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EFFECTS OF LIGANDS ON VARIOUS NMR PARAMETERS OF β-METHOXYISOBUTYLMERCURY COMPOUNDS

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Effects of ligands on various nmr parameters have been studied for $(CH_3)_2C(OCH_3)CH_2HgL$, and a linear relationship is found between $^1J_{HgC}$ and $^2J_{HgH}$. With regard to $\delta 199_{Hg}$ and $\delta 13_C$ vs. $^2J_{HgH}$, deviations from linearity occurring for the CN and SCN ligands are discussed in terms of π-bonding effect.

INTRODUCTION

C-13 nmr spectroscopy is very useful for elucidation of the nature of metal-carbon bondings of organometallic compounds.[1)] For example, the properties of π- and σ-bondings between metal and carbon have been compared in Zeise's type salts and β-methoxyalkylmercuric chlorides by their metal-carbon direct coupling constants and C-13 chemical shifts.[2)]

In the present paper, effects of ligands on the mercury-carbon bonding of β-methoxyisobutylmercury compounds, $(CH_3)_2C(OCH_3)CH_2HgL$, are closely studied in terms of mercury-proton and mercury-carbon coupling constants, together with carbon-13 and mercury-199 chemical shifts.

EXPERIMENTAL

β-Methoxyisobutylmercury compounds, ($L= OAc^-$, Cl^-, Br^-, SCN^-, I^-, and CN^-), were prepared and purified according to the usual method from β-methoxyisobutylmercuric acetate and the corresponding salts (NaL or KL).[3)] Nmr samples were made in 40 mol % chloroform solutions. Carbon-13 nmr spectra at room temperature were obtained on JEOL PS-100 and Hitachi R-26-FT spectrometers operating at 25.2 and 10.0 MHz, respectively. Spectra were scanned many times using JEOL JEC-5 and Northern NS-560 spectrum computers in order to obtain enhanced S/N values. Mercury-199 chemical shifts were determined by the usual INDOR method on JEOL 4H-100 and Hitachi R-20B spectrometers equipped with frequency synthesizers.

RESULTS and DISCUSSION

(1) Effects of ligands on nmr spin-spin coupling constants.

Table 1. NMR spin-spin coupling constants for $(CH_3)_2C(OCH_3)CH_2HgL$.[a)]

L	$^2J_{HgH}$	$^4J_{HgH}$	$^1J_{HgC}$	$^2J_{HgC}$	$^3J_{HgC}$	$^1J_{CH}$
OAc^-	211.2	22.2	1705	106	142	136
Cl^-	205.5	22.8	1642	103	142	137
Br^-	197.7	22.5	1579	103	142	136
SCN^-	195.0	28.8	1524	103	138	136
I^-	190.5	22.2	1504	102	134	136
CN^-	180.6	17.4	1452	63	107	134

a) Coupling constants in Hz.

Table 2. Carbon-13 and Mercury-199 chemical shifts for $(CH_3)_2C(OCH_3)CH_2HgL$.[a)]

L	$\underline{C}H_3$	$\underline{C}H_2$	$\underline{C}$	$O\underline{C}H_3$	$\underline{Hg}$
OAc^-	28.2	40.3	75.7	49.3	---
Cl^-	28.0	47.3	75.3	49.3	-1145
Br^-	28.9	51.5	76.0	49.8	-1234
SCN^-	28.0	50.8	76.0	49.3	-939
I^-	28.7	55.7	76.1	49.5	-1386
CN^-	29.3	44.7	77.3	50.0	-927

a) C-13 and Hg-199 chemical shifts are given in ppm unit relative to TMS and $Hg(CH_3)_2$, respectively.

All the coupling constants determined for $(CH_3)_2C(OCH_3)CH_2HgL$ are shown in Table 1. Both the mercury-proton and mercury-carbon coupling constants change according to the ligands. Remarkable variations of the geminal Hg-H and the direct Hg-C coupling constants ($^2J_{HgH}$ and $^1J_{HgC}$) are especially to be noted. A parallel change between the geminal Hg-H coupling constants of β-methoxyisobutylmercury compounds and methylmercury ones was found with respect to the ligands, which suggests that the effects of the ligands on $^2J_{HgH}$ are common to organomercurials. As shown in the last column in Table 1, however, the direct carbon-proton coupling constants ($^1J_{CH}$) of the methylene group attached directly to HgL group do not change all through the ligands, which is in accordance with the result of methylmercury compounds.[4)] Therefore, the observed changes of both $^1J_{HgC}$ and $^2J_{HgH}$ with the ligands are mainly attributed to the mercury atom.

As shown in Fig. 1 (A), a plot of $^{2}J_{HgH}$ against $^{1}J_{HgC}$ for these compounds gives a straight line which passes through the origin. A similar result has been reported with regard to $^{1}J_{PtC}$ and $^{2}J_{PtH}$ of trans-[PtMe(L)(AsMe$_3$)$_2$].5) It has also been suggested that the trans-influence of a ligand upon the spin-spin coupling constants is due to its σ-bonding property, and that the Fermi contact term is a dominant factor in the spin-spin interactions between carbon-13 and heavy metals.1,5) This term is considered to be closely related to the electron densities at the valence s orbitals.6) It is therefore strongly suggested that the mercury 6s valence orbital plays a very important role in the mercury-carbon σ-bonding.

(II) Effects of ligands on C-13 and Hg-199 chemical shifts.

The carbon-13 and mercury-199 chemical shifts ($\delta 13_C$ and $\delta 199_{Hg}$) of these compounds are shown in Table 2. Substantial changes of $\delta 13_C$ with the ligands are observed only with regard to the shifts of the methylene carbons. The values of $\delta 199_{Hg}$ are given in ppm unit relative to Hg(CH$_3$)$_2$, the Hg resonance frequency of which is equal to 10,746,468 Hz at 60 MHz for TMS protons.7) The large extent of high field shifts and sensitive variations of them with the ligands are both to be noted. Plots of the methylene carbon and the mercury-199 chemical shifts vs. $^{2}J_{HgH}$ are represented in Fig. 1 (B) and (C), respectively. Linear correlations are detected here except for the CN ligand concerning $\delta 13_C$ (Fig. 1 (B)), and except for the CN

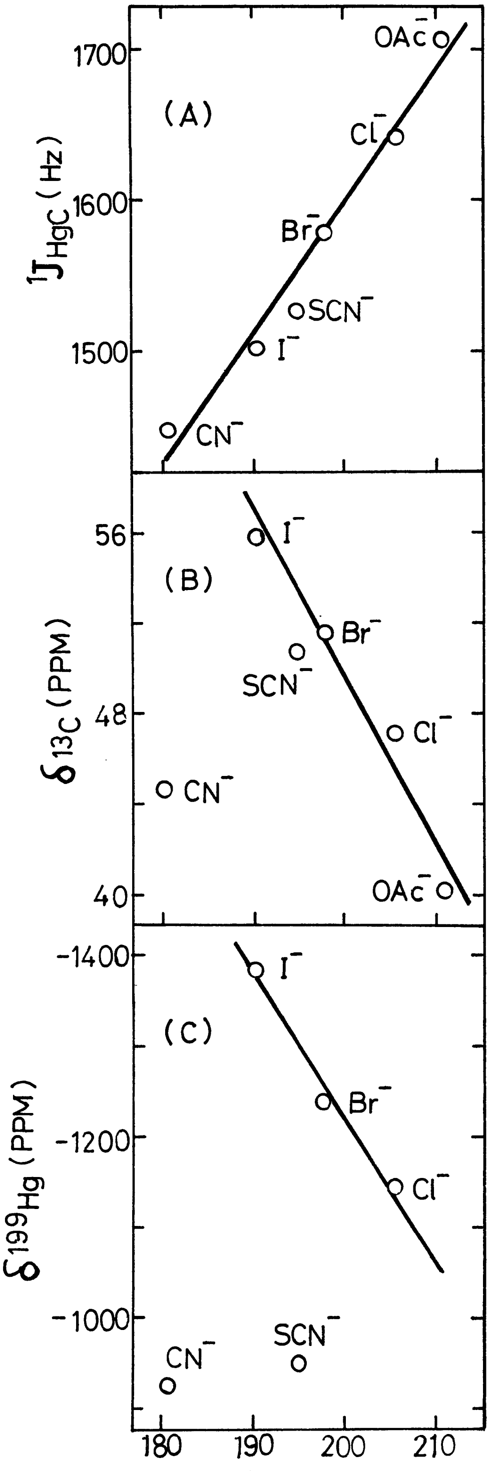

Fig. 1. Correlation of $^{2}J_{HgH}$ with $^{1}J_{HgC}$ (A), $\delta 13_C$ (B), and $\delta 199_{Hg}$ (C) of $(CH_3)_2C(OCH_3)CH_2HgL$.

and SCN ligands concerning $\delta 199_{Hg}$ (Fig. 1 (C)).

As far as the shieldings of heavier nuclei than proton are concerned, the paramagnetic term is a dominant factor and would depend upon the electron densities of the valence orbitals other than s orbitals. The large deviations of the Hg-199 chemical shifts of the CN and SCN ligands from linearity (Fig. 1 (C)) suggest that the interaction between the mercury (p + d) valence orbitals and π-electron of the CN triple bond is very different from the interaction between Hg and the halogen ligands. A similar result has been reported with regard to the tin-119 chemical shifts of ethyltin derivatives,8) where π-bonding is suggested to be important with regard to the unsaturated ligands in contrast with the halogens. The large deviation from linearity regarding the methylene carbon shift of β-methoxyisobutylmercuric cyanide (Fig. 1 (B)) can also be interpreted as due to the influence of the π-bonding property of the CN ligand. As for the SCN mercurial, the small deviation of $\delta 13_{C}$ may reflect the interference of sulfur atom with the effect of the CN triple bond.

In conclusion the coupling constants of $^{1}J_{HgC}$ and $^{2}J_{HgH}$ are a good measure of σ-bonding between mercury and carbon, whereas the strong π-bonding effect of the CN ligand is reflected in the chemical shifts of $\delta 199_{Hg}$ and $\delta 13_{C}$ of the organomercurials. It is worthwhile to mention that the order of the mercury-carbon dissociation energies of CH_3HgL is $Cl^- > Br^- > I^- > CH_3^-$.9) If the dissociation energy for CH_3HgCN is determined, it will be possible to decide the relative importance of σ- and π-bonding effects on the mercury-carbon bond strength.

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