Intramolecular π Coordination in γ-Phenylpropylmercurials

William Kitching,* Gregory M. Drew, and Vincent Alberts

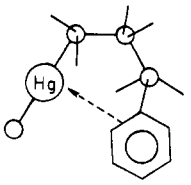
Department of Chemistry, University of Queensland, Brisbane, Australia

Received August 12, 1981

The ^{13}C and ^{199}Hg nuclear magnetic resonance spectra of series of 3-(*p*-substituted-phenyl)-2-methoxypropylmercuric chlorides and 3-(*p*-substituted-phenyl)-2-methyl-2-methoxypropylmercuric chlorides have been obtained. Variations in spectral parameters with the para substituent, solvent, concentration, and temperature are fully in accord with the conclusion that γ-phenylpropylmercuric halides exist (in poorly donor solvents) largely as intramolecular π complexes. Spectral comparisons for *n*-butyl-, 3-phenylpropyl-, and 3-(cyclopropyl)propylmercuric chlorides indicate that the π-donor ability of the 3-cyclopropyl group is insignificant.

Introduction

Some years ago Kiefer and co-workers reported extensive ^1H NMR data for certain 3-aryl-2-methyl-2-methoxypropylmercuric derivatives in which the 3-aryl group was, in the main, a para-substituted phenyl group.[1-3] Variations in the degree of magnetic inequivalence displayed by the methylene protons, and the four-bond ^{199}Hg–CH_3 coupling constant strongly indicated a chelate effect involving the π system of the 3-aryl group. Changing the para substituent from methoxy to trifluoromethyl induced changes explicable in terms of stronger donor action by the *p*-anisyl group. More classical approaches such as temperature, solvent, and concentration changes produced the anticipated variations in the ^1H NMR spectra, and the conformation permitting Hg–arene interaction (A) agreed



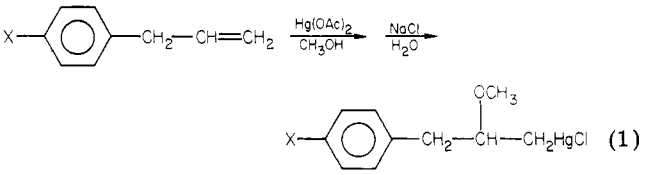
A

with the crystal structure[1] of 3-(*p*-methoxyphenyl)-2-methyl-2-methoxypropylmercuric chloride.

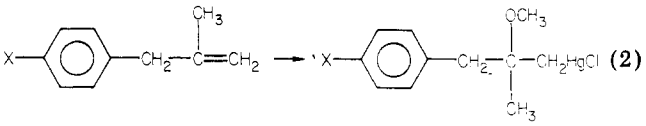
We have reported the ^{13}C and ^{199}Hg NMR spectra of several classes of organomercurials and developed conclusions concerning some of the determinants of ^{13}C–^{199}Hg coupling and ^{199}Hg chemical shifts.[4-8] If γ-phenylpropylmercuric chlorides did indeed possess a clear-cut (1–2 kcal/mol) conformational energy minimum, it appeared that the ^{13}C and ^{199}Hg NMR parameters should follow certain trends if our previous generalizations on these matters were valid. We have, therefore, obtained the ^{13}C and ^{199}Hg NMR spectra of two series of oxymercurials: 3-(*p*-substituted-phenyl)-2-methoxypropylmercuric chlorides and 3-(*p*-substituted-phenyl)-2-methyl-2-methoxypropylmercuric chlorides. The unsubstituted 3-phenylpropylmercuric chloride has also been examined, along with 3-(cyclopropyl)propyl and *n*-butylmercuric chlorides. Effects of para substituents on the spectra, as well as solvent, concentration, and temperature changes, have been evaluated.

Results and Discussion

Compounds. The mercurials I and II were prepared in a standard way by methoxymercuration (mercuric acetate in methanol) followed by treatment with aqueous sodium chloride (eq 1, 2). Some of the mercurials were



I, X = H, OCH_3, CF_3



II, X = H, CH_3, OCH_3, CF_3

crystalline, while others were viscous oils.

3-Phenylpropylmercuric chloride was synthesized from the bromide, which in turn was obtained from the reaction of mercuric bromide and 3-phenylpropylmagnesium bromide. Condensation of cyclopropylcarbinyl bromide with diethyl sodiomalonate followed by hydrolysis and decarboxylation provided 3-(cyclopropyl)propanoic acid which was reduced to the alcohol. Bromination (PBr_3/ether) yielded the bromide which was converted to the bromomercurial via the Grignard reagent in the normal way. The bromomercurial was metathesized with a slight excess of silver acetate, and the acetatomercurial was converted to the chloromercurial which was fully characterized. The constitutions of the mercurials follow from the syntheses, the ^1H, ^{13}C, and ^{199}Hg spectra, and from the analyses of the crystalline derivatives.

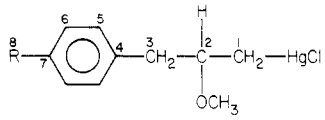
^{13}C Spectra. Examination of series I was conducted initially to establish that significant changes in the vicinal ^{13}C–^{199}Hg coupling occurred, as the substituent and concentration varied. The data are in Table I and confirm variations in $^3J_{^{13}C-^{199}Hg}$ of such a magnitude that further measurements were warranted.

The important aspect of the date in Table I is the variation of the ^{199}Hg coupling to C_3 (*vic* coupling), particularly with substituent. Thus an increase of some 21 Hz is observed when R is changed from OCH_3 to CF_3, with R = H exhibiting an intermediate value. A small decrease (~3 Hz) is also observed when the concentration is reduced from 0.4 M to 0.2 M for R = OCH_3. These changes encouraged examination of series II oxymercurials, the series studied initially (by ^1H NMR) by Kiefer and co-

(1) Kiefer, E. F.; Waters, W. L.; Carlson, D. A. *J. Am. Chem. Soc.* **1968**, *90*, 5127.
(2) Kiefer, E. F.; Gericke, W. *J. Am. Chem. Soc.* **1968**, *90*, 5131.
(3) Kiefer, E. F.; Gericke, W.; Amimoto, S. T. *J. Am. Chem. Soc.* **1968**, *90*, 6246.
(4) Kitching, W.; Praeger, D.; Doddrell, D.; Anet, F. A. L.; Krane, J. *Tetrahedron Lett.* **1975**, 759.
(5) Anet, F. A. L.; Krane, J.; Kitching, W.; Doddrell, D.; Praeger, D. *Tetrahedron Lett.* **1974**, 3255.
(6) Barron, P. F.; Doddrell, D.; Kitching, W. *J. Organomet. Chem.* **1977**, *139*, 369.
(7) Kitching, W.; Drew, G. M.; Adcock, W.; Abeywickrema, A. *J. Org. Chem.* **1981**, *46*, 2252.
(8) Kitching, W.; Drew, G. M. *J. Org. Chem.* **1981**, *46*, 2695.

0276-7333/82/2301-0331$01.25/0 © 1982 American Chemical Society

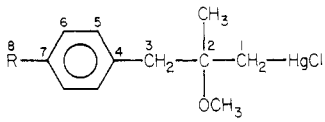
Table I. ^{13}C NMR Data[a] for



R	solvent	carbon number 1	2	3	4	5	6	7	8	OCH_3
H	$CDCl_3$ (0.4 M)	34.87 (1546.7)	78.0	42.0 (73.3)	137.4	129.0	129.7	127.2		56.2
OCH_3	$CDCl_3$ (0.4 M)	34.2	80.0	40.8 (70.3)	129.1	130.6	114.7	159.0	55.4	56.0
	$CDCl_3$ (0.2 M)	34.2 (1551.1)	80.0	40.7 (67.4)	129.1	130.6	114.7	159.1	55.5	56.0
CF_3	$CDCl_3$ (0.4 M)	35.8 (1555.2)	79.8	42.6 (91.6)	141.7	130.0	125.7 [3.7]	129.2 [27.1]	123.6 [271.8]	56.2

[a] Chemical shifts (ppm) relative to internal Me_4Si. Values in parentheses are ^{13}C–^{199}Hg couplings (Hz), and values in brackets are ^{13}C–^{19}F couplings (Hz).

Table II. ^{13}C NMR Data[a,b] for



R	solvent	carbon number 1	2	3	4	5	6	7	8	CH_3	OCH_3
H	$CDCl_3$ (0.4 M)	41.9 (1612.6)	77.8	44.8 (61.5)	137.7	128.7	130.3	127.1		27.1 (198.6)	49.5
	$CDCl_3$-pyridine[c] (0.4 M)	41.0 (1656.6)	77.4	44.7 (73.3)	137.4	128.0	129.8	126.4		26.5 (186.1)	48.9
OCH_3	$CDCl_3$ (0.2 M)	41.4 (1608.9)	78.0	43.8 (54.2)	129.7	131.2	114.6	159.2	55.5	27.0 (208.1)	49.5
	$CDCl_3$ (0.4 M)	41.4 (1611.1)	77.9	43.8 (55.7)	129.6	131.2	114.6	159.2	55.4	27.0 (208.1)	49.5
	$CDCl_3$ (0.6 M)	41.4 (1613.3)	77.9	43.8 (56.4)	129.6	131.2	114.5	159.1	55.4	27.0 (207.4)	49.4
	$CDCl_3$-pyridine[c] (0.4 M)	40.5 (1699.1)	77.4	43.7 (65.9)	129.2	130.7	113.8	158.5	54.7	26.4 (195.6)	48.6
CH_3	$CDCl_3$ (0.4 M)	41.5 (1614.8)	77.8	44.2 (55.7)	137.3	130.2	129.7	134.6	21.1	27.1 (206.6)	49.5
	$CDCl_3$-pyridine[c] (0.4 M)	40.6 (1657.3)	77.3	44.2 (66.9)	136.3	129.7	128.9	134.2	20.5	26.5 (194.2)	48.9
CF_3	$CDCl_3$ (0.4 M)	42.5 (1587.0)	77.8	45.3 (79.1)	141.9	130.7	125.3 [4.4]	129.4 [32.3]	124.1 [271.8]	27.1 (181.7)	49.6
	$CDCl_3$-pyridine[c] (0.4 M)	41.0 (1667.6)	77.3	45.2 (92.3)	141.7 [1.4]	130.2	124.7 [3.6]	127.5 [33.0]	123.7 [271.8]	26.5 (165.6)	48.9

[a] Chemical shifts (ppm) are relative to internal Me_4Si. [b] Values in parentheses are ^{13}C–^{199}Hg couplings (Hz), and values in brackets are ^{13}C–^{19}F couplings (Hz). [c] $CDCl_3$-pyridine refers to 80:20 by volume

workers.[1,2] The full listing of the ^{13}C data for series II is listed in Table II.

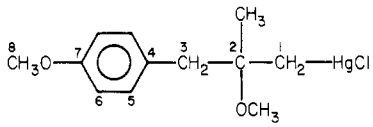
The series II oxymercurials have the advantageous feature that two vicinal ^{199}Hg–^{13}C couplings (to C_3 and CH_3) can be measured. The salient features of the data in Table II are the following: (a) For 0.4 M solutions in $CDCl_3$, the *vic* ^{13}C–^{199}Hg coupling to C_3 is ~55 Hz for donor R groups (OCH_3, CH_3) and increases to 79 Hz for R = CF_3, with R = H exhibiting an intermediate value (61.5 Hz). In contrast, the *vic* coupling to CH_3 is ca. 207 Hz for R = OCH_3, CH_3, 199 Hz for R = H, and 182 Hz for R = CF_3. (b) For 0.4 M solutions, in 80:20 $CDCl_3$:pyridine, a significant increase in all *vic* couplings to C_3 occurs (compared with data for $CDCl_3$ solutions), whereas significant reductions occur in ^3J to CH_3. The variations with R are comparable with the changes observed for $CDCl_3$ solvent. (c) For R = OCH_3, concentration changes from 0.2 to 0.6 M ($CDCl_3$) induce slight increases in ^3J (of C_3) but a marginal decrease in ^3J to CH_3.

We also examined the effect of temperature on the ^{13}C spectra of the *p*-anisyl derivative, and the results are shown in Table III.

The chief feature to emerge from this study is the reduction in ^3J to C_3 (55.7 → 50.6 Hz) with decreasing temperature, but the increase (208 → 223.7 Hz) in ^3J to CH_3.

The large difference in the ^3J values to C_3 and CH_3 in these systems (~50–90 Hz compared with 180–210 Hz) is particularly noteworthy, as are the changes in these couplings with substituent and the less pronounced but significant variations with concentration, solvent, and temperature. We have demonstrated previously that *vic* ^{199}Hg–^{13}C coupling is strongly dihedral-angle dependent, of the Karplus type.[4,5] For example, in alkylmercuric chlorides, couplings of ca. 75 and 275 Hz are associated with dihedral angles of ca. 60° and 180°, respectively, although a β-methoxy group may have a slight effect on these couplings. It is quite clear, then, that in the present series the average dihedral angle between ^{199}Hg and C_3 and

Table III. ^{13}C NMR Data[a,b] for



temp, K	carbon number 1	2	3	4	5	6	7	8	CH_3	OCH_3
303	41.4 (1611.1)	77.9	43.8 (55.7)	129.6	131.2	114.6	159.2	55.4	27.0 (208.1)	49.5
274	41.4 (1615.6)	77.8	43.6 (53.5)	129.6	131.2	114.5	159.1	55.4	27.0 (210.3)	49.5
233	41.2 (1631.7)	77.6	42.6 (50.6)	129.3	131.1	114.2	158.8	55.4	27.0 (223.7)	49.6

[a] Values in parentheses are ^{13}C-^{199}Hg couplings (Hz). Chemical shifts in ppm. [b] 0.4 M in $CDCl_3$.

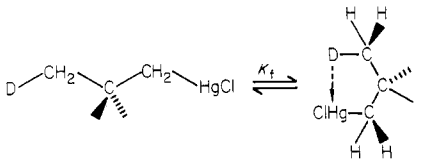
Table IV. ^{199}Hg Chemical Shifts[a] for 2-Methoxy-3-phenylpropylmercuric Chloride

p-$RC_6H_4CH_2CH(OCH_3)CH_2HgCl$, R =	conditions: 0.2 M $CDCl_3$	0.4 M $CDCl_3$	0.4 M (80:20) $CDCl_3$-pyridine	0.3 M (65:35) $CDCl_3$-pyridine
OCH_3	174.0	172.3	177.3	180.6
H		168.1	175.1	178.7
CF_3		157.9	173.5	180.3
p-$RC_6H_4CH_2C(CH_3)(OCH_3)CH_2HgCl$, R =	0.2 M $CDCl_3$	0.4 M $CDCl_3$	0.6 M $CDCl_3$	0.4 M (80:20) $CDCl_3$-pyridine
OCH_3	154.5	154.4	154.2	158.2
CH_3		154.6		157.9
H		149.1		154.5
CF_3		149.1		156.8

[a] Positive values are to lower field. Chemical shifts in ppm.

between ^{199}Hg and CH_3 must be quite different and approach ~60° and 160–170°, respectively. The variations in *vic* couplings with a para substituent cannot be attributed to any direct interaction (of the substituent) with the coupling ^{13}C and ^{199}Hg nuclei as the substituent is simply too remote from them. Rather, the (average) dihedral angle changes (as evidenced by changes in ^3J) must be associated with a change in conformational equilibria, regulated by the donor ability of the aryl group. The responses listed above to the classical tests for intramolecular interaction (concentration, temperature, etc.) favor this conclusion.

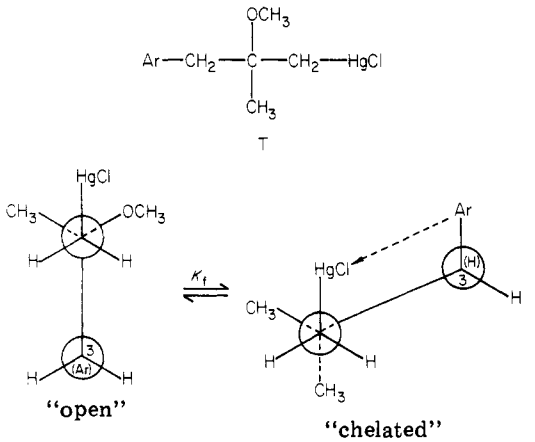
Kiefer and co-workers[1,2] argued that an equilibrium of the form shown in eq 3 was primarily responsible for the spectral variations they observed. K_f should be larger as



(3)

donor ability increased (e.g., electron-donating para substituents) and also at lower concentrations where competition from intermolecular coordination would diminish. On the other hand, addition of sufficient external donor, e.g., a strongly coordinating solvent, would reduce the requirement for the chelate effect and reduce K_f. Variation of the ^{13}C parameters with temperature verifies the existence of a preferred conformation, the nature of which can be reasonably inferred if the "spectral characteristics" of one limiting conformation are available.

To discuss our data (^3J values) in terms of the model above, it is necessary to decide the preferred conformations for both the chelated and open arrangements, so that dihedral angles can be estimated. The favored open and chelated arrangements are shown in eq 4.



(4)

Notice that the dihedral angles between Hg and CH_3 are 180° in the "chelated" form and 60° in the open form, but 60° to C_3 in the chelated form and 180° in the open form. Thus an overwhelming predominance of chelated form should be characterized by ^3J values of ca. 200–230 Hz to CH_3 and ca. 50 Hz to C_3. (These values are adjusted downwards slightly for the suppressing effect of β-methoxy substitution on ^3J.)[4] As K_f is reduced by various changes, $^3J(CH_3)$ should decline and $^3J(C_3)$ increase, given the dihedral angle changes associated with the open ⇌ chelated interconversion.

The ^3J values listed in Table II are in accord with this analysis and vary in the anticipated way with para substituent. Thus K_f should be larger for p-CH_3 and p-OCH_3 and smallest for p-CF_3. At lower concentrations, K_f should be larger and accompanied by a decline in $^3J(C_3)$ but an

Table V. ^{13}C and ^{199}Hg NMR Data[a] for R-$\overset{3}{C}H_2\overset{2}{C}H_2\overset{1}{C}H_2HgCl$ (all 0.4 M in $CDCl_3$)

R	temp, °C	carbon position 1	2	3	other		^{199}Hg shift, ppm
CH_3	room	33.06 (1439.7)	30.49 (85)	27.83 (176.6)	13.47		159.7
CH_3	0	33.2 (1429)	30.5 (85)	27.9 (174.4)	13.5		158.3
C_6H_5	room	30.1 (1488)	29.4 (91.6)	38.7 (134)	140.6 (ipso)		191.7
					128.6 (*o*)		
					128.9 (*m*)		
					126.6 (*p*)		
	0	30.0 (1491)	29.4 (93)	35.4 (131.1)			192.8
	−40	29.9 (1504)	29.4 (95.3)	38.2 (129.2)			193.8
c-C_3H_5	room	32.83 (1442.6)	28.44 (85.7)	39.29 (163.4)	10.28	4.60	161.0
	0	32.92 (1447.8)	28.44 (85.7)	39.29 (164.9)	10.28	4.57	159.5
	−40	33.12 (1462.4)	28.47 (87.2)	39.24 (168.5)	10.25	4.51	156.3

[a] Values in parentheses are ^{13}C–^{199}Hg couplings (Hz). Chemical shifts in ppm.

increase in $^3J(CH_3)$. The effects of lower temperature for the *p*-OCH_3 derivative are confirmatory, with a significant reduction in $^3J(C_3)$ and increase (208 → 223.7 Hz) in $^3J(CH_3)$ as required for increasing K_f. It is very likely that for the *p*-OCH_3 case at 233 K ($^3J_{CH_3}$ = 223 Hz) a limiting value of ^3J is attained, with the chelated conformer essentially exclusive. Assuming the ^3J values for the *p*-OCH_3 case at 233 K are close to the limiting values, then for $\varphi = 60°$, $J \sim 50$ Hz, and for $\varphi = 180°$, $J \sim 230$ Hz. It is then possible to calculate the free energy difference between open and chelated forms as being ca. 1.3 kcal/mol, a value close to the rough estimate of Kiefer.[1] The addition of pyridine (20% by volume) would be expected to quench to a significant degree, intramolecular coordination, and this is confirmed by the increase in $^3J(C_3)$ and decrease in $^3J(CH_3)$ for all cases.

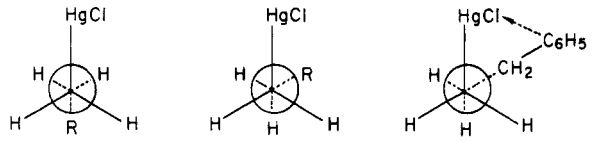
^{199}Hg Spectra. The relative ^{199}Hg shifts for both series of oxymercurials are assembled in Table IV.

For series I, it is clear that the *p*-anisyl compound has the lowest field ^{199}Hg resonance, some 14 ppm removed from that of the *p*-CF_3 derivative. Granted that intramolecular coordination is more important for the *p*-anisyl derivative, it may have been thought that its ^{199}Hg resonance should have been at higher field. However ^{199}Hg is one nucleus, for which *increased* electron density appears to result in *low-field* shifts.[7,8] Thus the order of ^{199}Hg shifts is agreeable with the conclusion of enhanced π coordination in the *p*-anisyl compound. Increasing amounts of the coordinating pyridine cause shifts to lower field (increased electron density at Hg) and a substantial compression in the range of ^{199}Hg shifts from ~14 ppm for 0.4 M $CDCl_3$ solutions to ~2 ppm for the 65:35 $CDCl_3$–pyridine system. This is expected for a much reduced population of the π-coordinated arrangement, and in the limit, the ^{199}Hg shifts for the three derivatives should be almost identical. Changing the concentration from 0.4 M → 0.2 M should increase K_f, with a move to lower field as observed. Considerations of the same type apply to series II, although the range of shifts is smaller. Again the resonance for the *p*-CF_3 compound is to higher field of *p*-OCH_3 (by ~5 ppm). All resonances are affected by pyridine (move to lower field), with the range of shifts (OCH_3, CF_3) being reduced to ~1.4 ppm. The general behavior of the ^{199}Hg shifts is in accord with the conclusion that π coordination is more pronounced for anisyl and increases with dilution and can be quenched by the addition of a superior ligand such as pyridine.

In view of the frequent comparisons between phenyl and cyclopropyl as π-donor groups, we decided to compare the ^{13}C and ^{199}Hg spectral characteristics of *n*-butyl-, 3-phenylpropyl-, and 3-(cyclopropyl)propylmercuric chlorides to determine if the γ-cyclopropyl group could function as a π donor toward -HgCl, as phenyl evidently does.

The ^{13}C and ^{199}Hg data are shown in Table V.

Vicinal ^{199}Hg–^{13}C coupling constants (^3J) have been reported[4] for the compounds RCH_2CH_2HgCl, where R = CH_3, CH_3CH_2, *i*-$(CH_3)_2CH$, and *t*-Bu and ^3J = 190, 183, 212, 227 Hz, respectively. In the (reasonable) absence of any specific interaction with the alkyl (R) groups, the moderately increasing ^3J values may be associated with an increased population of the rotamer A, with dihedral



A B C

angle 180°. For $J \approx 200$ Hz, it may be calculated that the populations of A and B are ca. 60–70% and 40–30%, respectively. If we accept that the steric size of benzyl is no smaller than that of methyl,[9] the quite low value (~130 Hz) of ^3J for the 3-phenylpropylmercurial at first seems anomalous as it corresponds to ~70–75% population of the *gauche* B (R = $CH_2C_6H_5$). However it is in C (B with R = $CH_2C_6H_5$) that the π-donor ability of phenyl towards -HgCl can be exercised. We conclude that in 3-phenylpropylmercuric chloride at room temperature (in $CDCl_3$) the favored conformation is that one stabilized by a Hg–phenyl π interaction. This conclusion is supported by the ^{199}Hg shift (ca. 190 ppm the lowest field position of all observed in this study), some 30 ppm to low field of the signal for the *n*-butyl compound under identical conditions.

Regarding the 3-cyclopropyl compound, there is a clear similarity between its ^{199}Hg shifts (~160 ppm) and *vic* ^{199}Hg–^{13}C couplings (~165 Hz) and those of the *n*-butyl derivative (~160 ppm and ~175 Hz). However, these data are quite different from those (discussed above) for the corresponding phenyl compound and permit the conclusion that π-donor action by the 3-cyclopropyl group is insignificant. This is supported by the trends in the *vic* ^{13}C–^{199}Hg couplings and ^{199}Hg shifts (for this compound) with temperature, as both are in the wrong direction for a favored π interaction. The magnitudes of *vic* ^1H–^{199}Hg coupling constants also indicate a greater population of the *gauche* rotamer (see C) for the phenyl compound than for *n*-butyl or the 3-cyclopropyl derivative. The (average) *vic* $^3J_{^{199}Hg-^1H}$ are 312 (phenyl), 274 (*n*-butyl), and 278 Hz (cyclopropyl), requiring a greater average dihedral angle between HgCl and the C_2 protons, in the phenyl derivative. The essential lack of π-donor action by the 3-cyclopropyl

(9) Whitesides, G. M.; Sevenair, J. P.; Goetz, R. W. *J. Am. Chem. Soc.* **1967**, *89*, 1135.

group toward -HgCl is not surprising when the radial and energy characteristics of the appropriate orbitals are considered. Some of the expected consequences of arene–mercury coordination have been discussed previously.[1,2]

Experimental Section

Compounds. The oxymercurials were synthesized in a standard oxymercuration sequence as described below for the *p*-methoxy derivative:

3-(*p*-Methoxyphenyl)-2-methylpropene (1.23 g, 7.6 mmol) in methanol (~7 mL) was added to mercuric acetate (2.44 g, 7.7 mmol) in methanol (15 mL) and acetic acid (4 drops), and the mixture was stirred for 1 h (no yellow precipitate with aqueous sodium hydroxide). This solution was filtered into an aqueous sodium chloride solution (~0.6 M) to produce the chloromercurial as an oil, which was crystallized from aqueous methanol as fine white crystals (1.74 g, 54%), mp 75.5–76 °C. Anal. Calcd for $C_{12}H_{17}ClHgO_2$: C, 33.56; H, 3.96. Found: C, 33.77; H, 4.07.

3-(*p*-(Trifluoromethyl)phenyl)-2-methyl-2-methoxypropylmercuric chloride was obtained similarly, mp 83–84 °C. Anal. Calcd for $C_{12}H_{14}ClF_3HgO$: C, 30.83; H, 3.00. Found: C, 30.99; H, 3.15.

3-(*p*-Methylphenyl)-2-methyl-2-methoxypropylmercuric chloride had mp 78.9–79 °C. Anal. Calcd for $C_{12}H_{17}ClHgO$: C, 34.86; H, 4.12. Found: C, 34.87; H, 4.31.

The remaining members of the 2-methyl series of oxymercurials and all members of the parent series were viscous oils which could not be crystallized. However, the method of synthesis and ^1H, ^{13}C, and ^{199}Hg NMR spectra confirm the assigned structures.

3-Phenylpropylmercuric chloride was obtained via the Grignard reagent of 3-phenylpropyl bromide and mercuric bromide. Treatment with silver acetate provided a solution of the acetatomercurial which was filtered into aqueous sodium chloride. The resulting chloromercurial was recrystallized from ethanol–hexane, mp 51–52 °C; ^1H NMR (100 MHz; $CDCl_3$) δ 7.4 (5 H, m, phenyl), 2.8 (2 H, t, CH_2(benzylic)), 2.12 (2 H, p, CH_2–CH_2Hg; $J_{^{199}Hg-^1H}$ = 312 Hz), 2.0 (2 H, t (distorted), CH_2Hg, $J_{^{199}Hg-^1H}$ = 200 Hz) (all $J_{^1H-^1H} \approx 7$ Hz). Anal. Calcd for $C_9H_{11}HgCl$: C, 30.41; H, 3.10. Found: C, 30.47; H, 3.19.

***n*-Butylmercuric chloride** was prepared analogously and had mp 126–126.5 °C. Anal. Calcd for C_4H_9HgCl: C, 16.38; H, 3.07. Found: C, 16.47; H, 3.11. The 300-MHz ^1H spectrum ($CDCl_3$) showed resonances at δ 2.11 (t, $J \sim 7$ Hz, CH_2HgCl, $J_{^{199}Hg-^1H}$ = 197 Hz), 1.73 (p, $J \sim 7$ Hz, CH_2–CH_2Hg, $J_{^{199}Hg-^1H}$ = 274 Hz), 1.42 (sextet, $J \sim 7$ Hz, CH_3CH_2), and 0.96 (t, $J \sim 7$ Hz, CH_3).

3-(Cyclopropyl)propylmercuric chloride was obtained by treating the Grignard reagent from 3-(cyclopropyl)propyl bromide (see below) with mercuric bromide, followed by conversion to the acetate and precipitation of the chloride, which was recrystallized from ethanol; mp 78.5–79 °C. Anal. Calcd for $C_6H_{11}HgCl$: C, 22.56; H, 3.45. Found: C, 22.59, H. 3.46. The 300-MHz ^1H NMR spectrum ($CDCl_3$ solvent) exhibited the following: δ 1.31 (q, $J \sim 7$ Hz, c-$C_3H_5CH_2$), 1.86 (p, $J \sim 7$ Hz, CH_2–CH_2; $J_{^{199}Hg-^1H}$ = 278 Hz), 2.10 (t, $J \sim 7$ Hz, CH_2Hg; $J_{^{199}Hg-^1H}$ = 195 Hz), and the cyclopropyl resonances of δ 0.05 (2 H), 0.45 (2 H), and 0.70 (1 H). The ^{13}C and ^{199}Hg NMR shifts are discussed in the text.

3-(Cyclopropyl)propyl bromide was obtained by brominating (phosphorus tribromide in ether) the alcohol. The bromide (bp 59 °C (22 mm)) exhibited ^1H NMR absorptions centered at δ 3.5 (t, CH_2Br) and (1–2.3, *m* 4 H) CH_2–CH_2) and the characteristic cyclopropyl resonances.

NMR Spectra. ^{13}C spectra were obtained for the indicated concentrations and solvents (see text) on a JEOL FX-100 spectrometer at 25.04 MHz. ^{199}Hg spectra were obtained on the same spectrometer modified for multinuclear observation (17.822 MHz), and 10-mm tubes were employed. The ^{199}Hg shifts in Tables IV and V are relative to the highest field data point, and more positive shifts are to lower field. More discussion of the experimental details is presented elsewhere.[7] ^1H spectra were obtained at 100 or 300 MHz for $CDCl_3$ solutions.

Summary

Examination of the ^{13}C and ^{199}Hg NMR spectra of certain 3-(*p*-substituted-phenyl)-2-methoxypropylmercuric chlorides strongly supports the view that in poorly coordinating solvents, these mercurials exist largely as intramolecular π complexes. The study further illustrates the use of ^{13}C–^{199}Hg vicinal coupling constants in conformational analysis and sheds further light on the factors affecting ^{199}Hg shifts.

Acknowledgment. We gratefully acknowledge the support of the Australian Research Grants Committee.

Registry No. I (X = H), 79663-94-8; I (X = OCH_3), 79663-95-9; I (X = CF_3), 79663-96-0; II (X = H), 4175-60-4; II (X = CH_3), 79663-97-1; II (X = OCH_3), 4175-61-5; II (X = CF_3), 21388-54-5; 3-phenylpropylmercuric chloride, 41408-75-7; *n*-butylmercuric chloride, 543-63-5; 3-(cyclopropyl)propylmercuric chloride, 79663-98-2; 3-phenylpropene, 300-57-2; 3-(*p*-methoxyphenyl)propene, 140-67-0; 3-(*p*-trifluoromethylphenyl)propene, 1813-97-4; 3-phenyl-2-methylpropene, 3290-53-7; 3-(*p*-methylphenyl)-2-methylpropene, 40296-92-2; 3-(*p*-methoxyphenyl)-2-methylpropene, 20849-82-5; 3-(*p*-trifluoromethylphenyl)-2-methylpropene, 53482-96-5; 3-phenylpropyl bromide, 637-59-2; 3-(cyclopropyl)propyl bromide, 78300-38-6.