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# METAL–SILICON BONDED COMPOUNDS

## XVIII *. A $^{199}$HG FT NMR STUDY OF SOME SILYLMERCURY DERIVATIVES AND SELECTED ORGANOMERCURY COMPOUNDS

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## Summary

The $^{199}$Hg NMR spectra were determined for a series of silylmercury derivatives of the form Hg(SiRR′R″)$_2$ by Fourier transform techniques. A linear correlation between the chemical shift, $\delta(^{199}\text{Hg})$, and the sum of the orbital electronegativities on silicon is reported for symmetric species. The chemical shifts are also linearly dependent on the lowest energy UV absorption maximum for these derivatives. These observations are discussed in terms of the current theories dealing with chemical shifts of heavy nuclei. The $^{199}$Hg–$^{29}$Si coupling constants have been tabulated with evidence presented indicating that these are dominated by the Fermi contact interaction. It has been found that these are dependent on the same energy terms as observed for the chemical shift. Limited studies are reported on solvent, concentration, and temperature dependence of the $\delta(^{199}\text{Hg})$ for these derivatives.

## Introduction

We have a continuing interest in the preparation, reactivity, structures, and spectroscopic properties of silylmetallic compounds, and, as a result, have sought a variety of means to characterize these derivatives. One such approach is to investigate directly one of the nuclei which is involved in the silicon–metal bond. For the silylmercurials, either $^{199}$Hg or $^{29}$Si may serve as an NMR probe and should provide essentially the same type of information. In this study, we have chosen the $^{199}$Hg nucleus as the probe for exploration of the substituent effects on the $^{199}$Hg chemical shift, $\delta(^{199}\text{Hg})$, and on the $^{199}$Hg–$^{29}$Si coupling constants of a wide variety of silylmercury derivatives. These studies have been extended to include a few new organomercury compounds and other complexes of mercury in order to provide

*(Continued on p. 41)*

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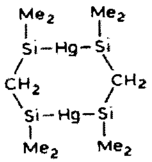
* For part XVII see ref. 1.

TABLE 1

$^{199}$Hg CHEMICAL SHIFTS AND COUPLING CONSTANTS FOR SILYLMERCURY DERIVATIVES

| Compound | Solvent[a] | Concenration[b] | δ (ppm)[c] | $^1J(^{199}Hg-^{29}Si)$ | $^1K$[d] | Σ χ[e,f] | UV absorption max. $cm^{-1} \times 10^4$ | |
|---|---|---|---|---|---|---|---|---|
| | | | | | | | $C_6H_{12}$ | THF |
| 1 $Li_2Hg(SiMe_2Ph)_4$ | Cyclopentane | 0.045 | 1681[h] | | | | | |
| 2 $LiHg(SiMe_3)_3$ | DME | 0.54 | 1137[h] | | | | | |
| 3 $[(Me_3Si)_3Si]_2Hg$ | $C_6D_6/C_6F_6$ 80/20 | 0.087 | 987[i] | 432 | 1015 | 6.39[e] | 2.564 | 2.564 |
| 4 $(Et_3Si)_2Hg$ | $C_6D_6/C_6F_6$ 80/20 | 10.1 | 849[h] | 955 | 2245 | 6.69[e] | | |
| 5 $(Et_3Si)_2Hg$[j] | – | – | 807 | 957 | | | | |
| 6  | Cyclopentane<br>9% $C_6F_6$ vol. | 0.07 | 740[h] | 958 | 2252 | | 2.299 | |
| 7 $(EtMe_2Si)_2Hg$ | $C_6D_6/C_6F_6$ 80/20 | 0.99 | 596[h] | 972 | 2285 | 7.19[e] | | |
| 8 $(n\text{-}PrMe_2Si)_2Hg$ | $C_6D_6/C_6F_6$ 80/20 | 0.58 | 574[h] | 968 | 2275 | 7.23[e] | | |
| 9 $[CH_2{=}CH(CH_2)_4SiMe_2]_2Hg$ | $C_6D_6/C_6F_6$ 80/20 | 0.89 | 572[i] | 975 | 2292 | 7.23[e] | | |
| 10 $[CH_2{=}CH(CH_2)_3SiMe_2]_2Hg$ | $C_6D_6/C_6F_6$ 80/20 | 1.32 | 567[i] | 976 | 2294 | 7.26[e] | | |
| 11 $(Me_3Si)_2Hg$ | $C_6D_6/C_6F_6$ 80/20 | 0.94 | 499[i] | 981 | 2306 | 7.44[f] | 2.564 | |
| 12 $(Me_3SiCH_2SiMe_2)_2Hg$ | $C_6D_6/C_6F_6$ 80/20 | 0.66 | 493[i] | 972 | 2285 | 7.41[e] | | |
| 13 $(CH_2{=}CHCH_2SiMe_2)_2Hg$ | $C_6D_6/C_6F_6$ 80/20 | 0.69 | 491 | 1050 | 2468 | 7.41[e] | | |
| 14 $[CH_2{=}CH(CH_2)_2SiMe_2]_2Hg$ | $C_6D_6/C_6F_6$ 80/20 | 0.34 | 460[c] | 1033 | 2428 | 7.48[e] | | |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| **15** $(Me_3Si)_2Hg$[k] | – | – | 456 | 990 | | | | |
| **16** $(PhCH_2SiMe_2)_2Hg$ | $C_6D_6/C_6F_6$<br>47/33 | 0.44 | 454 | 1111 | 2611 | | | |
| **17** $(Me_3Si)_2Hg$[j] | DME<br>$C_6D_6/C_6F_6$<br>9.7/2.4 | 0.47 | 411 | 1031 | 2423 | 7.65[e] | | 2.703 |
| **18** $(CH_2{=}CHSiMe_2)_2Hg$ | $C_6D_6/C_6F_6$<br>80/20 | 0.53 | 376 | 1031 | 2423 | | | |
| **19** $(Me_2PhSi)_2Hg$ | $C_6D_6/C_6F_6$<br>80/20 | 0.27 | 360 | 1037 | 2437 | 7.71[f] | 2.584 | |
| **20** $Me_3SiHg(SiH_3)$[k] | Benzene | | 327 | | | | | |
| **21** $(MePh_2Si)_2$ | $C_6D_6/C_6F_6$<br>80/20 | 0.27 | 294 | 1111 | 2611 | 7.98[f] | 2.635 | |
| **22** $(H_3Si)_2Hg$[k] | Benzene | | 196 | | | | | |
| **23** $Me_3SiHgGeH_3$[k] | Benzene | | 159 | | | | | |
| **24** $Me_3SiHgMe$[j] | | | | 1367 | | | | |
| **25** $Me_3SiHg$-n-Pr[i] | | | 56 | 1234 | | | | |
| **26** $Me_3SiHg$-n-Bu[j] | | | 49 | 1226 | | | | |
| **27** $Me_3SiHgCH_2Cl$[j] | | | | 1137 | | | | |
| **28** $Me_2Hg$ | $C_6F_6$ 10%<br>$HgMe_2$ 90% | – | 0 | | | | | |
| **29** $Me_2Hg$[l] | $C_6H_6$<br>10/90 | – | −11 | | | | | |
| **30** $(Me_3SiCH_2)_2Hg$ | $C_6D_6/C_6F_6$<br>33/67 | 3.63 | −58 | | | | | |
| **31** $(H_3Ge)_2Hg$ | | | −147 | | | | | |
| **32** $Me_3SiHg$-i-Pr[j] | – | – | −159 | 1084.9 | | | | |
| **33** $(ClSiMe_2)_2Hg$ | $C_6D_6/C_6F_6$ | 0.20 | −160 | 1392 | 3272 | 8.51[f] | 2.809 | |
| **34** $Me_3SiHgEt$[j] | – | – | −199 | 1213 | | | | |
| **35** $Me_3SiHg$-t-Bu[j] | – | – | −299 | 995.6 | | | | |
| **36** $(ClSiMe_2)_2Hg$ | DME<br>$C_6D_6/C_6F_6$<br>10/20 | 0.21 | −315[h] | 1516 | 3657 | 8.51[f] | | 3.125 |
| **37** $(MeCl_2Si)_2Hg$ | $C_6D_6/C_6F_6$<br>80/20 | 0.17 | −658[g] | 2020 | 4748 | 9.58[f] | 3.023 | |
| **38** $(MeCl_2Si)_2Hg$ | DME<br>$C_6D_6/C_6F_6$<br>15/4 | 0.23 | −843[g] | 2395 | 5629 | | | |

TABLE 1 (continued)

| Compound | Solvent[a] | Concenration[b] | $\delta$ (ppm)[c] | $^{1}J(^{199}Hg-^{29}Si)$ | $^{1}K$[d] | $\Sigma\chi$ | UV absorption max. $cm^{-1} \times 10^4$ | |
|---|---|---|---|---|---|---|---|---|
| | | | | | | | $C_6H_{12}$ | THF |
| **39** $(Cl_3Si)_2Hg$ | $C_6D_6/C_6F_6$ 80/20 | saturated | −1001[g] | | | 10.65[f] | 3.226 | |
| **40** $(Cl_3Si)_2Hg$ | DME<br>$C_6D_6/C_6F_6$ 12.4/2 | 0.74 | −1177[g] | 3864 | 9082 | | | 3.704 |
| **41** $Hg(NO_3)_2$[m] | 70% $HNO_3$ | 4.0 | −2532 | | | | | |
| **42** $HgI_2$ | DMSO | 1.2 | −3127 | | | | | |
| **43** $K_2HgI_4$[n] | $H_2O$ | saturated | −3451 | | | | | |

[a] Solvent compositions are reported in terms of weight % unless otherwise noted. [b] Concentrations are given in molality unless otherwise specified. [c] The standard taken as zero is 90/10 $HgMe_2/C_6F_6$ which resonates at a frequency of 17.913266 in a field in which hexafluorobenzene lock signal is at 93.653631 MHz. Chemical shifts taken from the literature have been adjusted to correspond to this work. In most cases heat dimethylmercury was a common reference, but in some cases another compound or the actural resonance frequency was used. Due to these adjustments, the error in chemical shifts may exceed ±1 ppm for literature values. [d] The reduced coupling constant is given by $^{1}K_{AB} = \frac{2\pi\gamma_A\gamma_B}{h}$. [e] Empirical values obtained from the least-squares fit from Fig. 2. [f] Electronegativity values were obtained from ref. 15. [g] The values given are for the lowest energy band given in ref. 3. [h] Sample tamperature 30°C. [i] Sample temperature 26°C. [j] Ref. 16. [k] Ref. 17. [l] A.P. Tupciauskas, N.M. Sergeyev, Yu. A. Ustynyuk, and A.N. Kashin, J. Magn. Resonance, 7 (1972) 124. [m] G.E. Maciel and M. Borzo, J. Magn. Resonance, 10 (1973) 388. [n] S.S. Dharmatti, C.R. Kanekar, and S.C. Mathur, Proc. 2nd. U.N. Intern. Conf. Peaceful Uses Atomic Energy, 28 (1958) 644.

additional data on which to base some empirical correlations between $^{199}$Hg chemical shifts and various substituent effects and spectral properties.

Although it is too early in the development of the theory dealing with chemical shifts of heavy metal nuclei to make quantitative predictions concerning these parameters, a qualitative discussion of the factors which determine chemical shifts is presented. These terms are then used in conjunction with our experimental observations to provide insight into those factors which are of major importance in the determination of $\delta(^{199}Hg)$.

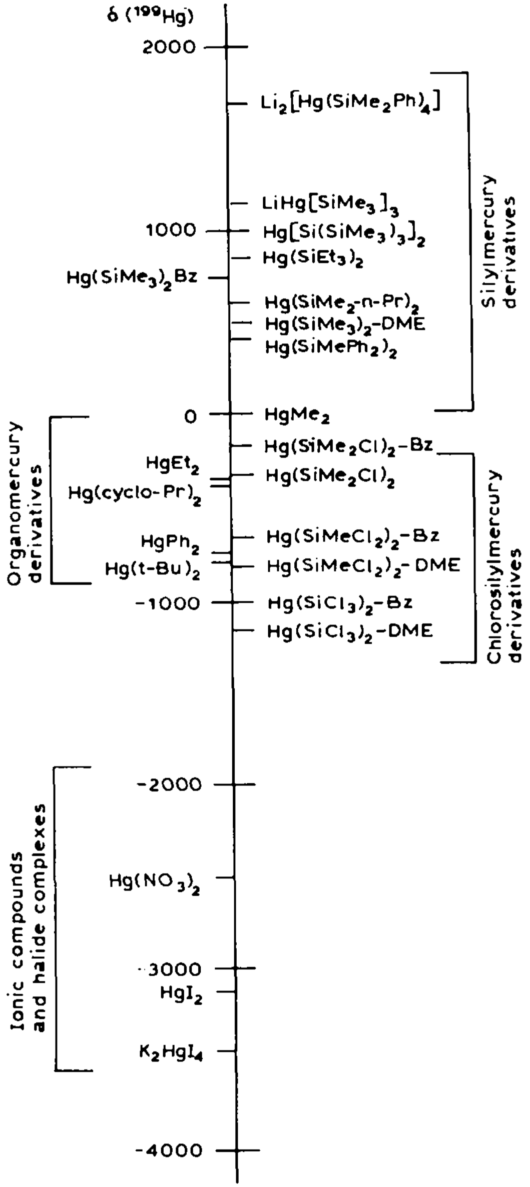


Fig. 1. The chemical shift range for $^{199}$Hg in a variety of organomercury, silylmercury and simple mercury derivatives.

## Experimental

*General experimental techniques.* All manipulations were carried out using standard techniques. The silylmercury derivatives are generally sensitive to oxygen and water and, therefore, were handled in Schlenk ware, in an inert atmosphere box, or by use of high vacuum techniques. All solvents were dried over molecular sieve, $LiAlH_4$, or Na metal as appropriate.

*Compound preparation:* All organomercury compounds were prepared from the appropriate Grignard reagent and $HgCl_2$ or $HgBr_2$ by standard techniques. The silylmercury compounds had been previously prepared and analyzed by mass spectrocopy [2] as well as by other techniques [3–6].

*NMR studies.* NMR samples were prepared in the inert atmosphere box or on the vacuum system. In all cases the samples were degassed by several freeze-pump-thaw cycles and then sealed. Samples were covered with aluminum foil and stored in a freezer to minimize decomposition. Routine $^1H$ NMR spectra were run on a Varian A-60A or on a T-60A spectrometer. Some $^1H$ NMR spectra and all $^{199}Hg$ NMR spectra were run on a JEOL JNM-4H-100 equipped with a PFT 100 pulse Fourier transform package and an EC 100 data system. The $^1H$ mode used a fixed frequency deuterium lock at 15.28730 MHz. The $^{199}Hg$ spectra were obtained on 8 mm samples using an internal fixed frequency fluorine lock at 93.653631 MHz giving a frequency of 17.913266 MHz for 90% $HgMe_2/10\%C_6F_6$. Samples with potential $^1H$–$^{199}Hg$ coupling were proton noise decoupled with a 2.5 kHz 30 watt signal. The sample temperature was maintained at approximately 30°C by a variable temperature controller. Complete concentration, solvent, and run conditions are given in Table 1.

TABLE 2

$^{199}Hg$ CHEMICAL SHIFT TRENDS FOR HALIDE AND PSEUDO HALIDE DERIVATIVES

| $K_2HgX_4$ [a] | $HgX_2$ [a] | $Cp(CO)_3WHgX$ [b] | MeHgX [c] | $\delta(^{199}Hg)$ (ppm) |
|---|---|---|---|---|
| | | | $Me_2Hg$ [d] | −93 |
| | | $[Cp(CO)_3W]_2Hg$ | | −348 |
| $K_2Hg(CN)_4$ | | | | −502 |
| | | | MeHgCl [e] | −728 |
| | | | MeHgBr [e] | −842 |
| | | $Cp(CO)_3WHgSCN$ | | −924 |
| | | $Cp(CO)_3WHgCl$ | | −997 |
| | $Hg(CN)_2$ | | | −1021 |
| | | | MeHgI [e] | −1045 |
| | | $Cp(CO)_3WHgBr$ | | −1200 |
| $K_2HgCl_4$ | | | | −1331 |
| | | $Cp(CO)_3WHgI$ | | −1529 |
| | $HgCl_2$ | | | −1541 |
| $K_2HgBr_4$ | | | | −1921 |
| | $HgBr_2$ | | | −2231 |
| | $HgI_2$ | | | −3127 |
| $K_2HgI_4$ | | | | −3451 |

[a] $H_2O$ sat. [b] In DMSO-$d_6$, taken from M.J. Albright and J.P. Oliver, J. Organomet. Chem., 92 (1979) 99. [c] Pyridine solvent. [d] W.G. Schneider and A.D. Buckingham, Discuss. Farraday Soc., 34 (1961) 837. [e] G.E. Maciel and M. Borzo, J. Magn. Resonance, 10 (1973) 388.

## Results and discussion

The chemical shifts for a wide variety of both inorganic and organometallic mercury derivatives have been obtained during the past several years [7]. We have now added an extensive group of compounds containing Si–Hg bonds to this list so that the total chemical shift range reported is from $Li_2Hg(SiMe_2Ph)_4$ at 1681 ppm, the least shielded, to $K_2HgI_4$ at −3451 ppm, the most shielded [8]. These are depicted graphically in Fig. 1 which serves as a quick guide to the chemical shifts of mercury as a function of its substituents with the precise values listed in Table 1. Although it is not possible to provide a detailed explanation for the chemical shifts of heavy metals based on theory at this time, it should be possible to develop some understanding of those factors which are of most importance and to develop some empirical correlations which should prove both useful from the practical standpoint, and, ultimately aid in our understanding of the factors which govern the observed changes in chemical shift of the mercury nucleus.

The factors which should be taken into account in a discussion of chemical shift may be most readily understood by examination of the formalism presented by Saika and Slichter [9]. They separated the screening contributions into three terms:

$$\sigma = \sigma_{\text{diamagnetic}} + \sigma_{\text{paramagnetic}} + \sigma_{\text{other}} \qquad (1)$$

The diamagnetic term * is small (usually less than 10 ppm) relative to the observed chemical shift changes for mercury and will be neglected [8]. The term which is designated "other" has contributions from several sources which may be of importance in the systems under consideration. There is an intra-atomic contribution arising from magnetic anisotropy and a solvent interaction. Both terms may contribute to the chemical shift variations but are difficult to evaluate. The solvent effect will be discussed as it applies to the silylmercury derivatives, but other contributions will be neglected.

The remaining term, $\sigma_{\text{paramagnetic}}$, dominates the chemical shift of heavy nuclei. This term arises from the nonspherical distribution of electron density in the vicinity of the nucleus, with the contributions to it altered as a function of the interaction between the ground state and excited states. The equation formulated for this term by Karplus and Pople [10] is given by:

$$\sigma_{para} = \frac{-e^2h^2}{2m^2c^2} \langle r^{-3} \rangle_{2p} (\Delta E_{\text{av}})^{-1} \Sigma Q_{\text{AB}} \qquad (2)$$

where the three parameters $r^{-3}$, $\Delta E_{\text{av}}$ and $Q_{\text{AB}}$ are of interest to us. The first of these is the mean value of $r^{-3}$ where $r$ is the distance between the nucleus and the $2p$ electrons and may be evaluated from the expression:

$$\langle r^{-3} \rangle_{2p} = \frac{1}{3}\left(\frac{Z_{2p}}{2a_0}\right)^3 \qquad (3)$$

The dependence on the cube of the effective nuclear charge indicates the high degree

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* The $\sigma_d$ term is dependent on states with no angular momentum, and as pointed out by a referee, the Hg atom makes extensive use of the $\sigma s$ orbitals in bonding. This may cause the $\sigma_d$ term to be larger, however, it is still unlikely to exceed 50 or 100 ppm and, thus, represents only a small contribution to the total chemical shift range for the mercury derivatives.

of dependence of the paramagnetic term on charge distribution with an increase in electron density leading to increased shielding or to a decrease in frequency at constant field.

The second variable, $\Delta E_{av}$, is an approximation for the actual electronic excitation energies, $\Delta E_{i\text{-}j}$ [11]. If the mean excitation energies can be assumed to be constant, then the relative chemical shifts may be calculated on the basis of changes in the other variables. For a series of hydrocarbons, it has been shown that $\Delta E_{av}$ decreases as the energy of the maximum absorption decreases [12], and this approximation may be extended to these systems. A decrease in $\Delta E_{av}$ would decrease the shielding by increasing the absolute magnitude of $\sigma_{para}$.

The last variable, $\Sigma\ Q_{AB}$, is the sum of the $2p$ atomic orbital coefficients from the molecular orbitals. However, along with the average excitation energy approximation, the summation is done over Q. It is comprised of the elements of the bond order matrix for the atomic orbitals which represents the molecular orbitals. This summation reflects changes in the orbital angular momentum. Qualitatively, an increase in bond order would cause a decrease in the shielding. With this qualitative estimate of the way these factors will effect the chemical shift in hand, we are now in a position to examine various series of compounds where we have some control over the individual terms.

Data for four homologous series, $K_2HgX_4$, $HgX_2$, MeHgX, and $Cp(CO)_3WHgX$ have been collected in Table 2. In each of these series, the halide substitution should have similar effects on the chemical shifts providing that the halide substitution dominates the observed changes. This is observed with the increase in shielding in the order Cl < Br < I in all cases.

This order is inconsistent with dominance of the $\Delta E$ term since the spectrochemi-

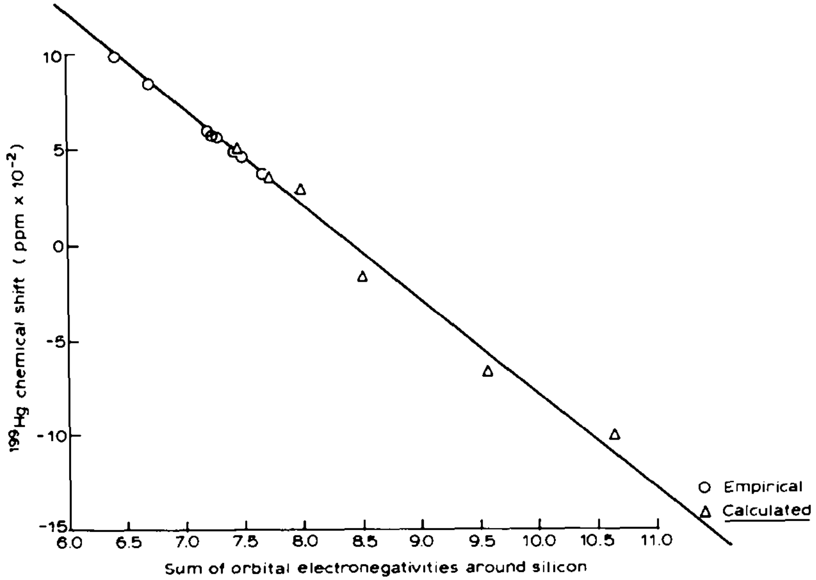

Fig. 2. A least squares fit of the sums of orbital electronegativities vs. $^{199}$Hg chemical shifts. Data used for the least squares fit are for samples **11**, **19**, **21**, **33**, **37**, and **39** listed in Table 1. The empirical values are for samples **3**, **4**, **7**, **8**, **9**, **10**, **12**, **13**, **14**, and **18** in Table 1.

TABLE 3

RELATIVE CHEMICAL SHIFT DIVIDED BY THE NUMBER OF HYDROGENS $\beta$ TO THE MERCURY FOR SOME ORGANOMERCURY COMPOUNDS[a]

| Compound | $\delta_{rel}/\beta$-H's (ppm)[b] | $\delta_{rel}$ (ppm) | $\delta$ (ppm)[c] |
|---|---|---|---|
| $Me_2Hg$[c] | - | 0 | −11 |
| $Bu_2Hg$[c] | 51.25 | 205 | −216 |
| $(C_6H_{13})_2Hg$[d] | 51.5 | 206 | −217 |
| $(C_6H_{11})_2Hg$[d] | 54.5 | 218 | −229 |
| n-$Pr_2Hg$[e] | 60.0 | 240 | −251 |
| $(PhCH_2CH_2)_2Hg$[f] | 60.5 | 242 | −253 |
| $Et_2Hg$[g] | 47.17 | 283 | −294 |
| $Et_2Hg$(neat)[e] | 55.0 | 330 | −341 |
| (1,1-$Me_2$-cyclo-Pr)$_2$Hg[h] | 83.5 | 334 | −345 |
| cyclo-$Pr_2Hg$[h] | 48.75 | 390 | −401 |
| i-$Pr_2Hg$[i] | 49.58 | 595 | −606 |
| $(CH_2{=}CH)_2Hg$[c] | 162.00 | 648 | −643 |
| $(PhCH_2)_2Hg$[c] | - | 700 | −711 |
| $Ph_2Hg$[c] | 185.5 | 742 | −753 |
| t-$Bu_2Hg$[j] | 46.0 | 828 | −839 |

[a] Based on an assumption postulated in ref. 14 which indicates a constant value of 56 ppm/$\beta$-H's is expected for dialkylmercury compounds. [b] Chemical shift relative to $Me_2Hg$ divided by the total number of $\beta$-hydrogens. [c] A.P. Tupčiauskas, N.M. Sergeyev, Yu. A. Ustynyuk, and A.N. Kashin, J. Magn. Resonance, 7 (1972) 124. [d] Molal concentration $(C_6H_{13})_2Hg$, 1.92; $(C_6H_{11})_2Hg$, 1.89; solvent 50/50 $C_6D_6/C_6F_6$. [e] Ref. 14. [f] G.E. Maciel and M. Borzo, J. Magn. Resonance, 10 (1973) 388. [g] 2.49 molal, solvent 80/20 $C_6D_6/C_6F_6$. [h] P.A. Scherr, Ph.D. Dissertation, Wayne State University, Detroit, Michigan, 1970. [i] 3.65 molal, solvent 48/52 $C_6D_6/C_6F_6$. [j] 0.76 molal solvent 60/40 $C_6D_6/C_6F_6$.

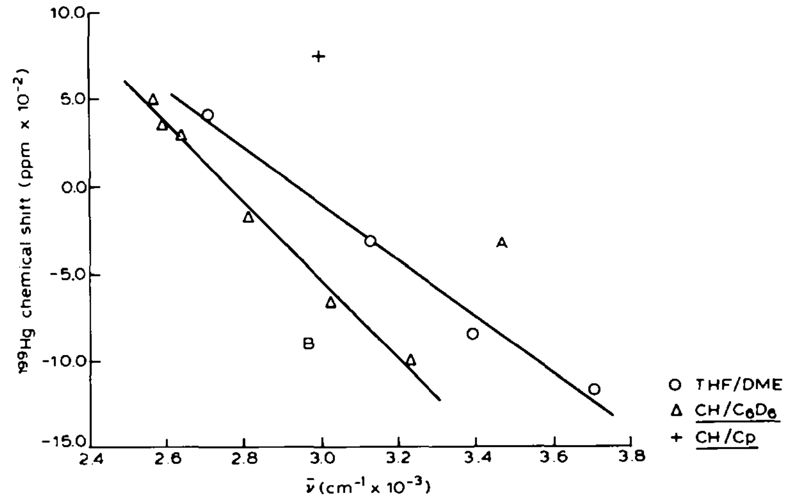

Fig. 3. A least squares fit of $^{199}$Hg chemical shifts vs. the lowest observed UV absorption of the silylmercury derivative. Data used for the least-squares fit are for samples **17**, **36**, **38**, and **40** for A (ether solvent) and **11**, **19**, **21**, **33**, **37** and **39** for B (hydrocarbon solvent) taken for Table 1. + Is for the cyclic compound, **6**.

TABLE 4

CONCENTRATION DEPENDENCE STUDY OF THE $^{199}$Hg CHEMICAL SHIFT OF $[(CH_3)_3SiCH_2]_2Hg$

| Concentration[a] (molal) | δ[b] (MHz) | Relative δ | |
|---|---|---|---|
| | | Hz | ppm |
| 0.349 | 17.909855 | −101 | 5.64 |
| 0.719 | 17.909879 | −77 | 4.30 |
| 0.983 | 17.909889 | −67 | 3.74 |
| 1.274 | 17.909907 | −49 | 2.73 |
| 1.67 | 17.909925 | −31 | 1.73 |
| 2.49 | 17.909956 | 0 | 0 |

[a] In 80/20 $C_6D_6/C_6F_6$ by weight. [b] Internal $C_6F_6$ lock at 26°C.

cal series (which should reflect $\Delta E$) is in the order I < Br < Cl < CN and similarly one may expect that the bond order increase in the series Cl < Br < I [13]. Again, this order would lead to the opposite ordering. The remaining factor is the variation in the electron density on mercury which would be anticipated to increase. The decreasing in ionic character of the Hg–X bond which follows the order Hg–Cl > Hg–Br > Hg–I and appears to provide the dominant effect leading to the increase in shielding observed. A similar ordering has been observed for the MeHgX species, where again the dominant term must be the increase of electron density on the Hg atom.

Although many of the data on $^{199}$Hg chemical shifts are organomercury derivatives, no significant correlations have been obtained. The total range observed for these derivatives is approximately 1200 ppm with that for the saturated alkyls extending over 600 ppm. It is clear that increasing chain length and branch tend to increase the shielding of the $^{199}$Hg nucleus. The only correlation which has been made is that between the number of $\beta$-H atoms and chemical shift by Dessy [14] which when extended to 10 compounds, Table 3, gives a value of 52.5 ppm/$\beta$-hydrogen which includes within $\pm 7.5$ ppm associated with solvent, etc. and represents a reasonable correlation considering the simplicity of the approach and the magni-

TABLE 5

TEMPERATURE DEPENDENCE STUDY OF THE $^{199}$Hg CHEMICAL SHIFT OF $[(CH_3)_3SiCH_2]_2Hg$

| Temperature (°C) | δ[a] (MHz) | $\Delta T$ (°C) | Relative δ | |
|---|---|---|---|---|
| | | | Hz | ppm |
| 26 | 17.909956 | 0 | 0 | 0 |
| 27 | 17.909958 | 1 | 2 | 0.11 |
| 31 | 17.909962 | 5 | 6 | 0.34 |
| 36 | 17.909967 | 10 | 11 | 0.61 |
| 42 | 17.909970 | 16 | 14 | 0.78 |
| 51 | 17.909976 | 25 | 20 | 1.12 |
| 57 | 17.909979 | 31 | 23 | 1.28 |

[a] 2.49 molal in 80/20 $C_6D_6/C_6F_6$ by weight, internal $C_6F_6$ lock.

tude of the chemical shifts involved. The unsaturated and aromatic derivatives are still more shielded, but no attempt has been made to account for these chemical shift changes.

Turning now to the silylmercury derivatives, which represent the main focus of the paper, we see in Table 1 that the chemical shift for this series of compounds is very broad encompassing nearly 3000 ppm from the least shielded complex reported, $Li_2Hg(SiMe_3)_4$, to quite highly shielded species such as $(Cl_3Si)_2Hg$. The compounds listed show a wide range of substitution on silicon and, thus, should permit us to isolate various factors which may influence the chemical shifts as a function of the substituent.

One of the simplest approaches to take is to examine the variation of $\delta(^{199}Hg)$ as a function of the electronegativity [15] of the substituent groups on silicon for the symmetrically substituted compounds. These data are provided in Table 1 along with the chemical shifts and are plotted in Fig. 2. The chemical shift values used were obtained under the same conditions and yielded a least squares fit with a standard deviation of 0.174. The trend shown is for increasing shielding with increasing electronegativity of the substituents. This indicates that the dominant effect is not the dependence on charge which would yield the opposite trend as observed in the halide series, but must arise either from the change in bond order or an increase in $\Delta E_{av}$. There is no convenient way to measure bond order in these systems, but the optical spectra have been obtained previously [3]. The low energy transitions primarily involve mercury orbitals which are perturbed by the substituent. The energies for the lowest lying bands are given in Table 1. The data for the chemical shifts obtained in DME solvent are plotted in Fig. 3 vs. the absorption maxima obtained in THF solutions for a series of derivatives. The least squares fit of

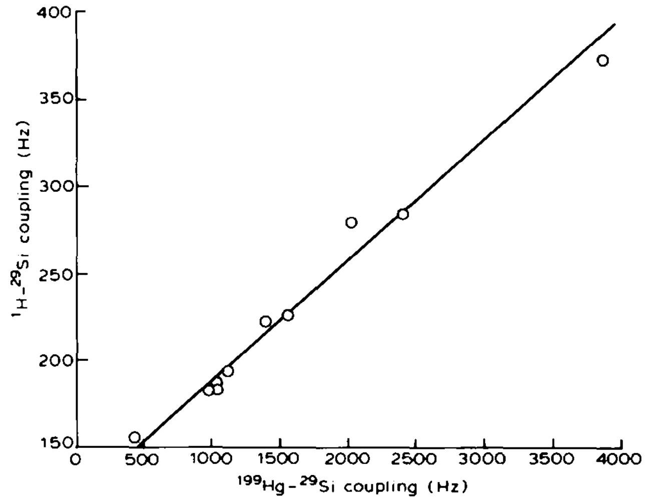

Fig. 4. A plot of the $^1J(^1H\text{-}^{29}Si)$ vs. $^1J(^{199}Hg)$ for a series of HSiRR′R″ and $Hg(SiR'R'')_2$ derivatives. The data plotted are for compounds **11**, **17**, **3**, **33**, **36**, **37**, **38**, **40**, **19**, and **21** from Table 1. The Si–H coupling constants are 184 Hz(**11**), 222.3 Hz(**4**), 279.5 Hz(**37**), 188 Hz(**19**), and 194 Hz(**11**) taken from M.A. Jensen, J. Organomet. Chem., 11 (1968) 423; for sample **3** the $^1H\text{–}^{29}Si$; coupling constant used for 155 Hz taken from H. Burger and W. Kelean, ibid., 18 (1969) 299. The remaining values for samples **36**, 226 Hz, **38**, 284 Hz, and **40**, 372 Hz were obtained in the present work (DME solvent).

these data gives a line with a standard deviation of 0.0463. The data obtained in less strongly coordinating solvents (data from Table 1) are plotted in Fig. 3 and give a line displaced from that obtained in the ether solvents with a standard deviation of 0.0231. The value for the cyclic mercury derivative is shown on the figure but was not included in the fit because it is known to be non-linear [5], and this change in geometry would alter the orbital energies and cause it to fall off the correlation line as indicated.

These observations which shows that there is a linear relationship between $\delta(^{199}Hg)$ and the UV transitions and that this relationship is maintained on changing from polar to non-polar solvents with large changes occurring both for $\delta(^{199}Hg)$ and for the UV transitions strongly supports the dominance of the $\Delta E_{av}$ term on $\delta(^{199}Hg)$ for this series of compounds.

Examination of the limited data reported from other groups, which are given in Table 1, indicates that the same general trends may be observed for unsymmetrically substituted derivatives [16,17], but other factors also must play a role making any quantitative predictions meaningless. It should even be noted that the symmetrical compound, $(H_3Si)_2Hg$, appears to give anomalous results [17]. Finally, there are significant concentration, temperature, and solvent dependences observed for the chemical shifts and even for the coupling constants. Limited data for the changes in the chemical shifts as a function of concentration and of temperature are presented in Table 4 and 5, respectively.

Turning our attention to the Si–Hg coupling, we again find a very wide range of values dependent upon the substituents and on the solvent. A plot of the one bond coupling constants, $^1J(^{199}Hg-^{29}Si)$ for a number of symmetrically substituted silylmercury derivatives vs. the one bond $^1H-^{29}Si$ coupling constants, $^1J(^1H-^{29}Si)$, for the parent silanes yields a linear relationship, shown in Fig. 4, between these coupling constants. This indicates that the factors governing the magnitudes of these

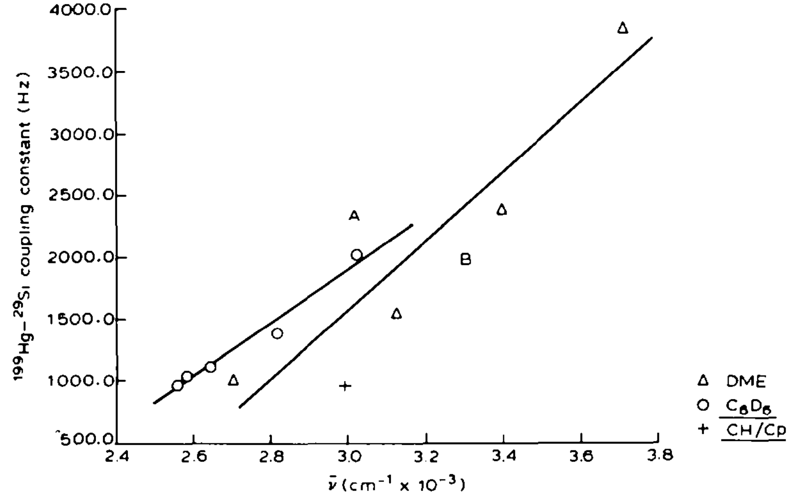

Fig. 5. A plot of $^1J(^{199}Hg-^{29}Si)$ coupling constants vs. the maximum of the lowest energy UV absorption band of the symmetrical silylmercury derivatives. The data used for the least-squares fit are for samples **11**, **19**, **21**, **33**, and **37** for A (hydrocarbon solvent) and **1**, **17**, **36**, **38**, and **40** and B (DME solvent). + Taken from Table 1 is for the cyclic compound, **6**.

two coupling constants are related and supports the suggestion that Si–Hg coupling is dominated by the Fermi contact interaction since it has been established [18] that the $^{1}H-^{29}Si$ coupling is governed by this term.

Several other correlations have been attempted in an effort to provide a convenient means of predicting the $^{29}Si-^{199}Hg$ coupling constants and/or chemical shift. In Fig. 5A a plot of $^{1}J(^{199}Hg-^{29}Si)$ vs. the observed electronic transitions for several symmetrical silylmercury species in hydrocarbon solvent shows a linear relationship with the transition energy, a similar plot (Fig. 5B) for several of the derivatives in DME solvent shows the same trend, but the least squares fit is very poor ($\sigma = 362$) indicating other contributions are important in coordinating solvents.

The conclusion reached is that the coupling constants measured for a series of symmetrically substituted silylmercury derivatives obtained under the same conditions have a linear dependence on the lowest energy electronic transition observed in the molecules. This is consistent with the formalism used to describe the coupling interactions which have been developed [19] and occurs even though there are many factors which contribute to the magnitude of the coupling constants such as bond angle and hybridization of the bonding orbitals used by mercury; thus, the deviation observed for the cyclic derivative $\overline{HgSi(Me_2)CH_2Si(Me_2)HgSiCH_2Si}(Me_2)$ is expected because of the deviation of the Si–Hg–Si unit from linearity.

Finally Fig. 6 shows a plot of the observed one bond $^{29}Si-^{199}Hg$ coupling constant vs. the $^{199}Hg$ chemical shift for a wide variety of symmetrically substituted compounds and includes data obtained under a wide variety of conditions and in different solvent systems. The figure shows a smooth trend between these parameters with the only exception observed for $[(Me_3Si)_3Si]_2Hg$ (★) which has an extremely small value for its $^{199}Hg-^{29}Si$ coupling constant. Attempts to find this type of correlation for the unsymmetrically substituted compounds given in Table 1 shows that none exists for the limited number of samples available.

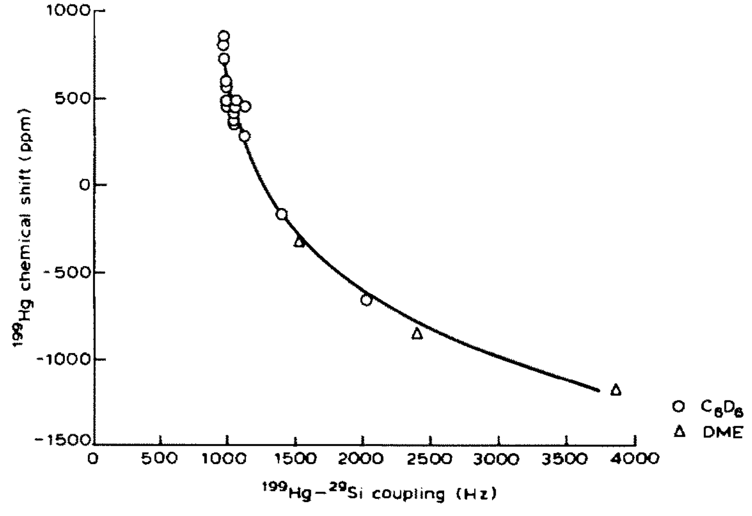

Fig. 6. An empirical plot of $^{1}J(^{199}Hg-^{29}Si)$ vs. the $^{199}Hg$ chemical shift for the symmetrical silylmercury derivatives given in Table 1. ★ Is for compound 3, $[(Me_3Si)_3Si]_2Hg$.

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