9. Kato, T.; Kodama, T.; Nakagawa, T.; Matsui, Y.; Suzuki, S.; Shiromaru, H. *Chem. Phys. Lett.* **1991**, *180*, 446.
10. Kukolich, S. G.; Huffman, D. R. *Chem. Phys. Lett.* **1991**, *182*, 263.
11. Liehr, A. D. *Ann. Rev. Phys. Chem.* **1962**, *13*, 47.
12. Su, W. P.; Schriffer, J. R.; Heeger, A. *Phys. Rev.* **1983**, *B22*, 2099; *ibid,* **1983**, *B28*, 1138; *Phys. Rev. Lett.* **1979**, *42*, 1698.
13. Harigaya, K. *Phys. Rev.* **1992**, *B45*, 13676. Friedman, B. *Phys. Rev.* **1992**, *B45*, 1454. Fu, R. T.; Sun, X.; Chen, Z. *Chinese Phys. Lett.* **1992**, *9*, 541.
14. Lee, K. H.; Paek, U. *J. Phys. Chem. Solids* **1993**, *54*, 565.
15. Fu, R. T.; Lee, K. H.; Park, T. Y.; Sun, X.; Yu, Z. G. *Bull. Korean Chem. Soc.* **1994**, *15*, 112.
16. Fu, R. T.; Fu, R.; Lee, K. H.; Sun, X.; Ye, H. J.; Yu, Z. G. *Bull. Korean Chem. Soc.* **1993**, *14*, 740.
17. Bendale, R. D.; Stanton, J. F.; Zener, M. *Chem. Phys. Lett.* **1992**, *194*, 467.
18. Shastry, B. S. *J. Phys.* **1983**, *A16*, 2049.
19. Friedman, B.; Harigaya, K. *Phys. Rev.* **1993**, *B47*, 6975.
20. Varma, C. M.; Zaanen, J.; Raghavachari, K. *Science* **1991**, *254*, 989.
21. Schluter, M.; Lannoo, M.; Needels, M.; Baraff, G. A.; Tomanek, D. *Phys. Rev. Lett.* **1992**, *68*, 526.
22. You, W. M.; Wang, C. L.; Zhang, F. C.; Su, Z. B. *Phys. Rev.* **1993**, *B47*, 4765.

Solid-State ^{31}P NMR Chemical Shielding Tensors in Binuclear Platinum Diphosphite Complexes

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The principal elements of the ^{31}P NMR chemical shielding tensors have been determined for three binuclear platinum diphosphite complexes, $K_4[Pt_2(P_2O_5H_2)_4]\cdot 2H_2O$ ("Pt_2"), $K_4[Pt_2(P_2O_5H_2)_4Cl_2]\cdot 2H_2O$ ("Pt_2Cl_2"), and $K_4[Pt_2(P_2O_5H_2)_4Br_2]\cdot 2H_2O$ ("Pt_2Br_2"), by using a Herzfeld-Berger graphical method for interpreting the ^{31}P MAS spectrum. The orientations of ^{31}P chemical shielding tensor relative to the molecular axis system are partially assigned with combination of the longitudinal relaxation study of HPO_3^{2-} and the reference to known tensor orientations of related sites; the most chemical shielding component, δ_{33}, is directed along the P-Pt bond axis. A discussion is given in which the experimental principal elements of the ^{31}P chemical shielding tensor are related with the Pt-Pt bond distances in binuclear platinum diphosphite complexes.

Introduction

Solid-state NMR spectroscopy of S=1/2 nuclei, principally ^{13}C and ^{31}P, has been utilized to yield information concerning the molecular geometry, electronic structure, and motion of molecules in organometallic systems. ^{31}P NMR spectroscopy has been more frequently used than ^{13}C in the organometallic studies, because of the 100% natural abundance and the relatively high sensitivity of the ^{31}P nucleus. ^{31}P chemical shielding tensors have been successfully correlated with the molecular structural parameters such as bond angles and bond distances in phosphido-bridged complexes and phosphates.[1,2] Similarly, the correlation between the ^{31}P isotropic chemical shift and the cation charge of orthophosphates has been investigated.[3] The *cis-trans* isomerization of $(R_3P)_2MCl_2$ (M=Pd, Pt)[4,5] and the determination of NMR parameters in cyclic/acyclic phosphine complexes[6,7] have been studied by ^{31}P CP/MAS NMR spectroscopy. In addition, the effects of molecular motion for solid P_4[8] and phase transition for P_4S_3[9] on ^{31}P NMR spectra have been investigated. Two-dimensional ^{31}P CP/MAS NMR techniques have been applied to separate the unresolved interactions in the metal phosphine complexes.[10]

Binuclear platinum diphosphite complexes, $K_4[Pt_2(P_2O_5H_2)_4]\cdot 2H_2O$ ("Pt_2"), $K_4[Pt_2(P_2O_5H_2)_4X]\cdot 2H_2O$ ("Pt_2X"), and $K_4[Pt_2(P_2O_5H_2)_4X_2]\cdot 2H_2O$ ("Pt_2X_2"; X=Cl, Br, I), have attracted attention because they can be used to prepare linear chain structures with the electrical properties of a semiconductor.[11~15] The semiconductivity of these complexes have been indirectly investigated by the determination of the intermetallic bond distances from X-ray crystallography. The intermetallic bonding have also been characterized from electronic and vibrational spectroscopic data.[16~18] Herein, three principal elements and the partial orientation of the ^{31}P chemical shielding tensors for Pt_2, Pt_2Cl_2, and Pt_2Br_2 were determined by using the solid-state ^{31}P MAS spectroscopy. Consequently, the NMR results will be related to the Pt-Pt distances in the molecular structures, Pt_2 and Pt_2X_2, to access information about the changes in the Pt-Pt bond that are so important to conduction in the Pt_2X system.

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Experimental

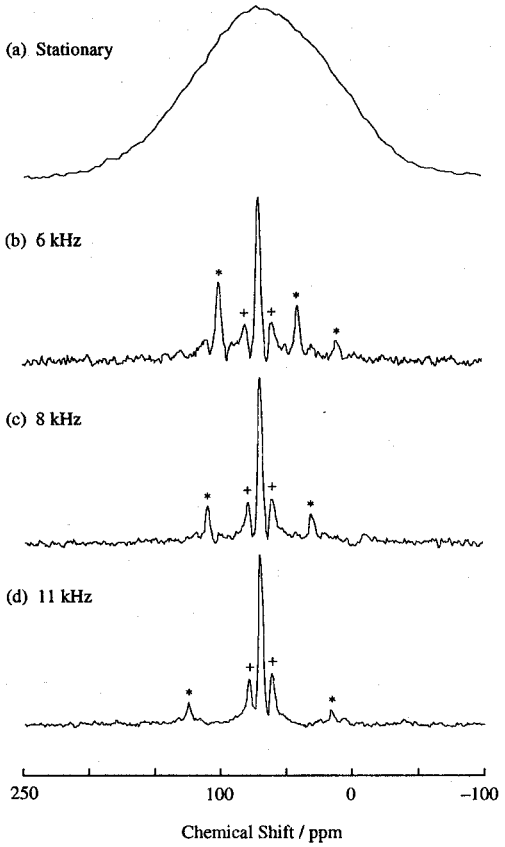
Sample Preparation. $K_4[Pt_2(P_2O_5H_2)_4]\cdot 2H_2O$ ("Pt_2"), $K_4[Pt_2(P_2O_5H_2)_4Cl_2]\cdot 2H_2O$ ("Pt_2Cl_2"), and $K_4[Pt_2(P_2O_5H_2)_4Br_2]\cdot 2H_2O$ ("Pt_2Br_2") were prepared by the literature method.[19,20] All chemicals were obtained from Aldrich Chemical Company, Inc.

Solid-State ^{31}P NMR Spectroscopy. Solid-state ^{31}P powder patterns were taken on stationary samples with a Bruker MSL200 solid-state NMR spectrometer operating at 80.98 MHz using a high power probe with a solenoidal coil. The 90° pulse length was 2 μs and the spectra were acquired as simple Bloch decays. The ^{31}P MAS (Magic Angle Spinning) spectra were acquired on Bruker MSL200 and 500 solid-state NMR spectrometers using a 15 kHz CP/MAS probe and a 4 mm ZrO_2 rotor with a Kel-F cap. The magic angle was adjusted by examining the ^{79}Br NMR signal of KBr.[21] Powdered samples, 70 to 100 mg, were loosely packed into the rotor along with alumina as an inert filler. At 80.98 MHz resonance frequency (MSL200), the 90° pulse was 5 μs and the spectra were acquired as simple Bloch decays. At 202.46 MHz (MSL500), an 8.9 μs (<90° tip angle) pulse was used. The ^{31}P chemical shift values recorded on the δ-scale are referenced to 85% H_3PO_4 as external standard. All spectra are exponentially filtered (200 Hz), Fourier transformed, and manually phased.

Solid-State ^{31}P NMR Chemical Shielding Tensors. A Herzfeld-Berger graphical method[22] was used to obtain three principal elements (δ_{11}, δ_{22}, and δ_{33}) of the ^{31}P chemical shielding tensors from the intensities of the spinning sidebands and the isotropic chemical shift, δ_{iso}, in the ^{31}P MAS spectra. The effects of dipolar and J couplings between ^{31}P and ^{195}Pt nuclei on the relative intensities of the ^{31}P MAS peaks[23] were neglected.

Results and Discussion

Shown in Figure 1 are the featureless ^{31}P NMR powder pattern at stationary and well-resolved ^{31}P MAS NMR spectra at three different spinning rates of Pt_2. It is difficult to reliably extract the principal elements of the ^{31}P chemical shielding tensor from the powder pattern. In principle, an analysis of the ^{31}P NMR powder patterns can be made by using ^{31}P Zeeman and chemical shielding interactions and dipolar and J coupling interactions between ^{31}P and ^{195}Pt nuclei. However, because the chemical shift anisotropy interaction for the phosphorus site is relatively small with respect to both dipolar and J coupling interactions between ^{31}P and ^{195}Pt nuclei, the ^{31}P powder pattern is featureless at 4.7 Tesla. Thus, the uncertainty in the fit of a simulated ^{31}P powder pattern to the experimental powder pattern is unacceptably large. For this reason, the principal elements of the ^{31}P chemical shielding tensor were acquired from a Herzfeld-Berger graphical analysis of the ^{31}P MAS spectra. In the MAS experiment, it is possible to focus on the spinning sidebands of the S=0 Pt isotopomer; thus the ^{195}Pt (S=1/2) spectral component shown as crosses (+) in Figure 1 is excluded from the analysis. It is usual to analyze below 2-3 kHz slow spinning spectra to obtain the reliable data. However, in this work, above 6 kHz spinning rate spectra have been used

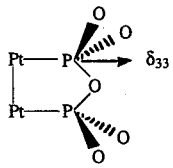
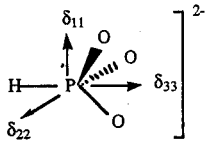


Figures 1. Solid-state ^{31}P powder pattern of $K_4[Pt_2(P_2O_5H_2)_4]\cdot 2H_2O$ ("Pt_2") and ^{31}P MAS spectra at different spin rates, ν_r. Asterisks (*) and crosses (+) represent the spinning sidebands and the J coupling peaks to ^{195}Pt, respectively. Experimental parameters are as follows: (a) ν_L=80.98 MHz, ν_r=0 kHz, NS=30, RD=120 s; (b) 202.46 MHz, 6 kHz, 16, 100 s; (c) 202.46 MHz, 8 kHz, 8, 100 s; and, (d) 202.46 MHz, 11 kHz, 8, 100 s.

to avoid the overlap between the spinning sidebands of the S=0 Pt isotopomer and the ^{195}Pt (S=1/2) spectral bands. Solid-state ^{31}P chemical shielding tensor for three binuclear platinum diphosphite complexes are listed in Table 1. The values of isotropic ^{31}P chemical shift (δ_{iso}) are essentially the same in solution as in the solid-state; there is an upfield shift going from Pt_2 to Pt_2Cl_2 and Pt_2Br_2. The values of δ_{11} and δ_{33} show upfield shifts while δ_{22} nearly constant.

The orientation of the ^{31}P chemical shielding tensor elements relative to the molecular axis system cannot be obtained from a Herzfeld-Berger graphical analysis of the S=0 Pt isotopomers. Single crystal NMR studies were attempted for Pt_2, but were unsuccessful due to a lack of a large crystal. The ^{31}P chemical shielding tensor orientations have not been determined experimentally in this study, though the most shielded element, δ_{33} is believed to be parallel to the ^{195}Pt-^{31}P bond axis. The ^{31}P chemical shielding tensor orientation assigned partially is shown in Table 1, as is the tensor orientation for a related ^{31}P site in the phosphite anion and the phosphines. In the solution-state ^{31}P NMR study by Farrar and Locker of HPO_3^{2-}, the orientation of the ^{31}P chemical shielding tensor elements as shown in Table 1 was determi-

Table 1. Solid-State ^{31}P NMR Chemical Shielding Tensors and Pt-Pt Distances for Binuclear Platinum Diphosphite Complexes

Compound	Solid-State[a]			Orientation	Solid-State		Solution-State[b]		d(Pt-Pt)[c]
	δ_{11}	δ_{22}	δ_{33}		δ_{iso}	J_{Pt-P} (Hz)	δ_{iso}	J_{Pt-P} (Hz)	(Å)
$K_4[Pt_2(P_2O_5H_2)_4]\cdot 2H_2O$	138	66	6		69.8	3120	69.4	3095	2.925 (1)
$K_4[Pt_2(P_2O_5H_2)_4Cl_2]\cdot 2H_2O$	92	59	−69		27.5	ca.2460	28.0	2170	2.695 (1)
$K_4[Pt_2(P_2O_5H_2)_4Br_2]\cdot 2H_2O$	96	60	−71		28.2	2185	24.0	2230	2.723 (4)
	Solution-State								
HPO_3^{2-}[d]	93	93	−30						

[a] Obtained by using a Herzfeld-Berger method. Error limits are ±5 ppm. [b] King, C.; Roundhill, D. M.; Dickson, M. K.; Fronczek, F. R. *J. Chem. Soc. Dalton Trans.* **1987**, 2769. [c] Ref. 12. [d] Ref. 24. Tensor orientation shown in the table based upon 3-fold site symmetry at phosphorus.

ned by the longitudinal relaxation study of the P-H spin system.[24] A single crystal ^{31}P NMR study of chlorotris(triphenylphosphine)rhodium(I) showed that the most shielded element is almost parallel to the Rh-P bond axis.[25] Also, the most shielded elements of the ^{31}P chemical shielding tensor in a number of solid phosphines were taken to lie along the C_3 (or *pseudo* C_3) axis.[26]

In the Ramsey approach,[27,28] the NMR chemical shielding of a nucleus can be decomposed into diamagnetic and paramagnetic contributions, which are generally opposite in sign. Because the coordination at phosphorus is not changed in the series of Pt_2, Pt_2Cl_2, and Pt_2Br_2, the diamagnetic contribution to the chemical shielding tensor elements should remain nearly constant. The range of chemical shift for ^{31}P is quite large. The chemical shifts on the δ-scale for the bare ^{31}P nucleus and free ^{31}P atom are 356 and −605 ppm, respectively, relative to 85% H_3PO_4.[29] In fact, highly shielded tensor elements are relatively rare in ^{31}P NMR, with P_4 ($\delta_{11}=-190$, $\delta_{22}=-597$, and $\delta_{33}=-597$ ppm)[8] and related systems such as P_4S_3 ($\delta_{11}=101$, $\delta_{22}=44$, and $\delta_{33}=-406$ ppm)[9] being some of the few examples. The fact that the value of δ_{33} is not close to that for a free ^{31}P atom for any of the binuclear platinum diphosphite complexes listed in Table 1 suggests a large paramagnetic contribution. We speculate that one of the significant changes occurring at the platinum metal center is a change in coordination number from four (Pt_2) to six (Pt_2Cl_2 and Pt_2Br_2), with the higher symmetry of the six-coordinate site affecting the paramagnetic contribution. Also, the increase in the P-Pt distances (and the decrease in the Pt-Pt distances) from Pt_2 to Pt_2Cl_2 and Pt_2Br_2 is an important factor affecting the more paramagnetic chemical shielding at ^{31}P nucleus on the P-Pt bond axis. We have found a good linear relationship between the Pt-Pt distances and the most shielded chemical shielding tensor element, δ_{33}; more shielded δ_{33} value implies more semiconductivity in the linear chain structures.

Figure 2 compares the ^{31}P MAS spectra for Pt_2, Pt_2Cl_2, and Pt_2Br_2. The spectra are similar to solution-state ^{31}P NMR spectra, though the line width, ~430 Hz (FWHH), obscures all but the single bond J coupling between ^{31}P and ^{195}Pt nuclei. The 33.7% natural abundant ^{195}Pt leads to a doublet in the ^{31}P spectrum which is superimposed upon the ^{31}P

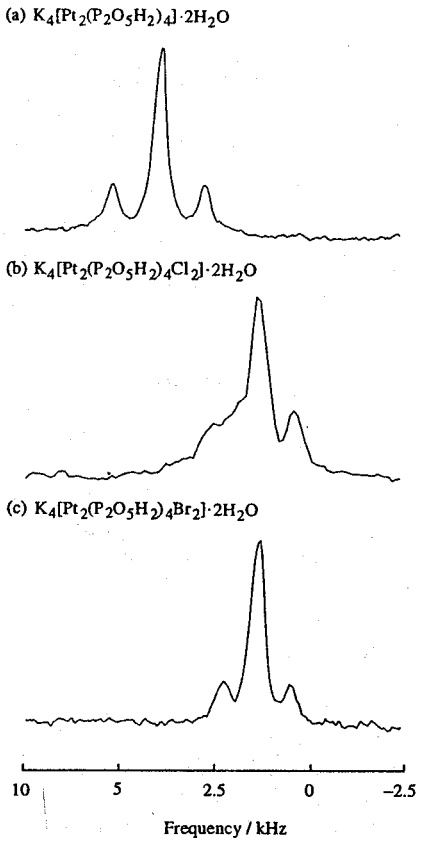


Figure 2. Solid-state ^{31}P MAS spectra of $K_4[Pt_2(P_2O_5H_2)_4]\cdot 2H_2O$ ("Pt_2"), $K_4[Pt_2(P_2O_5H_2)_4Cl_2]\cdot 2H_2O$ ("Pt_2Cl_2"), and $K_4[Pt_2(P_2O_5H_2)_4Br_2]\cdot 2H_2O$ ("Pt_2Br_2") at $\nu_r=10$ kHz and $\nu_L=80.98$ MHz. The spectra show a single peak at the ^{31}P isotropic chemical shift and a doublet due to J coupling between ^{31}P and ^{195}Pt nuclei. Experimental parameters are as follows: (a) $K_4[Pt_2(P_2O_5H_2)_4]\cdot 2H_2O$, NS=100, RD=30 s; (b) $K_4[Pt_2(P_2O_5H_2)_4Cl_2]\cdot 2H_2O$, 250, 30 s; and, (c) $K_4[Pt_2(P_2O_5H_2)_4Br_2]\cdot 2H_2O$, 88, 30 s.

singlet. The isotropic J coupling constants are given in Table 1; the J coupling constants decrease as going from Pt_2 to Pt_2Cl_2 and Pt_2Br_2. A decrease in the value of J (^{31}P-^{195}Pt) may be due to the longer P-Pt bond, with decreased *s*-orbital character in the P-Pt bonds, which can be explained on the basis of the Pople-Santry equation.[30] The doublet for the ^{31}P-^{195}Pt spin system in Pt_2Cl_2 is noticeably asymmetric in the MAS spectrum. An asymmetry of this type in a ^{31}P powder pattern has been shown to be a result of anisotropies of the ^{31}P chemical shielding and J coupling tensors in (^{31}P-^{195}Pt) [31] and (^{31}P-^{199}Hg) systems.[32,33]

Conclusions

The principal elements and the relative orientations of the ^{31}P chemical shielding tensors have been obtained for Pt_2, Pt_2Cl_2, and Pt_2Br_2 complexes in the solid state. The ^{31}P isotropic chemical shifts and J (^{31}P-^{195}Pt) coupling constants are essentially the same in solution as in the solid state. There is an upfield shift (more negative values on the δ scale) going from Pt_2 to Pt_2Cl_2 and Pt_2Br_2 complexes in δ_{33}, which is aligned with the P-Pt bond axis. The paramagnetic contribution to δ_{33} has been discussed based on the structural change at the platinum metal center. The results can be correlated with a decrease in the Pt-Pt distances in the order $Pt_2 > Pt_2Cl_2 \approx Pt_2Br_2$.

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References

1. Carty, A. J.; Fyfe, C. A.; Lettinga, M.; Johnson, S.; Randall, L. H. *Inorg. Chem.* **1989**, *28*, 4120.
2. Un, S.; Klein, M. P. *J. Am. Chem. Soc.* **1989**, *111*, 5119.
3. Turner, G. L.; Smith, K. A.; Kirkpatrick, R. J.; Oldfield, E. *J. Magn. Reson.* **1986**, *70*, 408.
4. Nelson, J. H.; Rahn, J. A.; Bearden, W. H. *Inorg. Chem.* **1987**, *26*, 2192.
5. Rahn, J. A.; Baltusis, L.; Nelson, J. H. *Inorg. Chem.* **1990**, *29*, 750.
6. Lindner, E.; Fawzi, R.; Mayer, H. A.; Eichele, K.; Pohmer, K. *Inorg. Chem.* **1991**, *30*, 1102.
7. Lindner, E.; Fawzi, R.; Mayer H. A.; Elchele, K.; Hiller, W. *Organometallics* **1992**, *11*, 1033.
8. Spiess, H. W.; Grosescu, R.; Haeberlen, U. *Chem. Phys.* **1974**, *6*, 226.
9. Bjorholm, T.; Jakobsen, H. J. *J. Magn. Reson.* **1989**, *84*, 204.
10. Wu, G.; Wasylishen, R. E. *Organometallics* **1992**, *11*, 3242.
11. Butler, L. G.; Zietlow, M. H.; Che, C.-M.; Schaefer, W. P.; Sridhar, S.; Grunthaner, P. J.; Swanson, B. I.; Clark, R. J. H.; Gray, H. B. *J. Am. Chem. Soc.* **1988**, *110*, 1155.
12. Roundhill, D. M.; Gray, H. B.; Che, C.-M. *Acc. Chem. Res.* **1989**, *22*, 55.
13. Filomena Dos Remedios Pinto, M. A.; Sadler, P. J.; Neidle, S.; Sanderson, M. R.; Subbiah, A.; Kuroda, R. *J. Chem. Soc., Chem. Commun.* **1980**, 13.
14. Che, C.-M.; Schaefer, W. P.; Gray, H. B.; Dickson, M. K.; Stein, P. B.; Roundhill, D. M. *J. Am. Chem. Soc.* **1982**, *104*, 4253.
15. Clark, R. J. H.; Kurmoo, M.; Dawes, H. M.; Hursthouse, M. B. *Inorg. Chem.* **1986**, *25*, 409.
16. Fordyce, W. A.; Brummer, J. G.; Crosby, G. A. *J. Am.. Chem. Soc.* **1981**, *103*, 7061.
17. Stein, P.; Dickson, M. K.; Roundhill, D. M. *J. Am.. Chem. Soc.* **1983**, *105*, 3489.
18. Alexander, K. A.; Bryan, S. A.; Fronczek, F. R.; Fultz, W. C.; Rheingold, A. L.; Roundhill, D. M.; Stein, P.; Watkins, S. F. *Inorg. Chem.* **1985**, *24*, 2803.
19. Alexander, K. A.; Bryan, S. A.; Dickson, M. K.; Hedden, D.; Roundhill, D. M. *Inorg. Synth.* **1986**, *24*, 211.
20. Che, C.-M.; Herbstein, F. H.; Schaefer, W. P.; Marsh, R. E.; Gray, H. B. *J. Am. Chem. Soc.* **1983**, *105*, 4604.
21. Frye, J. S.; Maciel, G. E. *J. Magn. Reson.* **1982**, *48*, 125.
22. Herzfeld, J.; Berger, A. E. *J. Chem. Phys.* **1980**, *73*, 6021.
23. Wu, G.; Wasylishen, R. E.; Curtis, R. D. *Can. J. Chem.* **1992**, *70*, 863.
24. Farrar, T. C.; Locker, I. C. *J. Chem. Phys.* **1987**, *87*, 3281.
25. Naito, A.; Sastry, D. L.; McDowell, C. A. *Chem. Phys. Lett.* **1985**, *115*, 19.
26. Penner, G. H.; Wasylishen, R. E. *Can. J. Chem.* **1989**, *67*, 1909.
27. Ramsey, N. F. *Phys. Rev.* **1950**, *78*, 699.
28. Goggin, P. L.; Goodfellow, R. J.; Haddock, S. R.; Taylor, B. F.; Marshall, I. R. H. *J. Chem. Soc., Dalton Trans.* **1976**, 459.
29. Malli, G.; Froese, C. *Int. J. Quantum Chem.* **1967**, *1S*, 95.
30. Nixon, J. F.; Pidcock, A. *Annu. Rev. N. M. R. Spectrosc.* **1969**, *2*, 345.
31. Power, W. P.; Wasylishen, R. E. *Inorg. Chem.* **1992**, *31*, 2176.
32. Power, W. P.; Lumsden, M. D.; Wasylishen, R. E. *Inorg. Chem.* **1991**, *30*, 2997.
33. Power, W. P.; Lumsden, M. D.; Wasylishen, R. E. *J. Am. Chem. Soc.* **1991**, *113*, 8257.