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A PROTON AND CARBON-13 NUCLEAR MAGNETIC RESONANCE STUDY OF NEOPENTYLMERCURY COMPOUNDS

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SUMMARY

Substituent effects on ^{199}Hg–^{1}H and ^{199}Hg–^{13}C spin–spin coupling constants have been studied for neopentylmercury derivatives, $(CH_3)_3CCH_2Hg$–R(or X), where R is covalently bonded Me, Et, t-Bu, neopentyl, and vinyl, and X is easily ionizable CN, Br, Cl, $OCOCH_3$, and ONO_2. Linear relationships exist between the methylene $J(^{13}CH)$ and ^{2}J(HgH), ^{4}J(HgH) and ^{2}J(HgC) and ^{3}J(HgC); but deviations from linearity occur for the chloride, bromide, acetate, and nitrate in the relationships between ^{2}J(HgH) and ^{4}J(HgH), ^{2}J(HgH) and ^{2}J(HgC). These deviations are discussed in terms of hyperconjugative p_π–d_π bonding between the methylene C–H bonds and mercury.

Although proton magnetic resonance (PMR) has often been used for structural[1-9] and bonding[10-13] studies of organomercury compounds, the use of carbon-13 magnetic resonance (CMR) for such studies is as yet unexplored. Mercury–carbon (^{199}Hg, spin 1/2, 16.86% natural abundance) coupling adjunct to mercury–proton coupling can provide useful information regarding the nature of bonding in these compounds. In this paper we report ^{199}Hg–^{1}H and ^{199}Hg–^{13}C coupling constants of model neopentylmercury compounds, $(CH_3)_3CCH_2Hg$–R(or X), and discuss their substituent-induced changes qualitatively in terms of bonding.

The usefulness of empirical correlations between these coupling constants in studying the changes in the bonding of mercury as the substituent changes from covalently bonded R to more ionizable X is demonstrated. The facile inter- and intra-molecular coordination of mercury, particularly when it has partial positive charge as in $RHg^{\delta+}$–$X^{\delta-}$ with nucleophilic ligands[13-16] and arene π systems[12] where mercury uses its $6p$ or $6(p+d)$ orbitals, is well known. In the present study, the coupling constant data of $(CH_3)_3CCH_2HgX$ suggest the involvement of these orbitals through hyperconjugation with the adjacent C–H bonds.

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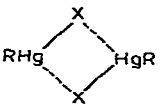
RESULTS

Tables 1 and 3 list the pertinent ^{1}H and ^{13}C data. The spectra of the R series were taken in neat liquids, and those of the X series (solids) in deuterochloroform at $35 \pm 1°$. The ^{1}H spectra of the R compounds were also measured in deuterochloroform, and no change in the mercury–proton coupling constants and proton chemical shifts was noted. But in the X compounds both the mercury–proton coupling constants and proton chemical shifts exhibited concentration dependence, and were measured at 1, 3, and 5 *M* concentrations (Table 2). The mercury–proton coupling constants extrapolated to zero concentration are given in Table 1.

The proton chemical shifts, however, are less concentration dependent than the mercury–proton coupling constants. Actually, in the 1–5 *M* concentration range investigated only the methylene protons shifted slightly ($\leqslant$ 2.4 Hz or 0.04 ppm) upfield with increasing concentration. It may be noted from Table 2 that this shift is in the opposite direction expected from simple ligand inductive effect due to the increased polarization of the $Hg^{\delta+}$–$X^{\delta-}$ bond at higher concentrations (see below). This effect probably is due to the diamagnetic shielding of protons by the Hg–X bond which, like the β proton shielding by C–X in the case of alkyl halides[17], overweighs the ligand inductive effect.

The CMR spectra of RHgX were run at 5 *M* concentrations, except that of neopentylmercuric nitrate which was run at 0.5 *M* because of its low solubility in $CDCl_3$. The ^{13}C chemical shifts were measured against external CH_3I, and were converted to the CS_2 scale by using +214 ppm for the chemical shift of CH_3I from CS_2. The concentration effect on mercury–carbon coupling constants was studied for neopentylmercuric chloride. The directly bonded mercury–carbon coupling was measured 1514, 1506, and 15.2 Hz at 5, 4, and 3 *M* concentrations, respectively. The geminal and vicinal couplings, however, were virtually unchanged in this concentration range.

The increase in the coupling constants of RHgX with concentration is similar to the effect of polar solvents, *e.g.*, acetone-d_6 and dimethyl sulfoxide-d_6 on mercury–proton coupling constants observed previously for neopentylmercuric chloride and bromide[18]. It is probably due to the solvent association with these compounds and, in the present case, to their intermolecular self-association, which results in the increased polarization of the Hg–X bond, thereby increasing the effective nuclear charge (Z_{eff}) of mercury and the fractional *s* character (α^2_{Hg}) of its orbital bonding to carbon. Both mercury–proton[19–21] and mercury–carbon[22] spin–spin couplings are generally conceded to occur through the Fermi contact mechanism to which Z_{eff} and α^2_{Hg} are the major contributors.



(or higher oligomers)

DISCUSSION

All the coupling constants increase roughly with the substituent electronegativity: $ONO_2 > OCOCH_3 > Cl \simeq Br > CN > R$. Electron withdrawal by mercury will

TABLE 1

PMR DATA OF $(CH_3)_3CCH_2Hg$–R(OR X)

Substituent R or X	*δ(CH$_2$)*[a] *(ppm)*	*δ(CH$_3$)*[a] *(ppm)*	*$^2J(HgH)$ (Hz)*	*$^4J(HgH)$ (Hz)*	*Remarks*
CH_3	1.17	0.90	102.0	6.1	CH_3: δ(H), 0.25 ppm; ^2J(HgH), 95.0 Hz
C_2H_5	1.18	0.98	92.0	5.3	C_2H_5: δ[H(CH$_3$)], 1.32 ppm; ^3J(HgH), 129.0 Hz
$C(CH_3)_3$	1.12	0.98	93.0	5.4	$C(CH_3)_3$: δ(H), 1.27; ^3J(HgH), 108.0 Hz
$CH_2C(CH_3)_3$	1.16	1.01	94.0	5.5	
$CH{=}CH_2$	1.36	1.00	109.0	6.3	$CH{=}CH_2$: $J(HH_{trans})$, 20.0 Hz; $J(HH_{cis})$, 14.0 Hz; $J(HH_{gem})$, 4.5 Hz
CN	1.97	1.05	173.0	10.6	
Cl	2.20	1.08	193.0	13.4	
Br	2.30	1.10	192.0	13.9	
$OCOCH_3$	2.18	1.08	204.0	13.9	$OCOCH_3$: δ(H), 2.06 ppm (singlet)
ONO_2[b]	2.48	1.11	222.0	16.5	

[a] From internal TMS. [b]Data at 0.5 *M* concentration in $CDCl_3$.

TABLE 2

CONCENTRATION DEPENDENCE OF ^{1}H CHEMICAL SHIFTS AND ^{199}Hg–^{1}H COUPLING CONSTANTS OF $(CH_3)_3CCH_2HgX$

Substituent X	*δ(CH$_2$) (ppm)*			*$^2J(HgH)$ (Hz)*			*$^4J(HgH)$ (Hz)*		
	5 M	*3 M*	*1 M*	*5 M*	*3 M*	*1 M*	*5 M*	*3 M*	*1 M*
CN	1.94	1.95	1.97	179.5	177.0	174.0	11.0	10.8	10.7
Cl	2.18	2.19	2.20	202.5	199.0	194.5	14.2	13.9	13.6
Br	2.28	2.29	2.30	200.0	197.0	193.5	14.4	14.2	14.0
$OCOCH_3$	2.14	2.16	2.18	210.0	208.0	205.0	14.3	14.1	14.0

TABLE 3

^{13}CMR DATA OF $(\overset{3}{C}H_3)_3\overset{2}{C}\overset{1}{C}H_2Hg$–R(OR X)

Substituent R or X	*^{13}C Chemical shifts (ppm)*[a]			*^{199}Hg–^{13}C coupling constants (Hz)*		
	C(1)	*C(2)*	*C(3)*	*HgC(1)*	*HgC(2)*	*HgC(3)*
CH_3	130.2	159.4	157.5	690	29.5	71.5
$CH_2C(CH_3)_3$	129.6	158.9	157.0	684	29.0	71.0
$\overset{4}{C}H{=}\overset{5}{C}H_2$[b]	137.0	159.0	157.1	820	31.0	75.0
CN	145.0	159.5	158.0	1404	51.0	120.0
Cl	140.0	159.3	158.5	1514	70.0	149.0
Br	136.2	158.9	158.4		69.5	148.0
$OCOCH_3$[c]	147.5	159.7	158.8		71.0	150.0
ONO_2	145.8	160.0	159.5		85.0	170.0

[a] Upfield from external CS_2. [b] δ(C(4)), 14 ppm; J(HgC(4)), 934 Hz. δ(C(5)), 59.4 ppm; J(HgC(5)), 38 Hz.
[c] Methyl carbon appeared at 168.4 ppm.

TABLE 4

^{13}C–H COUPLING CONSTANT DATA OF $(CH_3)_3CCH_2Hg$-R(OR X)

Substituent R or X	*J[^{13}CH(CH$_2$)] (Hz)*				*% s character CH$_2$*	*J[^{13}CH(CH$_3$)] (Hz)*
CH_3^{a}	126.5 (neat)				25.3	124.0
$CH_2C(CH_3)_3$	126.0 (neat)				25.2	124.0
CH=CH_2	127.5 (neat)				25.5	125.0
	5 *M*	3 *M*	1 *M*	0 *M* (*extrapolated*)		
CN	135.0	134.5	134.0	133.8	26.8	126.0
Cl	138.0	137.0	136.0	135.0	27.0	126.0
Br	139.0	137.5	136.0	135.5	27.1	126.0
$OCOCH_3$	139.0	138.0	137.0	137.0	27.3	126.0
ONO_2				138.0^b	27.6	126.5^b

^{a} $J[^{13}CH(CH_3)] = 129.8$ Hz. ^{b} Measured at 0.5 *M* concn. in $CDCl_3$.

increase with the polarization of the mercury–ligand bond and consequently, according to Bent's isovalent model[23] that "*s* character tends to concentrate in orbitals that are directed toward more electropositive groups", the *s* character of the methylene carbon orbitals involved in the C–H and C–C bonds will increase. The changes in the hybridization of the C–H bonds can be accurately estimated from the ^{13}C–H coupling constants by the method of Juan and Gutowsky[24]: % *s* character $= J(^{13}C\text{–}H)$ Hz/5. Pertinent data are given in Table 4. The *s* character of the methylene C–H bonds increases from 25.2 % in dineopentylmercury to 27.6 % (9.1 % increase) in neo-

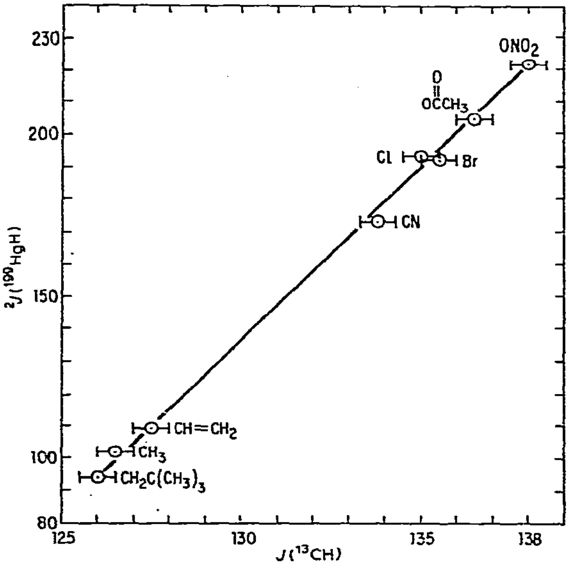


Fig. 1. Plot of $J(^{13}CH)$ *vs.* $^2J(^{199}HgH)$ of $(CH_3)_3CCH_2Hg$-R(or X).

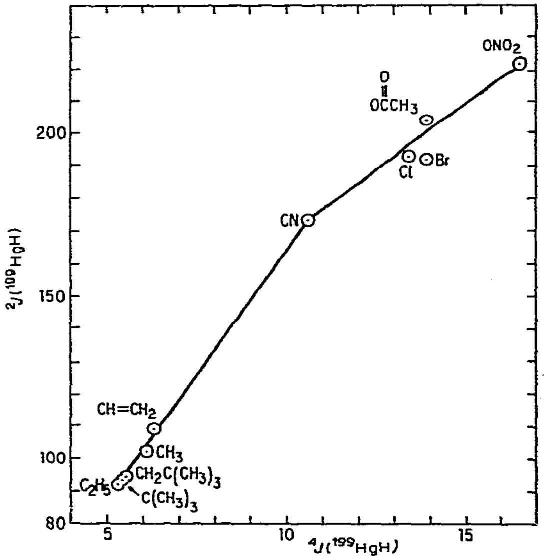
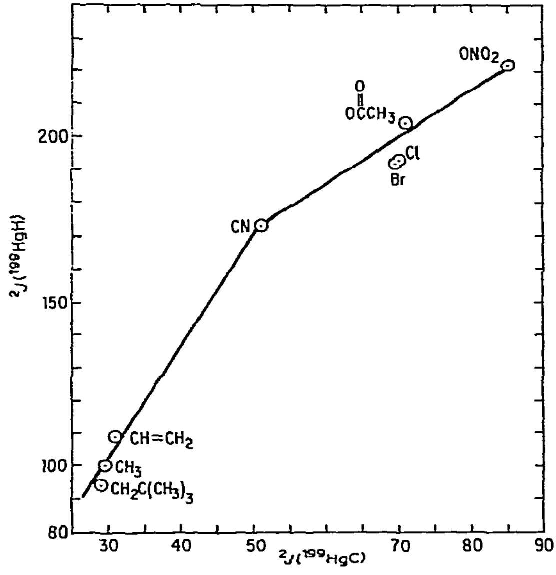


Fig. 2. Plot of $^2J(^{199}HgH)$ *vs.* $^4J(^{199}HgH)$ of $(CH_3)_3CCH_2Hg$-R(or X).



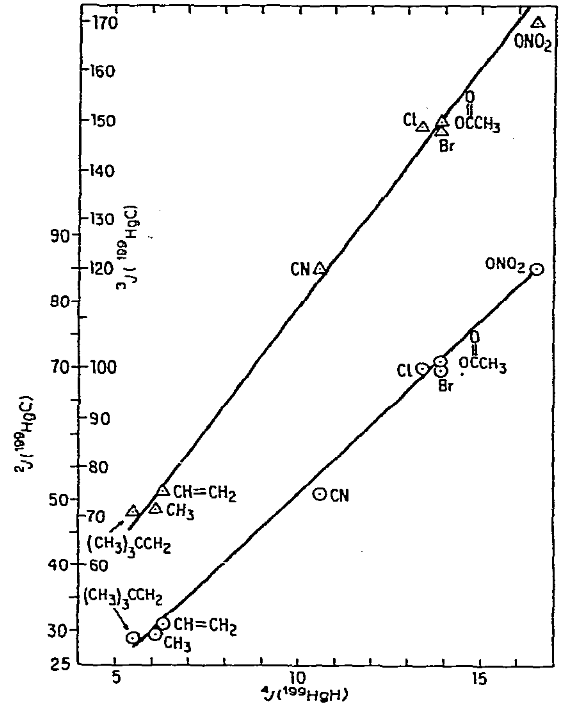


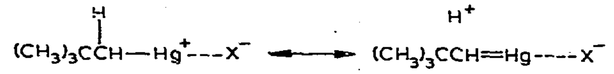
Fig. 3. Plot of $^2J(^{199}HgH)$ vs. $^2J(^{199}HgC)$ of $(CH_3)_3CCH_2Hg$-R(or X).

Fig. 4. Plots of $^4J(^{199}HgH)$ vs. $^2J(^{199}HgC)$ (⊙) and $^3J(^{199}HgC)$ (△) of $(CH_3)_3CCH_2Hg$-R(or X).

pentylmercuric nitrate. Consequently, the HgCH angle decreases resulting in the increase of the geminal mercury–proton coupling. It is interesting to note that the dependence of geminal HgCH coupling on the hybridization of C–H is linear (Fig. 1).

The changes in the hybridization of the C–C bond will be reflected in the coupling constants down the neopentyl chain (^2J(HgC), ^3J(HgC) and ^4J(HgH)). Of interest in this context are the relative changes in these coupling constants with the substituents. For example, Fig. 2 shows the relationship between geminal and four-bond mercury–proton coupling constants. While the R groups and the cyanide lie on a straight-line, deviations occur for the more ionizable chloride, bromide, acetate, and nitrate indicating a lower ^2J(HgH)/^4J(HgH) ratio in the X series (excluding CN) than in the R series. A similar relationship is observed between ^2J(HgH) and ^2J(HgC) (Fig. 3), again the same groups deviating from linearity. But excellent linear correlations exist between ^4J(HgH) and ^2J(HgC) and ^3J(HgC) (Fig. 4) suggesting that these coupling constants are affected rather proportionately by the hybridizational changes of the methylene carbon orbital in the C–C bond.

The deviations of the chloride, bromide, acetate and nitrate in Fig. 2 and 3 are interpreted in terms of the change in the ratio of the *s* character of the methylene carbon orbitals involved in the C–H and C–C bonds. In other words, this ratio is lower in the X series than in the R compounds and the cyanide. This imbalance in the distribution of the *s* character is rationalized in terms of p_π–d_π hyperconjugation between the methylene C–H bonds and the mercury atom:



$$(CH_3)_3C\overset{H}{\overset{|}{C}}H{-}Hg^{+}{-}{-}{-}X^{-} \longleftrightarrow (CH_3)_3C\overset{H^{+}}{C}H{=}Hg{-}{-}{-}{-}X^{-}$$

The effect of this bonding, because of the methylene carbon undergoing $sp^3 \rightarrow sp^2$ hybridizational change, will be such as to relatively lower the *s* character in the carbon orbitals of the C–H bonds and simultaneously increase it in the C–C bond.

The relationship between ^2J(HgC) and ^3J(HgC) (Fig. 5) is reasonably linear

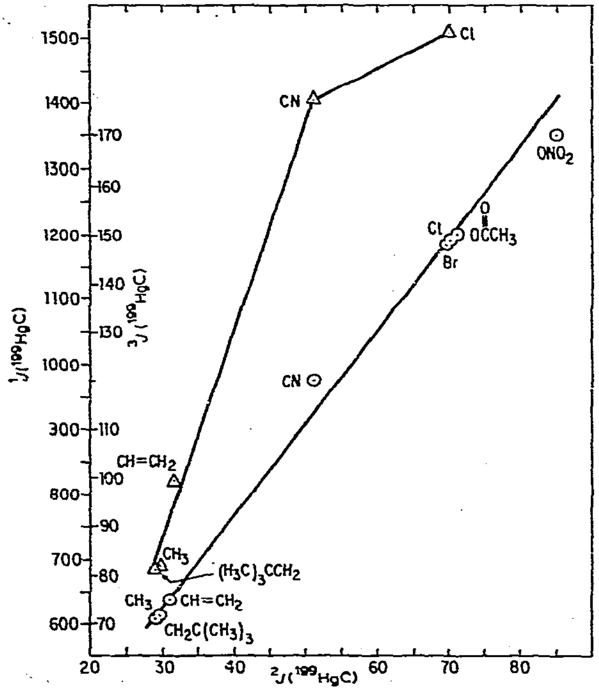


Fig. 5. Plots of $^2J(^{199}HgC)$ vs. ^3J(119HgC) (⊙) and $^1J(^{199}HgC)$ (△) of $(CH_3)_3CCH_2Hg$-R(or X).

despite the fact that they are supposed to have opposite signs[25]. However, a deviation in the relationship between ^1J(HgC) and ^2J(HgC) is indicated for the chloride, the only ionizable group for which the one-bond mercury–carbon coupling could be determined accurately. The ^1J(HgC) values for the other X compounds particularly the acetate and the nitrate could not be measured because of the poor satellite signal-to-noise ratio. The deviation of the chloride may be the result of the negative contribution to the directly bonded HgC coupling by the σ–π interaction of the incipient hyperconjugative double bond between carbon and mercury.

The dual behavior of the cyanide group

The behavior of the cyanide group is quite interesting because it exhibited the character of a typical ionizable ligand in the concentration studies, but seems to act more like an R group in the relationships of Fig. 2 and Fig. 3. In other words, as in the R series, the aforementioned hyperconjugation does not occur in neopentylmercuric cyanide. This border-line behavior of the cyanide apparently is due to the low polarizability of the Hg–CN bond, which is understandable in terms of the strong overlap between the 2*sp* orbital of the CN carbon and the 6*sp* orbital of mercury.

The R-like behavior of CN is also apparent from the ^{13}C data. For example, Weigert and Roberts[22,25] have correlated geminal mercury–carbon coupling to the corresponding mercury–proton coupling through the relationship:

$$^2J(\mathrm{HgC}) = 0.3\ ^2J(\mathrm{HgH}) \tag{1}$$

originally derived by Karabatsos[26] to correlate carbon–proton coupling with proton–proton coupling and later extended by Smith[27] to two-bond metal–proton coupling. Using eqn. 1, we have calculated the geminal mercury–carbon coupling constants from the corresponding mercury–proton data. The results are compared with the observed values in Table 5. The agreement is quite good for the R groups and the cyanide, but not for the chloride, bromide, acetate, and nitrate.

TABLE 5

COMPARISON OF THE CALCULATED AND OBSERVED GEMINAL MERCURY–CARBON COUPLING CONSTANTS OF $(CH_3)_3CCH_2Hg$–R(OR X)

Substituent R or X	$^2J(HgH)$ *(Hz)*	$^2J(HgC)$ *(Hz)*	
		Found	*Calcd.*
CH_3	102	29.5	30.6
$CH_2C(CH_3)_3$	94.0	29.0	28.2
$CH{=}CH_2$	109.0	31.0	32.7
CN	173.0	51.0	51.9
Cl	193.0	70.0	57.9 (77.7)[a]
Br	192.0	69.5	57.6 (76.8)[a]
$OCOCH_3$	204.0	71.0	61.2 (81.6)[a]
ONO_2	222.0	85.0	66.6 (88.8)[a]

[a] Values calculated from $^2J(\mathrm{HgC}) = 0.4\ ^2J(\mathrm{HgH})$ are given in parentheses.

The observed ^2J(HgC) values for the chloride, bromide, acetate, and nitrate are higher than the calculated probably because of the inherently lower ^2J(HgH) for these compounds. It is interesting to note, however, that their observed ^2J(HgC) values are lower than the ones calculated by using the proportionality constant = 0.4 in eqn. 1, a condition applicable to π systems[28]; thus indicating some sort of π bonding in these compounds, which is consistent with the above proposed hyperconjugation. In the case of the nitrate, the calculated 88.8 Hz for ^2J(HgC) from $^2J(\mathrm{HgC}) = 0.4\ ^2J(\mathrm{HgH})$ almost approaches the observed value of 85.0 Hz, suggesting a strong hyperconjugative $C(p_\pi)$–$Hg(d_\pi)$ bonding in this compound.

EXPERIMENTAL SECTION

General

Preparation and reactions of Grignard reagents were carried out under an atmosphere of prepurified nitrogen. The physical properties and analytical data of all the new compounds prepared during this study are given in Table 6. All melting

TABLE 6

PHYSICAL PROPERTIES AND ANALYTICAL DATA OF $(CH_3)_3CCH_2Hg{-}R$(OR X)

Substituent R or X	*B.p. (°C/mm) or m.p. (°C)*	n_D^{25}	*Yield (%)*	*Formula*	*Analysis. Found (calcd.) (%)*	
					C	*H*
CH_3	32.5/4.7	1.4880	91.2	$C_6H_{14}Hg$	25.47 (25.12)	4.95 (4.89)
C_2H_5	51–53/3.9	1.4985	75.0	$C_7H_{16}Hg$	27.68 (27.97)	5.52 (5.30)
$C(CH_3)_3$	51–52/1.7	1.4925	76.0	$C_9H_{20}Hg$	33.30 (32.90)	6.05 (6.09)
$CH{=}CH_2$	32/1.5	1.5085	73.5	$C_7H_{14}Hg$	28.60 (28.12)	4.47 (4.69)
CN	97–98		91.0	$C_6H_{11}NHg$	24.30 (24.20)	3.75 (3.70)
$OCOCH_3$	67[a]		100	$C_7H_{14}O_2Hg$	25.67 (25.41)	4.23 (4.23)
ONO_2	77–78[b]		90.0	$C_5H_{11}NO_3Hg$	18.12 (18.00)	3.30 (3.00)

[a] Sublimed at 50°/0.05 mm. [b] Sublimed at 100°/0.025 mm.

points, obtained on a Thomas–Hoover melting apparatus, and boiling points are uncorrected.

NMR spectra

Proton spectra were run on a Varian Associates A-60 spectrometer. The ^{13}C spectra were obtained on either Varian Associates HA-100 or Bruker HFX-90 spectrometer with wide-band decoupling from ^1H. The HA-100 operates at 25.1 MHz and the Bruker HFX-90 at 22.67 MHz. In all cases signal averaging was used (100–200 scans) to improve the signal-to-noise ratio.

Compounds

Neopentylmercuric chloride[29] and bromide[30] and dineopentylmercury[31] are known compounds, and were prepared by the reaction of neopentylmagnesium chloride, prepared in tetrahydrofuran, with $HgCl_2$ and $HgBr_2$. The chloride and bromide were purified by vacuum sublimation at 100° before further use.

$(CH_3)_3CCH_2HgR$

To a suspension of 6.142 g (0.02 mole) of neopentylmercuric chloride in 50 ml of anhydrous ether was added dropwise with stirring 0.03 mole of an appropriate Grignard solution in 10–50 ml of ether. After the addition of the Grignard was complete, the reaction mixture was stirred for 5 min and then decomposed with 50 ml of water. The ether layer was separated and dried over anhydrous sodium sulfate. Ether was removed by distillation. The remaining liquid was distilled under reduced pressure.

Vinylneopentylmercury was prepared by the same procedure, except that the addition of vinylmagnesium chloride (10 ml of 1.5 *M* solution in tetrahydrofuran) to a stirred suspension of neopentylmercuric bromide (7.03 g, 0.02 mole) instead of chloride in 50 ml of anhydrous ether was carried out at −20 to −30°.

$(CH_3)_3CCH_2HgX$

To a solution of neopentylmercuric chloride (3.07 g, 0.01 mole) in acetonitrile was added a solution of equimolar amount of an appropriate silver salt in 50–100 ml of acetonitrile. The mixture was stirred for 30 min and then filtered to remove insoluble silver chloride. Removal of acetonitrile from the filtrate *in vacuo* gave the desired neopentylmercuric salt as white solid. Analytical samples were generally prepared by vacuum sublimation.

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