly indicate a certain degree of B–C π bonding in alkenylboranes. Also the ^{13}C shift data demonstrate for the first time the presence of B–C π bonding in alkynylboranes.

Acknowledgment. Y.Y. wishes to express gratitude to Dr. K. Lee and Mr. M. Doi of the Department of Chemistry, Faculty of Science, Osaka University, for measuring the ^{13}C NMR spectra.

Registry No.—**1**, 6336-45-4; **2**, 55168-90-6; **3**, 55168-91-7; **4**, 55168-92-8; **5**, 56554-20-2; **6**, 24215-39-2; **7**, 56070-64-5; **8**, 56554-21-3; **9**, 30169-71-2; **10**, 18379-62-9; **11**, 2344-22-1; **12**, 97-94-9; **13**, 122-56-5; **14**, 56554-22-4.

References and Notes

(1) For preliminary communications, see Y. Yamamoto and I. Moritani, *Chem. Lett.*, 57, 439 (1975).
(2) Kuraray Co. Ltd., Osaka, Japan.
(3) (a) M. F. Lappert, "The Chemistry of Boron and Its Compounds", E. L. Muetterties, Ed., Wiley, New York, N.Y., 1967, p 482; (b) D. S. Matteson, *Prog. Boron Chem.*, **3**, 117 (1970); (c) D. S. Matteson, "Organometallic Reaction Mechanisms of the Nontransition Elements", Academic Press, New York, N.Y., 1974, p 296.
(4) D. S. Matteson, *J. Am. Chem. Soc.*, **82**, 4228 (1960).
(5) F. E. Brinckman and F. G. A. Stone, *J. Am. Chem. Soc.*, **82**, 6218 (1960).
(6) S. L. Stafford and F. G. A. Stone, *J. Am. Chem. Soc.*, **82**, 6238 (1960).
(7) T. D. Coyle, S. L. Stafford, and F. G. A. Stone, *J. Chem. Soc.*, 3103 (1961).
(8) C. D. Good and D. M. Ritter, *J. Am. Chem. Soc.*, **84**, 1162 (1962).
(9) M. F. Lappert and B. Prokai, *J. Organomet. Chem.*, **1**, 384 (1964).
(10) A. K. Holliday, W. Reade, K. R. Seddon, and I. A. Steer, *J. Organomet. Chem.*, **67**, 1 (1974).
(11) D. R. Armstrong and P. G. Perkins, *Theor. Chim. Acta*, **4**, 352 (1966).
(12) T. D. Coyle and F. G. A. Stone, *J. Am. Chem. Soc.*, **82**, 6223 (1960).
(13) T. D. Coyle, S. L. Stafford, and F. G. A. Stone, *Spectrochim. Acta*, **17**, 968 (1961).
(14) A. K. Holliday, W. Reade, R. A. W. Johnstone, and A. F. Neville, *Chem. Commun.*, 51 (1971).
(15) J. A. Pople and G. A. Segal, *J. Chem. Phys.*, **44**, 3289 (1966).
(16) G. Kuehnlenz and H. H. Jaffe, *J. Chem. Phys.*, **58**, 2238 (1973).
(17) N. L. Allinger and J. H. Siefert, *J. Am. Chem. Soc.*, **97**, 752 (1975), and references cited therein.
(18) J. B. Stothers, "Carbon-13 NMR Spectroscopy", Academic Press, New York, N.Y., 1972.
(19) G. C. Levy and G. L. Nelson, "Carbon-13 Nuclear Magnetic Resonance for Organic Chemists", Wiley-Interscience, New York, N.Y., 1972.

(20) For the preparation of alkyl- and alkenylboron derivatives, except **1**, see H. C. Brown, "Boranes in Organic Chemistry", Cornell University Press, Ithaca, N.Y., 1972; "Organic Syntheses via Boranes", Wiley, New York, N.Y., 1975. For the preparation of **1** see D. S. Matteson, *J. Am. Chem. Soc.*, **82**, 4228 (1960). For the alkynylboranes see D. S. Matteson and K. Peacock, *J. Org. Chem.*, **28**, 369 (1963).

(21) F. J. Weigert and J. D. Roberts, *Inorg. Chem.*, **12**, 313 (1973).

(22) D. J. Hart and W. T. Ford, *J. Org. Chem.*, **39**, 363 (1974).

(23) M. W. Rathke and R. Kow., *J. Am. Chem. Soc.*, **94**, 6854 (1972).

(24) G. E. Maciel, "Topics in Carbon-13 NMR Spectroscopy", Vol. 1, G. C. Levy, Ed., Wiley-Interscience, New York, N.Y., 1974, p 53.

(25) Private communication from Professor W. T. Ford.

(26) The assumption 2 may be unpardonable. However, the preparation of RCH=CHB(R')Cl (R' = alkyl) is highly difficult. Other assumptions, 1 and 2, are reasonable.

(27) A referee suggests that the comparison to an isopropyl cation is oversimplified. Both electron density and bond order contribute heavily to the paramagnetic term of the ^{13}C screening constant. The downfield shifts of C_2 must be due not only to decreased electron density but also to decreased π bond order.

Nuclear Magnetic Resonance Studies. IV.[1] The Carbon and Phosphorus Nuclear Magnetic Resonance of Phosphine Oxides and Related Compounds

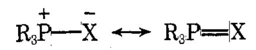
Thomas A. Albright, Walter J. Freeman,* and Edward E. Schweizer*

Department of Chemistry, University of Delaware, Newark, Delaware 19711

Received April 29, 1975

The ^{13}C and ^{31}P NMR of 16 phosphine oxides and sulfides are examined. Changes in the ^{13}C and ^{31}P NMR of triphenylphosphine oxide, sulfide, and selenide with respect to changes in the P–X bond are discussed. Perturbations on the ^{13}C–^{31}P nuclear spin coupling are examined for this series of compounds and various alkyl-substituted diphenylphosphine oxides. Support is given for the theory of competitive dπ–pπ overlap with the PO bond for phenyl and vinyl substituted phosphine oxides.

Phosphorus, a second row atom, possesses empty d orbitals which may overlap with filled p orbitals on an adjacent atom. Thus the following resonance structures may be considered.



$$R_3\overset{+}{P}—\overset{-}{X} \longleftrightarrow R_3P{=}X$$

1a **1b**

X = O,S,Se

The formal PX double bond in **1b** is expected to be quite different from a normal pπ–pπ double bond of, for example, a carbonyl group. The d orbitals are diffuse and more directional than 3p orbitals and most of the electron density in a pπ–dπ bond is expected to lie in the vicinity of the X atom.[2] The physical evidence which has been used to imply dπ–pπ overlap in the phosphoryl bond is quite persuasive and includes X-ray fluorescence,[3] basicity data,[4] ^{13}C–H nuclear spin coupling,[5] bond dissociation energies,[2,6] bond lengths,[7] dipole moments,[8] NQR measurements,[4] and photoelectron spectra.[10] This is further corroborated by semiempirical[11] and ab initio[12] molecular orbital calculations. There is less evidence of multiple PX bonding for phosphine sulfides and selenides. The general view, however, seems to be that the P–S (and analogously, P–Se) bond is weaker and there is less π bonding than in the PO bond. Bond dissociation energies,[13] ir force constant calculations,[14] and semiempirical molecular orbital calculations[11] lend support for this notion.

It has been considered that an important consequence of a strong, multiple PX bond is that competitive π bonding from an additional, weaker π donor is diminished (e.g., a vinyl or phenyl group). Various physical techniques, especially ^{19}F NMR, have given support for this notion.[15] Thus, in a vinyl phosphine oxide the dπ–pπ contribution from the PO bond will decrease dπ–pπ bonding from the vinyl group to phosphorus. In vinyl phosphonium salts the ^{13}C and ^{31}P NMR data strongly suggest dπ–pπ overlap between the vinyl group and phosphorus.[16] These differences will be examined in this context.

Results and Discussion

The values of the ^{13}C chemical shifts, ^{31}P–^{13}C coupling constants, and ^{31}P chemical shifts are given in Tables I and II. The ^{13}C chemical shifts previously reported[17] for tri-*n*-butylphosphine oxide and sulfide agree with the values reported in Table I. The ^{13}C chemical shifts and couplings reported for triphenylphosphine oxide also agree with those previously reported by Gray.[18] The values of the ^{31}P chemical shift and ^{31}P–^{77}Se coupling agree with those given by Stec and coworkers.[19]

Quin noted[17] that the close proximity of the ^{13}C resonances for carbons 2 and 3 in tri-*n*-butylphosphine oxide and sulfide are difficult to assign and are subject to adjustment. We have reexamined this problem and make our assignments based on spectra determined at two different field strengths. Additionally, in the case of tri-n-butylphosphine oxide, T_1 values were determined by the inversion–recovery technique.[20] The T_1 values for a $CDCl_3$ solution (not degassed) of the four carbons are found to be 1.2, 1.7, 2.4, and 3.0 ± 0.6 sec, respectively, for carbons 1–4. This is the normal sequence for saturated alkyl chains.[21] Moreover, the closely spaced inner lines of the four-line pattern due to C-2 and C-3 in tri-*n*-butylphosphine oxide were readily assigned by careful adjustment of the delay time in the inversion–recovery sequence so that the two low-field lines due to C-3 where inverted while the two high-field lines were upright.[22] On this basis the assignments given by Quin[17] were confirmed, but a value of $^2J_{P-C} = 3.9 \pm 0.1$ Hz was found instead of the reported $^2J_{P-C} = 5$ Hz.

The ^{31}P chemical shift of triphenylphosphine sulfide (**3**) is deshielded by 13.9 ppm from triphenylphosphine oxide (**2**). This is consistent with an expected smaller contribution of resonance structure **1b** for the sulfide. Likewise, the ^{31}P resonance of **2** is shielded by 27.9 ppm from its phosphonium salt analog **16**, while the ^{31}P resonance of **3** is virtually unaffected upon protonation to **17**.[23] However, in triphenylphosphine selenide (**4**), the ^{31}P chemical shift is deshielded by only 6.5 ppm from the oxide **2** and is shielded by 7.4 ppm with respect to the sulfide **3**. This irregularity in the ^{31}P chemical shift of the selenide is not in accord with the expected changes in the P–Se bond as compared to the P–S and P–O bonds. For example, an ir force constant study gave the strengths of the P–X bond, and hence the order of contribution of resonance structure **1b**, as P–O > P–S ≫ P–Se.[25] Therefore, a straightforward interpreta-