Carbon-13 and Proton Nuclear Magnetic Resonance Spectra of Methylmercury Nitrate in Strong Acids

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(Received July 24, 1976)

Proton and carbon-13 nuclear magnetic resonance spectra and Raman spectra of some methylmercury compounds, CH_3HgX, were measured. The spin-spin coupling constants, $^2J(^{199}Hg–H)$ and $^1J(^{13}C–H)$ of methylmercury nitrate in some strong acids were found to increase when the proton resonance of the methyl group attached to the mercury shifts to lower magnetic field. It was also found that the C–H stretching bands of the methyl group shift to higher frequency in the strong acids. The results are explained by an increase of the effective positive charge on the mercury. As has been observed in other alkylmercury compounds, the spin-spin coupling constant between directly bonded mercury and carbon nuclei, $^1J(^{199}Hg–^{13}C)$, of some methylmercury compounds in organic solvents increased with the geminal spin-spin coupling constant, $^2J(^{199}Hg–H)$. The $^1J(^{199}Hg–^{13}C)$ value of methylmercury nitrate in strong acids was found to decrease, whereas the $^2J(^{199}Hg–H)$ values increased in these media. The lowering of the mercury-carbon bond strengths in the strong acids, which was revealed from the mercury-carbon stretching frequency in the Raman spectra, is considered one possible reason for the decrease of the $^1J(^{199}Hg–^{13}C)$ value.

In recent years a great deal of information on heavy atom–proton and –carbon-13 spin-spin couplings has accumulated, particularly for the mercury system. Hatton, Schneider, and Siebrand¹⁾ have shown that in a series of methylmercury compounds, CH_3HgX, the geminal spin-spin coupling constant, $^2J(^{199}Hg–H)$, is approximately accounted for by the Fermi contact mechanism. Henneike²⁾ has also shown from a semi-empirical molecular orbital study of a number of methylmercury compounds that the orbital contraction for the mercury 6S orbital with increasing electronegativity of the substituent, X, is an important contributing factor to the spin-spin coupling constant. Singh³⁾ and Ibusuki and Saito⁴⁾ have indicated that the Fermi contanct interaction is predominant in the mercury–proton and –carbon-13 spin-spin coupling constants by showing linear relationships between the spin-spin coupling constants $^1J(^{199}Hg–^{13}C)$ and $^2J(^{199}Hg–H)$ which pass almost through the origin for neopentylmercury compounds, $(CH_3)_3CCH_2HgX$, and 2-methoxy-2-methylpropylmercury compounds, $(CH_3)_2C(OCH_3)CH_2HgX$, respectively.

In parallel with these studies, the proton and carbon-13 nuclear magnetic resonance spectra of a variety of organomercury compounds have been used for structural and bonding studies,⁵⁻²⁶⁾ because the $^1J(^{199}Hg–^{13}C)$ and $^2J(^{199}Hg–H)$ values are influenced markedly by substituents at the mercury.

In the present paper, the proton and carbon-13 nuclear magnetic resonance spectra of methylmercury nitrate, CH_3HgNO_3, in some strong acids were studied to find out the effect of the effective positive charge on the mercury on the spin-spin coupling constants, $^1J(^{199}Hg–^{13}C)$, $^2J(^{199}Hg–H)$, and $^1J(^{13}C–H)$. The Raman spectra of methylmercury nitrate were also measured in the strong acids; the results are discussed with the nuclear magnetic resonance spectral date.

Experimental

Preparation of Compounds. Methylmercury bromide was prepared by Grignard reaction of methylmagnesium bromide and mercury dibromide in ether and purified by recrystallization from methanol. Methylmercury cyanide and nitrate were obtained by stirring a mixtures of methylmercury bromide and appropriate silver salts in methanol for 5 h at ambient temperature. After filtering off the silver bromide, concentration of the filtrate at reduced pressure yielded crystalline compounds. The compounds were dried *in vaccuo* and were stored in a desiccator.

NMR Spectra. The Proton magnetic resonance spectra were measured on a JEOL model JNM-PS-100 spectrometer operating at 100 MHz. The chemical shifts were measured relative to internal tetramethylsilane and sodium 2,2-dimethyl-2-silapentane-5-sulfonate, DSS. The spin-spin coupling constants, $^1J(^{13}C–H)$ and $^2J(^{199}Hg–H)$, and the chemical shift of the methyl group, $\delta(Hg–C\underline{H}_3)$, obtained for methylmercury compounds in about 10 wt% solution are shown in Table 1. The values of dimethylmercury¹⁶⁾ and methylmercury ion²¹⁾ also appear in Table 1.

The carbon-13 nuclear magnetic resonance spectra were run on a JEOL model JNM-PFT-100 pulse Fourier transform spectrometer operating at 25.14 MHz. Broad band proton noise decoupling was employed to eliminate the spin-spin coupling with the protons and to enhance the signal-to-noise ratio. $(CD_3)_2CO$ was used as a lock signal. Good spectra were obtained generally by scanning 1500—2000 times. The spin-spin coupling constant, $^1J(^{199}Hg–^{13}C)$, for some methylmercury compounds in about 20 wt% solution is shown in Table 1.

Raman Spectra. The Raman spectra were recorded on a JEOL model JRS-02AS spectrometer using laser light of 4880 A. The mercury-carbon and carbon-hydrogen stretching frequencies of methylmercury nitrate in some strong acids are shown in Table 2. The concentration of the compounds was about 20 wt%. The data of some other methylmercury compounds²⁷⁻²⁹⁾ are also added for comparison.

Solvents. The organic solvents dried over a desiccant were purified by distillation. Inorganic acids obtained from commercial sources were used without further purification.

Results and Discussion

The proton magnetic resonance data of methylmercury nitrate in Table 1 show that the chemi-

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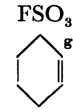
Table 1. Proton and carbon-13 NMR data of some methylmercury compounds, CH_3HgX, in several solvents

X	Solvent	$^1J(^{13}C\text{-}H)$ (Hz)	$^2J(^{199}Hg\text{-}H)$ (Hz)	$^1J(^{199}Hg\text{-}^{13}C)$ (Hz)	$\delta(C\underline{H}_3)$ (ppm)	$\delta(\underline{C}H_3)$ (ppm)
CH_3		129.6a)	104.3b)	690a)		
CN	Pyridine	132.0	177.6	1235	0.69	6.0c)
Br	Pyridine	135.6	214.5	1530	0.98	1.1c)
Br	DMSO	138.5	221.5	d)	0.87	d)
NO_3	CH_3OH	139.2	251.3	1793	1.08	−3.7c)
NO_3	H_2O	141.0	256.5	1785	1.06	−1.2e)
NO_3	DMSO	139.0	260.3	1954	0.88	−0.9c)
NO_3	HNO_3(60%)	142.9	257.4	1691	1.31	−1.1e)
NO_3	$HClO_4$(10%)	142.2	262.0	d)	1.13	d)
NO_3	$HClO_4$(20%)	142.5	262.8	1761	1.20	−0.1e)
NO_3	$HClO_4$(40%)	142.5	263.8	d)	1.25	d)
NO_3	$HClO_4$(50%)	142.8	265.8	d)	1.29	d)
NO_3	$HClO_4$(60%)	143.9	270.6	1732	1.39	1.3e)
NO_3	$HClO_4$(70%)	144.3	273.9	1711	1.42	3.8e)
NO_3	H_2SO_4(95%)	145.3	274.0	1654	f)	4.0e)
NO_3	CF_3SO_3H	146.4	280.6	1667	f)	3.7e)
FSO_3g)	$FSO_3H\text{-}SO_2$		246		1.54	
 g)	$FSO_3H\text{-}SO_2$		240		1.46	

a) Ref. 12. b) Ref. 16. c) Internal TMS. d) Not measured. e) External TMS. f) DSS was decomposed. g) Ref. 21.

Table 2. The C–H and Hg–C stretching frequencies of some methylmercury compounds, CH_3HgX (in cm^{-1})

X	Solvent	ν_{asym}(C–H)	ν_{sym}(C–H)	ν(Hg–C)
CH_3a)	Neat	2965	2909	514
CNb)	H_2O	3008	2931	564
NO_3c)	H_2O	3025	2941	566
ClO_4c)	H_2O	3027	2941	569
NO_3	$HClO_4$(70%)	3048 br	2945	569
NO_3	H_2SO_4(95%)	3045 br	2946	562
NO_3	CF_3SO_3H	d)	d)	561

a) Ref. 27. b) Ref. 28. c) Ref. 29. d) Could not be observed because of strong background.

cal shift of the methyl group, $\delta(Hg\text{–}C\underline{H}_3)$, shifts to lower magnetic field and concomitantly the geminal spin-spin coupling constant, $^2J(^{199}Hg\text{–}H)$, increases as the acid strength becomes large or the concentration of the acid increases. The chemical shift of the methyl proton, $\delta(Hg\text{–}C\underline{H}_3)$, of methylmercury nitrate in the strong acids is comparable to that of the methylmercury ion measured by Olah and Clifford[21)] in a mixed solvent system, $FSO_3H\text{–}SO_2$, but the geminal spin-spin coupling constant, $^2J(^{199}Hg\text{–}H)$, of methylmercury nitrate is much larger than that of the methylmercury ion. The small $^2J(^{199}Hg\text{–}H)$ value of the naked methylmercury ion was predicted from the semiempirical molecular orbital calculation by Henneike.[2)]

A fairly linear relation between the chemical shift of the methyl proton, $\delta(Hg\text{–}C\underline{H}_3)$, and the geminal spin-spin coupling constant, $^2J(^{199}Hg\text{–}H)$, is shown in Fig. 1. The relation is quite similar to that obtained for other series of methylmercury compounds, *i.e.*, increase of the geminal coupling constants, $^2J(^{199}Hg\text{–}H)$, is followed by increase of the electronegativity of the substituents[10)] or by decrease of the pK_a values of carboxylic acids.[15)] But the relation is quite different from the relations obtained for dimethyllead dinitrate, dimethyltin oxide, and dimethylthallium nitrate in strong acids,[30)] in which the geminal spin-spin coupling constants, ^2J(M–H)(M=Sn, Pb, and Tl), decrease as the acid strength or the concentration of the acids increase.

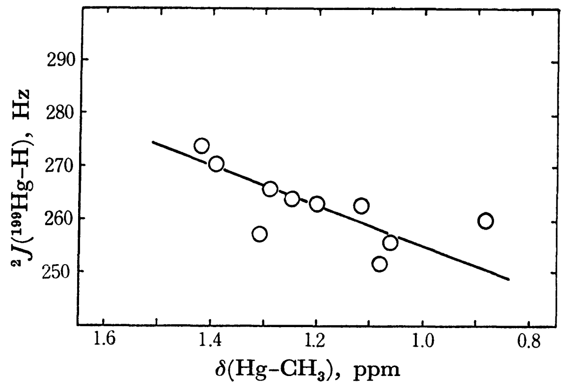


Fig. 1. Correlation between $\delta(Hg\text{-}CH_3)$ and $^2J(^{199}Hg\text{-}H)$ for methylmercury nitrate.

Woodward and co-worker[29,31)] have shown that there is the following equilibrium in an aqueous solution of methylmercury nitrate. Since the function of strong acids is to reduce the water activity below that necessary

$$CH_3HgONO_2 + H_2O \rightleftharpoons [CH_3HgOH_2]^+ + NO_3^-$$

to hydrate the cation fully, the equilibrium shown below may shift to the right in strong acids, where

$$[CH_3HgOH_2]^+ + Y^- + H^+ \rightleftharpoons [CH_3Hg^+\cdots Y^-] + H_3O^+$$

Y^- is the acid residue. In the $[CH_3Hg^+\cdots Y^-]$ species, the acid residue may coordinate weakly to mercury from the backside of the C–Hg bond. The effective positive charge, and therefore the orbital contraction of the mercury 6S orbital in the species, $[CH_3Hg^+\cdots Y^-]$, is probably larger than that of the hydrated species, $[CH_3HgOH_2]^+$, because the electron donating ability of the acid residue, Y^-, is considered to be smaller than water. The down field shift of the methyl proton, $\delta(\text{Hg–C}\underline{\text{H}}_3)$, and increase of the geminal spin-spin coupling constant, $^2J(^{199}\text{Hg–H})$, in strong acids, therefore, may be due to an increase of the species $[CH_3Hg^+\cdots Y^-]$ in these media.

As can be seen from Table 1, the $^1J(^{13}\text{C–H})$ value of the methyl group of the methylmercury nitrate increases when the acid strength or the concentration of the acids increases, although Henneike[2)] obtained little variation of the $^1J(^{13}\text{C–H})$ value for methylmercury compounds. Figure 2 gives a linear relation between the $^1J(^{13}\text{C–H})$ and $\delta(\text{Hg–C}\underline{\text{H}}_3)$ values, which is expressed by the following equation, where the values in parentheses are the errors estimated at the 95% confidence level and the r is the correlation coefficient. The result is quite similar to that obtained for

$$^1J(^{13}\text{C-H}) = 9.8(\pm 2.7)\delta(\text{Hg-C}\underline{\text{H}}_3) + 130.4(\pm 3.1) \quad r=0.955$$

dimethyltin oxide in strong acids.[30)] The dependence

$$^1J(^{13}\text{C-H}) = 5.6(\pm 1.6)\delta(\text{Sn-C}\underline{\text{H}}_3) + 130.4(\pm 2.1) \quad r=0.933$$

of the $^1J(^{13}\text{C–H})$ value on the chemical shift of the methyl protons is much more acute in the case of methylmercury nitrate. A linear relation is also obtained between the $^1J(^{13}\text{C–H})$ and $^2J(^{199}\text{Hg–H})$ values for methylmercury nitrate in strong acids(see Fig. 2), which is represented by the following equation:

$$^1J(^{13}\text{C-H}) = 0.22(\pm 0.11)^2J(^{199}\text{Hg-H}) + 84(\pm 22) \quad r=0.879$$

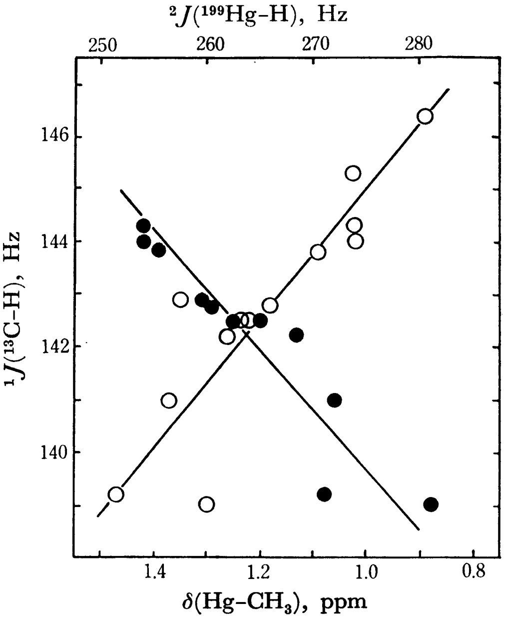


Fig. 2. Correlation between $^1J(^{13}\text{C-H})$ and $\delta(\text{Hg-CH}_3)$ (—●—) and $^2J(^{199}\text{Hg-H})$ (—○—) for methylmercury nitrate.

The C–H symmetric and asymmetric stretching bands shown in Table 2 shift to higher frequencies in strong acids. The values are rather larger than those of dimethylmercury.[27)] High C–H stretching freqeuencies of the methyl group of dimethyllead diperchlorate[32)] and dimethyltin diperchlorate[33)] in aqueous solutions relative to those of tetramethyl-lead and -tin,[34)] respectively, have been reported. Brown and Puckett[35)] have shown that in a variety of methyl compounds the spin-spin coupling constant, $^1J(^{13}\text{C–H})$, of the methyl group increases linearly with increasing C–H symmetric and asymmetric stretching frequencies and therefore with the C–H stretching force constant. By using the present values for methylmercury nitrate and the reported values of the $^1J(^{13}\text{C–H})$ and ν_{asym}(C–H) values of 32 methyl compounds, we obtained the following equation relating these quantities:

$$^1J(^{13}\text{C-H}) = 0.237(\pm 0.034)\nu_{\text{asym}}(\text{C-H}) - 576(\pm 102) \quad r = 0.933$$

They[35)] have shown theoretically that the C–H stretching force constant of these methyl compounds should depend on the C–H bond polarity, which will in turn depend on the electronegativity of the group attached to the methyl group. They concluded from these results that changes in the effective nuclear charge of carbon experienced by the electron in the C–H bonds can account for the principal variation in the $^1J(^{13}\text{C–H})$ value of the methyl groups[36)] and the assuming of a very large change in the hybridization parameter of carbon to fit the experimental value is not necessary. The increase of the $^1J(^{13}\text{C–H})$ value of methylmercury nitrate in strong acids, therefore, may be accounted for by the same principle. The result is in accordance with the increase of the species $[CH_3Hg^+\cdots Y^-]$ in strong acids, since in this species the effective positive charge on the mercury and therefore the electronegativity of the mercury, is considered to be large.

Table 1 gives the spin-spin coupling constant, $^1J(^{199}\text{Hg–}^{13}\text{C})$, of some methylmercury compounds. The value increases when the electron-withdrawing property of the substituent becomes large. A linear relation between the $^1J(^{199}\text{Hg–}^{13}\text{C})$ and $^2J(^{199}\text{Hg–H})$ values of these compounds in organic solvents and in water is shown in Fig. 3. The regression analysis for this relation gives the following equation:

$$^1J(^{199}\text{Hg-}^{13}\text{C}) = 7.65(\pm 0.80)^2J(^{199}\text{Hg-H}) - 144(\pm 173) \quad r = 0.997$$

Similar linear relations have been reported for 2-methoxy-2-methyl-propylmercury derivatives, $(CH_3)_2C(OCH_3)CH_2HgX$,[4)] and for neopentylmercury compounds, $(CH_3)_3CCH_2HgX$.[3)] The numerical values

$$^1J(^{199}\text{Hg-}^{13}\text{C}) = 8.47(\pm 2.32)^2J(^{199}\text{Hg-H}) - 98(\pm 140) \quad r=0.981^{***}$$

$$^1J(^{199}\text{Hg-}^{13}\text{C}) = 7.8^2J(^{199}\text{Hg-H}) - 59$$

*** The regression analysis was made by using the reported values.[4)]

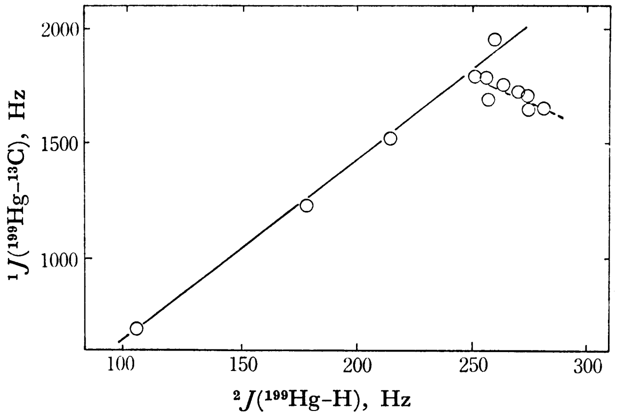


Fig. 3. Correlation between $^1J(^{199}Hg-^{13}C)$ and $^2J(^{199}Hg-H)$ for methylmercury compounds.

of these three equations are very similar. Although the lines do not pass exactly through the origin, the relations indicate that the Fermi contact term is mainly responsible for the spin-spin coupling constants, $^1J(^{199}Hg-^{13}C)$ and $^2J(^{199}Hg-H)$, in these cases. On the other hand, as can be seen from Table 1, the $^1J(^{199}Hg-^{13}C)$ value of methylmercury nitrate decreases when the acid strength increases, whereas the $^2J(^{199}Hg-H)$ value continues to incresae. These results cannot be explained by the simple assumption that the Fermi contact term plays a dominant role in the spin-spin coupling constant, $^1J(^{199}Hg-^{13}C)$.

According to the theory of spin-spin interaction developed by Ramsey,[37] the nuclear spin-spin coupling constant is, in addition to the Fermi contact interaction, affected by the following terms: 1) an orbital-dipole interaction between the magnitic field due to the orbital motion of the electron and the nuclear magnetic dipole (J_{orb}) and 2) a magnetic dipole-dipole interaction between the magnetic dipole of the spinning electron and the nuclear spin(J_{dipole}). Of these three basic interactions, the contact interaction is the main determinant of the nuclear spin-spin coupling constant, especially for H_2.[38] However, the J_{orb} and J_{dipole} terms have been found to be very important when one or both of the nuclei is electronegative, such as in the spin-spin coupling constant, $^1J(^{12}C-^{19}F)$ and $^{2,3}J(^{19}F-^{19}F)$.[39] In the spin-spin coupling constants, $^1J(^{13}C-^{13}C)$, the J_{dipole} term has been found to play a significant role.[39,40] Therefore, the contribution of the J_{orb} and J_{dipole} terms may be one reason for the decrease of the spin-spin coupling constant, $^1J(^{199}Hg-^{13}C)$, of methylmercury nitrate in strong acids. As can be seen from Table 2, the value of the mercury–carbon stretching frequency for methylmercury nitrate has a tendency to decrease in strong acids. The weakening of the mercury–carbon bond, therefore, may also be an another factor leading to a reduction of the $^1J(^{199}Hg-^{13}C)$ value. In an overlap population analysis of the molecular orbitals of the methylmercury compounds,[2] the overlap population between the mercury–carbon bond increases when the electronegativity of the substituent becomes large. The value of the overlap population of the hydrate species $[CH_3HgOH_2]^+$ is the largest among the methylmercury compounds. But the value of the naked methylmercury ion, CH_3Hg^+, is the smallest. Therefore, the bond properties for the mercury–carbon bond of the species $[CH_3Hg^+\cdots Y^-]$, which has been shown to be the predominant species of methylmercury nitrate in strong acids, may be in between those of the ions $[CH_3HgOH_2]^+$ and CH_3Hg^+.

We wish to express our hearty thanks to Professor Rokuro Okawara of Osaka University for his continuous encouragement throughout this study. We are also grateful to Dr. Teizo Kitagawa of the Protein Institute of Osaka University for the measurements of Raman spectra.

References

1) J. V. Hatton, W. G. Schneider, and W. Siebrand, *J. Chem. Phys.*, **39**, 1330 (1963).
2) H. F. Henneike, *J. Am. Chem. Soc.*, **94**, 5945 (1972).
3) G. Singh, *J. Organomet. Chem.*, **99**, 251 (1975).
4) T. Ibusuki and Y. Saito, *Chem. Lett.*, **1974**, 311.
5) F. A. Cotton and J. R. Leto, *J. Am. Chem. Soc.*, **80**, 4823 (1958).
6) R. E. Dessy, T. J. Flaut, H. H. Jaffé, and G. F. Reynolds, *J. Chem. Phys.*, **30**, 1422 (1959).
7) S. Brownstein, *Discuss. Faraday Soc.*, **34**, 25 (1962).
8) P. R. Wells and W. Kitching, *Tetrahedron Lett.*, **1963**, 1531.
9) M. M. Kreevoy and J. F. Schaeffer, *J. Organomet. Chem.*, **6**, 589 (1966).
10) W. Kitching, J. A. Smith, and P. R. Wells, *Chem. Commun.*, **1968**, 390
11) A. N. Nesmeyanov, L. A. Fedorov, R. B. Materikova, E. I. Fedlin, and N. S. Kochetkova, *Tetrahedron Lett.*, **1968**, 3753.
12) F. J. Weigert, M. Winkur, and J. D. Roberts, *J. Am. Chem. Soc.*, **90**, 1566 (1968).
13) E. F. Kiefer, W. L. Waters, and D. A. Carlson, *J. Am. Chem. Soc.*, **90**, 5127 (1968).
14) E. F. Kiefer and W. Gericke, *J. Am. Chem. Soc.*, **90**, 5131 (1968).
15) D. F. Evans, P. M. Ridout, and I. Wharf, *J. Chem. Soc., A*, **1968**, 2127.
16) R. Schefford, *Helv. Chim. Acta*, **52**, 56 (1969).
17) L. Lunazzi, M. Tiecoo, C. A. Boicelli, and F. Taddei, *J. Mol. Spectrosc.*, **35**, 190 (1970).
18) W. Kitching, B. F. Hegarty, and D. Doddrell, *J. Organomet. Chem.*, **21**, 29 (1970).
19) G. M. Cree, *J. Organomet. Chem.*, **27**, 1 (1971).
20) G. A. Olah and P. R. Clifford, *J. Am. Chem. Soc.*, **93**, 1262 (1971).
21) G. A. Olah and P. R. Clifford, *J. Am. Chem. Soc.*, **95**, 6067 (1973).
22) G. Singh and G. S. Reddy, *J. Organomet. Chem.*, **42**, 267 (1972).
23) R. A. Scherr and J. P. Oliver, *J. Am. Chem. Soc.*, **94**, 9026 (1972).
24) F. J. Weigert and J. D. Roberts, *Inorg. Chem.*, **12**, 313 (1973).
25) W. Adcock, B. D. Gupta, W. Kitching, D. Doddrell, and M. Geckle, *J. Am. Chem. Soc.*, **96**, 7360 (1974).
26) W. Adcock, B. D. Gupta, W. Kitching, and D. Doddrell, *J. Organomet. Chem.*, **102**, 297 (1975).
27) P. L. Goggin and L. A. Woodward, *Trans. Faraday Soc.*, **56**, 1591 (1960).

28) P. L. Goggin and L. A. Woodward, *Trans. Faraday Soc.*, **58**, 1495 (1962).

29) P. L. Goggin and L. A. Woodward, *Trans. Faraday Soc.*, **62**, 1423 (1966).

30) Y. Kawasaki and M. Aritomi, *J. Organomet. Chem.*, **104**, 39 (1976).

31) J. H. R. Clarke and L. A. Woodward, *Trans. Faraday Soc.*, **62**, 3022 (1966).

32) C. E. Fedline and R. S. Tobias, *Inorg. Chem.*, **5**, 354 (1966).

33) M. M. McGrady and R. S. Tobias, *Inorg. Chem.*, **3**, 1157 (1964).

34) E. R. Lippincott and M. C. Tobin, *J. Am. Chem. Soc.*, **75**, 4141 (1953).

35) T. L. Brown and L. C. Puckett, *J. Chem. Phys.*, **44**, 2238 (1966).

36) D. M. Grant and W. M. Litchiman, *J. Am. Chem. Soc.*, **87**, 3994 (1965).

37) N. F. Ramsey, *Phys. Rev.*, **91**, 303 (1953).

38) A. Carrington and A. D. McLachlan, "Introduction to Magnetic Resonance," Harper and Row, New York, N. Y. (1967).

39) A. C. Blizzard and D. P. Santry, *J. Chem. Phys.*, **55**, 950 (1971).

40) J. M. Schulman and M. D. Newton, *J. Am. Chem. Soc.*, **96**, 6295 (1974).