ties with pure (fluorene)Cr(CO)$_3$ left remaining. Solutions containing K$^+$(fluorenyl)Mo(CO)$_3^-$ were prepared as follows. Equimolar quantities of fluorenylpotassium and tris(acetonitrile)molybdenum tricarbonyl were placed in a 100-ml roundbottom flask under nitrogen. Fifty milliliters of freshly distilled dioxane (from Na) was placed in the flask. The mixture was then refluxed under nitrogen for 22 hr. After allowing the mixture to cool, it was filtered to remove unreacted starting materials. The amber yellow filtrate was used for the nmr spectrum discussed above.

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A Hydrogen-1 Nuclear Magnetic Resonance Study of Unsymmetrical Mercury Compounds from Bis(trimethylsilyl)mercury and Diorganomercurials

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In equilibrium systems containing two mercury compounds (A_2Hg, B_2Hg) the unsymmetrical species (AHgB) is usually the major product of the reaction

$$A_2Hg + B_2Hg \rightleftarrows AHgB \qquad (1)$$

particularly if A and B are of different electronegativity.[1,2] The situation is less clear when one of the substituents is a triorganosilyl group.

Bis(trimethylsilyl)mercury and dimethylmercury have been reported not to give the unsymmetrical compound $(CH_3)_3SiHgCH_3$ at room temperature.[3] Vyazankin, *et al.*, have reported that $(C_2H_5)_3SiHgC_2H_5$ slowly symmetrizes, although the compound is stable enough to be distilled under vacuum.[4] These reports imply that the symmetrical compounds are favored in diorganomercury–bis(triorganosilyl)mercury systems. However, Marano and MacDiarmid have reported low yields of $Cl_3SiHgC_2H_5$ from diethylmercury and bis(trichlorosilyl)mercury.[5]

To investigate the apparently anomolous behavior of these systems, the reactions of bis(trimethylsilyl)mercury with diorganomercury species were followed by pmr spectroscopy.

Experimental Section

Organomercury compounds either were commercial products or were prepared by standard methods. Bis(trimethylsilyl)mercury was made by Eaborn's method[6] and was sublimed before use. All manipulations involving silylmercury compounds were performed on a vacuum line or under a nitrogen or argon atmosphere dried by sodium–potassium alloy. Solvents were dried over alkali metal and stored on the vacuum line. Solvents used for the reactions are those indicated in Table I.

TABLE I

NMR DATA FOR TRIMETHYLSILYLMERCURY AND METHYLMERCURY SPECIES

	$(CH_3)_3SiHgR$		CH_3HgR
R	τ	$J_{^{199}Hg-Si-C-^1H}$, Hz	$J_{^{199}Hg-C-^1H}$, Hz
Trimethylsilyl	9.80^a	40.8^a	76.8^a
Methyl	9.86^a	53.5^a	$102.5^{d,e}$
Phenyl	9.79^b	55.4^b	$108.5^{d,e}$
Vinyl	9.83^a	54.2^a	$107.0^{d,e}$
Cyclopropyl	9.89^b	52.4^b	$103.5^{d,e}$
1-Propynal	9.82^b	70.6^b	148^b
Bis(trimethylsilyl)amido	9.73^b	79.2^b	157.2^b
Benzyl	9.87^b	55.0^b	107.2^b
Pentachlorophenyl	9.83^c	72.2^c	$\ldots^f$

[a] In cyclopentane. [b] In 1,2-dimethoxyethane. [c] In benzene. [d] In Freon 11. [e] H. D. Visser, Ph.D. Thesis, Wayne State University, 1969. [f] Not measured.

Samples were prepared by placing the diorganomercurial and the bis(trimethylsilyl)mercury in an nmr tube, adding solvent from the vacuum line, and sealing off the tube under vacuum.

The appearance of unsymmetrical species could be easily observed by pmr. Significant quantities of the mixed species could be observed when the samples were left at room temperature: 2 min for bis[(trimethylsilyl)amido]mercury, 1 hr for dipropynal- and dibenzylmercury, 1 day for diphenyl- and divinylmercury, several days for dicyclopropylmercury, and several weeks for bis(pentachlorophenyl)- and dimethylmercury. Except for $(CH_3)_3SiHgCH_3$, decomposition of the unsymmetrical compounds was more rapid than for the bis(trimethylsilyl)mercury. Mercury was precipitated and resonances assignable to $(CH_3)_3SiR$ were observed.

Nmr spectra were obtained on a Varian Associates A-60A spectrometer at ambient temperatures unless otherwise noted. Coupling constants should be considered accurate to ±0.3 Hz.

Results and Discussion

Mixed species were detected when the organic group was methyl, phenyl, cyclopropyl, propynal, vinyl, pentachlorophenyl, benzyl, and the amide group bis(trimethylsilyl)amido. With dimethylmercury the equilibrium constant appeared to be close to the random value of 4.0, but decomposition of bis(trimethylsilyl)mercury prevented an accurate determination. With the other diorganomercurials the fairly rapid decomposition of the symmetrical compounds, probably by the reaction

$$RHgSi(CH_3)_3 \longrightarrow (CH_3)_3SiR + Hg \qquad (2)$$

prevented determination of the equilibrium constants, although they appeared to be much larger than the random value. The decomposition of $(CH_3)_3SiHgN(Si(CH_3)_3)_2$ was very rapid (within a few minutes at room temperature) and it was not possible to tell if the mixed species was favored.

These results show that, contrary to implications in the literature, unsymmetrical triorganosilylorganomercurials are the favored species in mixtures of bis(triorganosilyl)mercurials and diorganomercurials. In this regard silylmercury compounds more closely resemble organomercury compounds than may have been previously believed.

As expected the value of the ^{199}Hg–Si–C–^1H coupling in $(CH_3)_3SiHgR$ increases as the electronegativity of R increases (Table I). An interesting linear relationship was found between the values of $J_{^{199}Hg-Si-C-^1H}$ and $J_{^{199}Hg-C-^1H}$ in the related methyl compound CH_3HgR.

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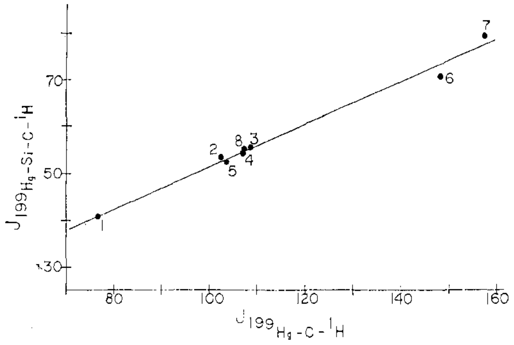

Figure 1.—Plot of $J_{^{199}Hg-Si-C-^{1}H}$ in $(CH_3)_3SiHgR$ *vs.* $J_{^{199}Hg-C-^{1}H}$ in CH_3HgR. R = (1) trimethylsilyl, (2) methyl, (3) phenyl, (4) vinyl, (5) cyclopropyl, (6) 1-propynal, (7) bis(trimethylsilyl)-amido, and (8) benzyl.

In Figure 1, $J_{^{199}Hg-Si-C-^{1}H}$ is plotted against $J_{^{199}Hg-C-^{1}H}$. The points fall on a line described by

$$0.453|J_{^{199}Hg-C-^{1}H}| + 6.0 = |J_{^{199}Hg-Si-C-^{1}H}| \qquad (3)$$

This linear relationship indicates that the mechanism of coupling is basically the same in both series of compounds.

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Preparation and Characterization of Some Mixed Halo-Nitrile Complexes of Rhodium(III)[1]

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A number of nitrile complexes of rhodium(III) have been reported and characterized by spectroscopic methods.[2] In all cases the complexes have been prepared using rhodium trichloride hydrate or the hexachlororhodate anion as the starting material. A search for new preparative methods for these complexes and an interest in the corresponding bromide complexes resulted in the study of the reactions of various nitriles with rhodium tribromide hydrate and tetraethylammonium nonachlorodirhodate. The increased solubility of this latter compound in warm nitriles facilitated the preparation of the respective monosubstituted and disubstituted complexes (especially those of the higher nitriles). The spectral properties of the new complexes were investigated in some detail to further our understanding of the donor properties of nitriles when they are coordinated to a non-first-row transition metal and to contrast the properties of the bromo complexes with the corresponding chloro species.

During the course of the study outlined above, the utility of proton nmr spectra in determining the structure of certain of these nitrile complexes was demonstrated. Thus the confirmation of the structure of the previously reported[2b] *trans*-$RhCl_3(C_2H_5CN)_3$ by proton nmr is also reported.

Experimental Section

Preparation of Tetraethylammonium Tetrabromodiacetonitrilerhodate(III).—$((C_2H_5)_4N)[RhBr_4(CH_3CN)_2]$ was prepared in a manner similar to that used for the analogous chloro complex.[2c] Upon mixing equimolar amounts of rhodium tribromide (hydrate) and tetraethylammonium bromide in acetonitrile, a green species was formed, possibly $((C_2H_5)_4N)_3RhBr_6$. This green product decomposed upon heating and the solution became red-brown. This green intermediate could be avoided by mixing the reactants directly in hot acetonitrile: rhodium tribromide dihydrate (0.195 g, 0.515 mmol) was dissolved in 25 ml of boiling acetonitrile and tetraethylammonium bromide (0.108 g or 0.515 mmol dissolved in a minimum amount of acetonitrile) was slowly added. The solution turned dark red. Upon standing overnight in the freezer some brown precipitate was obtained which was filtered and washed with ether. Addition of an equal amount of ether to the filtrate yielded additional brown precipitate. The two samples had identical infrared spectra. The final product was recrystallized from acetonitrile, washed with anhydrous ether, and dried under vacuum over P_2O_5. *Anal.* Calcd for $C_{12}H_{26}N_3RhBr_4$: C, 22.70; H, 4.13; N, 6.62. Found: C, 22.99; H, 4.01; N, 6.90.

Preparation of Aquotribromodiacetonitrilerhodium(III).—The complex $RhBr_3(H_2O)(CH_3CN)_2$ was prepared by dissolving rhodium tribromide dihydrate (0.20 g) in acetonitrile and refluxing the solution for 7 hr, during which time the solution changed from very dark brown to wine red. Removal of the solvent by means of a rotary evaporator produced dark brown crystals, which were recrystallized, washed, and dried as above. *Anal.* Calcd for $C_4H_8N_2ORhBr_3$: C, 10.85; H, 1.82; N, 6.33. Found: C, 11.66; H, 1.93; N, 6.37.

Preparation of *trans*-Trichlorotris(propionitrile)rhodium(III).—The *trans*-$RhCl_3(CH_3CH_2CN)_3$ complex was prepared in a fashion similar to the one used for the analogous acetonitrile complex.[2c] One gram of rhodium trichloride trihydrate was dissolved in 20 ml of absolute ethanol and propionitrile (10 ml) was added. The solution was refluxed until a yellow precipitate was obtained. Complete precipitation was accomplished by means of ether addition. The final product was recrystallized from propionitrile and washed and dried as above. The presence of the $RhCl_3(CH_3CH_2CN)_3$ species was verified by its visible and infrared spectra.[2b]

Preparation of Tetraethylammonium Tetrachlorobis(benzonitrile)rhodate(III).—$((C_2H_5)_4N)[RhCl_4(C_6H_5CN)_2]\cdot H_2O$ was prepared from $((C_2H_5)_4N)_3Rh_2Cl_9$. The starting material was stirred slowly with warming in benzonitrile until all of it had been dissolved leaving a reddish orange solution. The hot solution was filtered and the desired compound was obtained by slow addition of anhydrous ether. The pale orange (apricot) complex was washed and dried as above. *Anal.* Calcd for $C_{22}H_{32}N_3ORhCl_4$: C, 44.10; H, 5.38; N, 7.01. Found: C, 43.74; H, 5.01; N, 6.86.

Visible, Infrared, and Proton Nmr Spectra.—The visible spectra were obtained on a Perkin-Elmer Model 450 spectrophotometer or a Cary Model 15 spectrophotometer. The infrared spectra in the 4000–650-cm^{-1} region were taken on a Beckman Model IR-5A instrument and those in the 500–700-cm^{-1} region were recorded on a Beckman Model IR-11 or Perkin-Elmer FIS-3 spectrophotometer. All proton nmr spectra were obtained on a Varian Model A-60 high-resolution spectrometer at 60 Mc.

Results and Discussion

Infrared Spectra.—Since the mixed complexes prepared in this investigation contained nitriles and halides coordinated to the metal, it seemed feasible to determine their infrared spectra in the normal infrared range and in the far-infrared region to observe both the spectra of the coordinated nitriles and the coordinated halides. The values observed for the C≡N stretching frequencies in the various rhodium–nitrile

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[1] Taken in part from the thesis presented by B. D. C. for the Ph.D. degree from Louisiana State University in New Orleans.

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