Experimental and Theoretical Studies of Bis(perfluorovinyl)mercury, $Hg(CF{=}CF_2)_2$: Synthesis, Characterization, and Structure in the Gaseous and Crystalline Phases

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The low-temperature reaction between 2 equiv of (perfluorovinyl)lithium, derived from CF_3CH_2F and butyllithium, and mercury(II) chloride results in high yields of $Hg(CF{=}CF_2)_2$. Complete characterization of the air- and moisture-stable liquid product is afforded by multinuclear (^{13}C, ^{19}F, ^{199}Hg) NMR studies. Crystals of the compound [triclinic, $P\bar{1}$; $a = 4.956(4)$, $b = 5.733(4)$, $c = 6.394(4)$ Å; $\alpha = 104.57(5)$, $\beta = 109.32(6)$, $\gamma = 107.16(6)°$; $Z = 1$] were obtained by slow cooling; an X-ray structural determination at 110 K represents the first such report for a (perfluorovinyl)metal complex. The mercury is coordinated linearly [$r(Hg{-}C) = 1.998(5)$ Å], and π-stacking of the perfluorovinyl groups is observed. There is considerable variation in the C−F bond distances [1.286(6), 1.312(6), 1.362(6) Å] within each perfluorovinyl group. Structural data for the vapor-phase species were obtained by analysis of the electron-diffraction pattern. There appears to be free rotation of the perfluorovinyl groups around the Hg−C bonds, a significantly longer mercury−carbon distance [2.054(3) Å], and a similar, but smaller, variation in the C−F bond lengths. Theoretical optimization of the geometry at the MP2/DZP level predicts a shallow potential-energy minimum when the two perfluorovinyl groups are nearly perpendicular [$\Phi(C{=}C\cdots C{=}C) = 98.2°$] to one another. Analysis of the bonding in the molecule suggests that no significant $d(Hg) \rightarrow \pi^*(C{=}C)$ interaction is present.

Introduction

There has been a recent resurgence of interest in compounds containing fluorinated groups. Such materials can be “lightly” fluorinated, such as those found in pharmaceuticals and agrochemicals,[1] or highly fluorinated, for example materials for CVD applications and, more recently, in fluorous biphase work.[2] Metal complexes containing fluorinated ligands are also used as models for the chlorine−fluorine exchange processes involved in the synthesis of modern CFC replacements[3] and as transfer reagents.[4] Examples of complexes containing the smallest perfluoroalkyl ligand, CF_3, have been known for some time, and these exhibit a number of interesting properties, including a weakening of the C−F bonds on coordination;[5] attempts have been made to rationalize this behavior by modeling.[6] Unfortunately, the amount of structural data for complexes containing perfluorinated ligands is very much more limited than for their perprotio analogues, despite the fact that the perfluorinated compounds are often more thermally stable. Metal complexes containing the perfluorovinyl (1,1,2-trifluoroethenyl) group, $CF{=}CF_2$, are a case in point; no structural data have been published despite the first examples of such materials being reported in the 1960s.[7] By comparison structural data exist for a wide range of vinyl-containing compounds of main-group[8] and transition-metal elements,[9] and combined structural and theoretical modeling studies of divinylmercury[10] and vinylmercury hydrides[11] have been reported.

Recently we have published a method utilizing the CFC-replacement CF_3CH_2F in the synthesis of a wide range of perfluorovinyl-containing materials.[12] Further we have reported the first single-crystal structural data for a perfluorovinyl-containing compound, $PPh(CF{=}CF_2)_2$, and examples of metal complexes containing a related ligand.[13] A number of structural features were apparent from this work, including a significant degree of variation in the C−F bond distances of the $CF{=}CF_2$ group. We have undertaken, therefore, a thorough structural investigation of one example of a geometrically simple metal−perfluorovinyl system in both the solid and gas phases employing X-ray crystallography, electron diffraction, and ab initio

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calculations in an attempt to understand better the structure and bonding of such systems.

Experimental Section

Caution! Mercury-containing compounds are potentially highly toxic materials. All reactions and handling should be carried out in a well-ventilated hood or using vacuum-line manipulation.

General Methods. Reactions were carried out under dinitrogen in flame-dried glassware. Diethyl ether and THF were dried over sodium wire for ca. 1 d and subsequently refluxed over sodium/benzophenone under a nitrogen atmosphere. CF_3CH_2F (ICI Klea) and BuLi (2.5 M in hexanes, Acros) were used as supplied. Fluorine and mercury NMR spectra were recorded on a Bruker DPX200 spectrometer operating at 188.30 and 35.80 MHz, respectively, with peak positions being quoted relative to external $CFCl_3$ and $Hg(CH_3)_2$, respectively, using the high-frequency positive convention. Carbon NMR spectra were recorded on a Bruker AC300 spectrometer operating at 75.47 MHz and referenced to external $SiMe_4$. Infrared spectra were recorded for liquid samples held between KBr plates on a Nicolet PC-5 FTIR spectrometer. Elemental analyses were performed by the UMIST Chemistry Department's microanalytical service.

Bis(perfluorovinyl)mercury(II). Into a three-necked, round-bottom flask equipped with nitrogen inlet and magnetic stirrer maintained at −78 °C was introduced diethyl ether (100 cm^3) and CF_3CH_2F (3.30 g, 32.4 mmol). BuLi (26.0 cm^3, 2.5 M, 65 mmol) was added slowly over a period of ca. 0.5 h. The mixture was left to stir for 2 h after which $HgCl_2$ (4.00 g, 14.7 mmol) in THF (50 cm^3) was added slowly and left to stir overnight. After this time the solution was warmed to room temperature and a saturated aqueous solution of ammonium chloride was added (30 cm^3). The organic phase was separated and dried over magnesium sulfate and the solvents removed on a rotary evaporator. The crude material was distilled in vacuo (60−61 °C/20 mmHg) to yield 4.54 g, 85% of pure product: ^{19}F NMR ($CDCl_3$) δ −90.1 (dd, 1F, $^2J_{FF} = 38.1$ Hz, $^3J_{FF} = 74.3$ Hz), δ −124.5 (dd, 1F, $^2J_{FF} = 38.1$ Hz, $^3J_{FF} = 108.8$ Hz), δ −185.4 (dd, 1F, $^3J_{FF} = 74.3$ Hz, $^3J_{FF} = 108.8$ Hz); ^{13}C NMR (neat) δ 165.0 (dd, $^1J_{CF} = 310.6$ Hz, $^1J_{CF} = 265.9$ Hz, $^2J_{CF} = 32.5$ Hz), δ 161.7 (dd, $^1J_{CF} = 285.5$ Hz, $^2J_{CF} = 87.5$ Hz, $^2J_{CF} = 25.0$ Hz $J_{CF'} = 5.5$ Hz); ^{199}Hg NMR (neat) δ 957 (ttt, 1F, $^2J_{HgF} = 814.3$ Hz, $^3J_{HgF} = 224.0$ Hz, $^3J_{HgF} = 32.4$ Hz); IR (liquid, KBr plates, cm^{-1}) $\nu_{C=C}$ 1750 (s), ν_{C-F} 1275 (s), 1150 (s), 1050 (s). Anal. Calcd for C_4F_6Hg: Hg, 55.3; F, 31.6. Found: Hg, 54.9; F, 31.6.

X-ray Diffraction. A crystal of $Hg(CF{=}CF_2)_2$ was obtained from a sample held in a Pyrex capillary (o.d. 0.38 mm) mounted on a Stöe Stadi-4 diffractometer equipped with an Oxford Cryosystems low-temperature device. Crystallization was achieved by first establishing a stable solid-liquid equilibrium at 260 K and then cooling the sample at a rate of 10 K h^{-1}. A data set comprising a full sphere of data to $2\theta = 60°$ was collected at 110 K; an absorption correction was applied using ψ-scans. The structure was solved by placing the Hg atom at the origin and locating the C and F atoms in a subsequent difference synthesis (CRYSTALS).[14] Refinement was performed against F with 914 data with $F > 4\sigma(F)$. All atoms were modeled with anisotropic displacement parameters to give $R = 2.41\%$ and $R_w = 2.61\%$ for 53 parameters at convergence. Other data collection and refinement parameters are given in Table 1.

Electron Diffraction. Electron scattering intensities were recorded on Kodak electron image plates using the Edinburgh gas diffraction apparatus operating with an accelerating voltage of 40 kV.[15] With the sample and nozzle temperature maintained at ca. 353 and 361 K, respectively, three plates were exposed at the long camera distance (258 mm) and six at the short distance (95 mm). Scattering intensities for benzene were also recorded, to provide calibration of the camera distances. The plates were scanned using a PDS microdensitometer employing a 200 μm pixel size at the Royal Greenwich Observatory, Cambridge, U.K.[16] Analysis of the data made use of standard data reduction[17] and least-squares refinement[18] programs and scattering factors.[19] The s ranges, weighting points, and other experimental details are listed in Table 2.

Table 1. Crystal Data and Structure Refinement for $Hg(CF{=}CF_2)_2$ at 110 K

empirical formula	C_4HgF_6
fw	362.62
cryst system	triclinic, space group $P\bar{1}$
unit cell dimens	$a = 4.956(4)$ Å, $\alpha = 104.57(5)°$ $b = 5.733(4)$ Å, $\beta = 109.32(6)°$ $c = 6.394(4)$ Å, $\gamma = 107.16(6)°$
V	151.03 Å^3
Z	1.00
T	−163 °C
λ	0.710 73 Å
μ	2.553 cm^{-1}
ρ_{calc}	3.99 g cm^{-3}
R^a	0.0241
$R_w{}^b$	0.0261

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

Ab Initio Calculations. All computations employed the Gaussian 94 program.[20] Optimizations were carried out by employing a DZP quality basis set consisting of (a) a relativistic effective core potential on Hg,[21] with the corresponding split-valence basis set in the recommended [21/21/21] contraction augmented with one set of f functions (exponent 1.002),[22] and (b) Dunning's (9s5p) basis on C and F,[23] contracted to [6111/41] and augmented with a set of d-polarization functions (exponents 0.75 and 0.9, respectively). Using standard methods,[24] geometries were fully optimized using numerical gradients at the restricted Hartree−Fock (or self-consistent field, SCF) level. For the title compound, optimizations were performed in C_{2h} and C_2 symmetry, followed by numerical calculations of the harmonic vibrational frequencies and, for the C_{2h} form, by reoptimization at the electron-correlated MP2/DZP level. At that level, the value of the $C{=}C\cdots C{=}C$ dihedral angle, Φ, was further optimized by performing a rigid potential-energy scan in which this angle was varied first in steps of 30° between $\Phi = 0$ and 180° and, subsequently, in steps of 10° between $\Phi = 70°$ and 120°. All other parameters were fixed at the MP2/DZP values of the C_{2h} form. The latter points were fitted using a quadratic function.

Bonding in the molecule was investigated using a natural bond orbital (NBO) analysis scheme,[25] employing the SCF/DZP wave functions for the MP2/DZP optimized geometries. In this scheme, atomic charges are obtained from population analysis of the natural atomic orbitals (NPA charges)[25] and (covalent) bond orders are given according to Wiberg's definition.[26]

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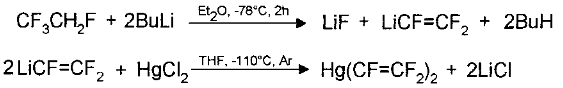
Table 2. Nozzle-to-Plate Distances, Weighting Functions, Correlation Parameters, Scale Factors, and Electron Wavelengths for the GED Study

nozzle-to-plate dist, mm	Δs^a	$s_{\min}{}^a$	$sw_1{}^a$	$sw_2{}^a$	$s_{\max}{}^a$	correlation param	scale factor k^b	electron wavelength,^{c} pm
257.83	0.2	4.0	4.2	13.0	15.2	0.207	0.851(10)	6.016
95.32	0.4	10.8	12.8	30.4	35.6	0.335	1.064(43)	6.015

[a] In nm^{-1}. [b] Figures in parentheses are the estimated standard deviations (1σ). [c] Determined by reference to the scattering pattern of benzene.

Scheme 1



$$CF_3CH_2F + 2BuLi \xrightarrow{Et_2O,\ -78°C,\ 2h} LiF + LiCF{=}CF_2 + 2BuH$$

$$2LiCF{=}CF_2 + HgCl_2 \xrightarrow{THF,\ -110°C,\ Ar} Hg(CF{=}CF_2)_2 + 2LiCl$$

To derive vibrational amplitudes (u) for the experimental GED refinements using a free-rotation model, additional optimizations (using analytical gradients) and frequency calculations were performed at the SCF level employing a basis set described as DZP′, i.e. equivalent to DZP but without the f-polarization functions on Hg. Force fields were evaluated for the stationary points with C_{2h}, C_{2v}, and C_2 (fully optimized) symmetry, as well as for points with Φ fixed at 45 and 135°.

Results

Synthesis and Spectroscopic Characterization of Bis(perfluorovinyl)mercury. A number of routes for the preparation of perfluorovinyl-containing compounds have been reported before. These are based upon silicon,[27] Grignard,[28] organocopper,[29] and organo-zinc[30] reagents as well as lithium compounds.[31] The majority of these routes rely on bromo- or chlorotrifluoroethene as the perfluorovinyl precursor, compounds which are becoming less readily available because of the damage that they inflict on the ozone layer and because of their potential as greenhouse gases. It has been demonstrated recently[12,32] that treatment of the CFC replacement CF_3CH_2F with 2 equiv of butyllithium in cold diethyl ether solution under anaerobic conditions results in (perfluorovinyl)lithium. To this solution, 0.5 equiv of a concentrated cold THF solution of mercury(II) chloride was added resulting in bis(perfluorovinyl)mercury(II), Scheme 1.

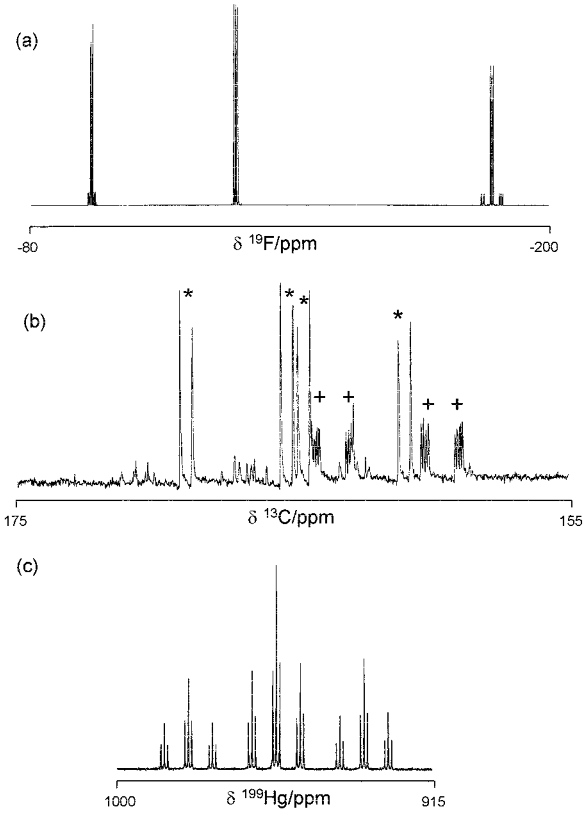


Figure 1. ^{19}F, ^{13}C, and ^{199}Hg NMR spectra of $Hg(CF{=}CF_2)_2$ dissolved in $CDCl_3$.

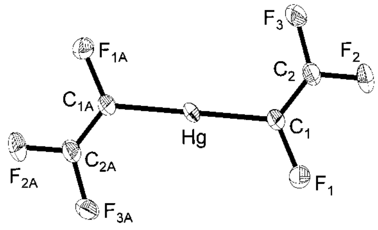


Figure 2. View of the molecular structure of $Hg(CF{=}CF_2)_2$ determined at 110 K showing the atom-numbering scheme used.

Prior to warming and working up the reaction mixture, a sample was withdrawn and the contents of the solution monitored using multinuclear NMR studies to determine the degree of substitution and the extent of reaction. The ^{19}F NMR spectra of these solutions, recorded at moderate resolution, clearly demonstrated that the HFC had been consumed, since the complex multiplet signals at δ −64.9 and −226.5 ppm arising from CF_3CH_2F[33] had been replaced by three sets of doublets of doublets at ca. −90.1, −124.5, and −185.4 ppm (Figure 1a). Each of these multiplets fell within the chemical-shift regions typical of the spectra recorded for perfluorovinyl complexes and were accompanied by ^{199}Hg satellites ($I = {}^1/_2$, 16.8%). These resonances were assigned on the basis of a previous analysis of this AA′MM′XX′ spin system[34] as F_2, F_3 and F_1 (Figure 2), respectively, in order of increasing chemical-shift value. After the reaction mixture was allowed to attain room temperature slowly overnight, saturated ammonium chloride solution was added. Extraction of the organic phase followed by drying and evaporation under vacuum resulted in a crude product from which, by distillation under reduced pressure (60−61 °C, 16 mmHg), the colorless, liquid product was obtained in greater than 80% yield. Although this compound has been prepared before, the only spectroscopic data available appear to be the IR[34] and ^{19}F NMR[35] spectra. Therefore, we have recorded and analyzed the ^{13}C and ^{199}Hg NMR spectra.

The ^{13}C NMR spectrum, Figure 1b, is interpreted in terms of two complex multiplets centered at 165.0 and 161.7 ppm. The first set of peaks (marked with asterisks) appear as a widely spaced doublet of doublets of doublets as a result of coupling

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Table 3. Bond Lengths (Å) and Angles (deg) Obtained from X-ray Diffraction Studies of $Hg(CF{=}CF_2)_2$

Hg_1-C_1	1.998(5)	$C_1{=}C_2$	1.312(6)
Hg_1-C_{1A}[a]	1.998(5)	C_2-F_2	1.286(6)
C_1-F_1	1.362(6)	C_2-F_3	1.324(6)
$C_1-Hg_1-C_{1A}$[a]	180	$C_1-C_2-F_2$	125.4(5)
$Hg_1-C_1-F_1$	118.4(3)	$C_1-C_2-F_3$	124.2(5)
$Hg_1-C_1-C_2$	125.4(4)	$F_2-C_2-F_3$	110.4(4)
$F_1-C_1-C_2$	116.3(4)		

[a] Symmetry transformations used to generate equivalent atoms: $-x$, $-y$, $-z$.

with the three nonequivalent fluorine nuclei. Two of the measured coupling constants are greater than 200 Hz, typical of $^1J_{C-F}$ coupling, and therefore, this multiplet is assigned to the nucleus C_2. The signal centered at 161.7 ppm is split into a larger number of components (marked with pluses) arising, presumably, from additional through-metal coupling to at least one of the fluorine nuclei of the other perfluorovinyl group. Such through-metal coupling has been noted previously in high-resolution ^{19}F NMR studies of related complexes.[35] The greater number of components for this signal and the observation of just one typical $^1J_{C-F}$ coupling constant value is consistent with this signal arising from carbon C_1. Bis-substitution of the complex is confirmed by the ^{199}Hg NMR spectrum; this consists of a triplet of triplets of triplets, Figure 1c, as a result of coupling with three sets of chemically equivalent pairs of fluorine nuclei. These experimental data do not appear to have been reported before, although they have been calculated on the basis of coupling constants obtained from ^{19}F NMR spectra.[35] The identity and purity of the product is confirmed unambiguously by elemental analysis.

X-ray Diffraction Analysis. Analysis of the crystallographic data shows that in the solid phase the title compound is centrosymmetric with the mercury atom occupying a crystallographic center of inversion. The molecule is planar and the mercury atom linearly coordinated to the two perfluorovinyl groups with a mercury−carbon distance of 1.998(5) Å. The molecular structure is shown in Figure 2, and bond lengths and distances are presented in Table 3; Cartesian coordinates are given in the Supporting Information. The Hg−C bond distance is significantly shorter than that found in $Hg(CF_3)_2$ [r(Hg−C) = 2.109(16) Å].[36] Interestingly, all three of the C−F bond lengths are different [$C_1-F_1 = 1.362(6)$, $C_2-F_2 = 1.286(6)$, and $C_2-F_3 = 1.324(6)$ Å]; the variation between the two extremes [0.076(8) Å] is nearly 10σ, and that between the two C_2-F distances [0.038(8) Å], nearly 5σ. The longest C−F distance is found for the C_1-F_1 bond which is consistent with a lengthening of the $C_\alpha-F$ bond observed in a number of structural studies on (perfluoroalkyl)metal-bound moieties.[37] Inspection of the packing diagram, Figure 3, shows that in the solid state the perfluorovinyl groups are stacked one upon another. Data for the intramolecular interactions reveal relatively close contacts between each of the fluorine atoms in one molecule with mercury centers in different, adjacent molecules. These interactions [$Hg\cdots F_1 = 2.964(5)$, $Hg\cdots F_2 = 3.503(5)$, and $Hg\cdots F_3 = 3.129(5)$ Å] undoubtedly contribute toward the differences between the three C−F bond distances. This variation in C−F bond distance is also consistent with that observed in the crystal structure of $PPh(CF{=}CF_2)_2$.[13] However a similar variation in C−F distances is not observed in the crystal structure of $[Cr(CO)_5CNCF{=}CF_2]$[38] nor in the single example of a mercury-bound perchlorovinyl complex, (3,4,7,8-tetramethyl-1,10-phenanthroline-*N*,*N′*)bis(trichlorovinyl)mercury,[39] in which the three C−Cl distances are reported to be essentially the same [1.726(9), 1.729(11), and 1.725(9) Å]. In this respect there appears to be a significant difference between the structure of the perchlorovinyl and perfluorovinyl complexes in the solid state. To investigate this further, gas-phase structural data were obtained from an electron-diffraction study supported by ab initio calculations.

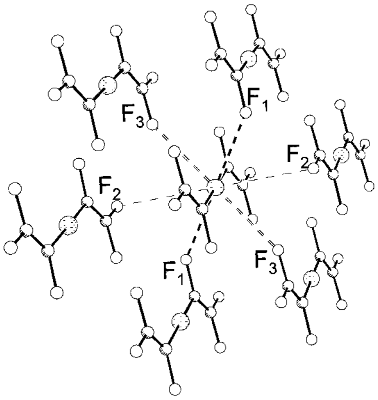

Figure 3. Packing diagram showing the intramolecular interactions between adjacent $Hg(CF{=}CF_2)_2$ molecules.

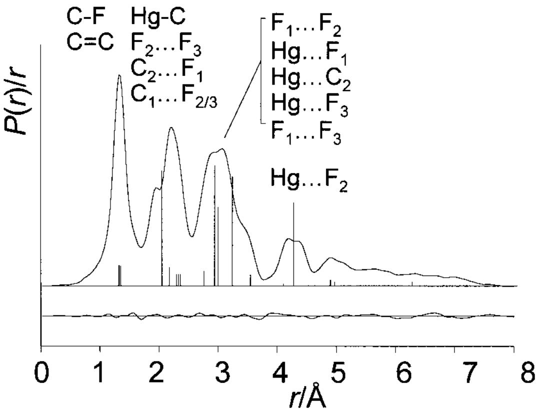

Figure 4. Observed and final weighted difference radial-distribution curves. Before Fourier inversion the data were multiplied by $s\,\exp[(-0.000\,02s^2)/(Z_{Hg} - f_{Hg})(Z_F - f_F)]$.

Electron Diffraction Analysis. Data were collected for gaseous $Hg(CF{=}CF_2)_2$ at 361 K as outlined in the Experimental Section. On the basis of the results of the ab initio calculations detailed below and of preliminary refinements of the experimental data, a model for $Hg(CF{=}CF_2)_2$ which assumed linear coordination at mercury, planar $Hg-CF{=}CF_2$ groups, and free rotation of the perfluoroethene groups about the Hg−C bonds was employed. As such, nine independent geometrical parameters are required to define the structure. Since the radial-distribution curve (Figure 4) contains only six distinct peaks, it was expected that strong correlation between parameters would make it difficult to refine all of the geometrical parameters simultaneously; in particular, the C=C and C−F bond lengths would be very similar to one another. The independent parameters (Table 4) needed to represent the five different bonded distances were chosen to be the mean of the C=C and

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Table 4. Geometrical Parameters (r_a/Å, $\angle_a$/deg) for the GED Study[a,b]

no.	param	r, $\angle$[c]	no.	param	r, $\angle$[c]
		(a) Independent			
p_1	$^1/_4[r(C_1{=}C_2) + r(C_1{-}F_1) + r(C_2{-}F_2) = r(C_2{-}F_3)]$	1.334(1)	p_6	$\angle C_1C_2F_2 - \angle C_1C_2F_3$	4.3(8)
p_2	$r(C_1{=}C_2) - {}^1/_3[r(C_1{-}F_1) + r(C_2{-}F_2) + r(C_2{-}F_3)]$	−0.011(10)	p_7	$\angle C_2C_1Hg$	123.9(7)
p_3	$r(C_1{-}F_1) - {}^1/_2[r(C_2{-}F_2) + r(C_2{-}F_3)]$	0.030(18)	p_8	$\angle F_1C_1Hg$	117.9(11)
p_4	$r(C_2{-}F_2) - r(C_2{-}F_3)$	−0.011[d]	p_9	$r(Hg{-}C_1)$	2.054(3)
p_5	$^1/_2(\angle C_1C_2F_2 + \angle C_1C_2F_3)$	124.8(5)			
		(b) Dependent			
d_1	$r(C_1{=}C_2)$	1.326(8)	d_5	$\angle C_1C_2F_2$	127.0(5)
d_2	$r(C_1{-}F_1)$	1.357(13)	d_6	$\angle C_1C_2F_3$	122.7(7)
d_3	$r(C_2{-}F_2)$	1.321(7)	d_7	$\angle C_2C_1F_1$	118.2(6)
d_4	$r(C_2{-}F_3)$	1.332(7)	d_8	$\angle F_2C_2F_3$	110.4(10)

[a] For atom-numbering scheme, see Figure 2. [b] Figures in parentheses are the estimated standard deviations (1σ). [c] For details of the refinements, see the text. [d] Fixed.

three C−F distances (p_1), the difference between the C=C distance and the mean of the three different C−F distances (p_2), the difference between $r(C_1{-}F_1)$ and the mean of the two $C_2{-}F$ distances (p_3), the difference between $r(C_2{-}F_2)$ and $r(C_2{-}F_3)$ (p_4), and the bond length r(Hg−C) (p_9). The other four parameters were defined to be the mean and the difference of angles $C_1C_2F_2$ and $C_1C_2F_3$ (p_5 and p_6, respectively), the angles C_2C_1Hg (p_7), and F_1C_1Hg (p_8).

Free rotation of the perfluoroethene groups was modeled by defining the molecule as a mixture of nine conformations. Each conformation was described by the same independent parameters, $p_1{-}p_9$, with a different C=C···C=C torsion angle (Φ) in the range 10−170°; $\Phi = 10°$ for the first conformation, $\Phi = 30°$ for the second, etc. An equal weighting was given to each conformation by setting the relative multiplicities of the torsion-sensitive distances appropriately.

The radial-distribution curve for $Hg(CF{=}CF_2)_2$, consisting of six distinct features, is shown in Figure 4. The peak at ca. 1.3 Å represents scattering from all bonding, light atom (non-Hg) scattering pairs in the molecule, i.e., 3 C−F and C=C. Peaks associated with scattering from atom pairs involving mercury are doublets,[40] and the peak at ca. 2.0 Å constitutes one element of such a doublet for the Hg−C distance. The other element forms part of the peak at ca. 2.2 Å, together with scattering from the light-atom, two-bond pairs. The broad peak centered at ca. 3.0 Å arises predominantly from the nonbonded scattering pairs $Hg\cdots F_1$, $Hg\cdots C_2$, and $Hg\cdots F_3$ and the doublet at ca. 4.3 Å from the $Hg\cdots F_2$ nonbonded pair. The broad continuum at $r > 4.5$ Å represents scattering from atom pairs arising from different vinyl groups, including all torsion-sensitive distances.

The r_a structure of $Hg(CF{=}CF_2)_2$ was refined. The program ASYM40[41] was used to convert the theoretical (HF/DZP level) Cartesian force field to one described by symmetry coordinates. In the absence of a full assignment of the experimental vibrational frequencies for the compound, the theoretical force constants were scaled empirically: 0.9 for bond stretches, 0.85 for bends, and 0.8 for out-of plane bends and torsions.[42] Root-mean-square amplitudes of vibration (u) were then calculated from the scaled force constants using ASYM40.[41] Values of amplitudes for the torsion-sensitive distances in the nine conformations describing the free rotation were interpolated from the additional force fields (HF/DZP′ level) described above.

The possibility of refining an r_α structure of $Hg(CF{=}CF_2)_2$ was considered. At the SCF/DZP level, there are predicted to be three very low frequency (<100 cm^{-1}) modes of vibration, at 8.6, 42.6, and 43.4 cm^{-1} (after scaling). An examination of the contribution to the perpendicular amplitude corrections (K) from each of these modes revealed not only the expected major contribution from the C=C···C=C torsional motion but also a significant contribution from the two Hg−C=C−F torsional motions. Thus, refinement of an r_α structure would demand the simultaneous modeling of both of these modes of vibration, as well as the C=C···C=C torsion, to obtain realistic K values from the force fields. The complexity of this model and the amount of information available from the experimental intensities was judged to negate the usefulness of such an approach.

Using starting values taken from the structure optimized ab initio at the MP2/DZP level, it was possible to refine eight of the nine independent geometrical parameters simultaneously. Introduction of p_4, defining the difference between $r(C_2{-}F_2)$ and $r(C_2{-}F_3)$, into the refinement yielded essentially the same R_G value and $p_4 = 0.070(15)$ Å; the refined values of $r(C_2{-}F_2)$ and $r(C_2{-}F_3)$ were 1.352(10) and 1.283(11) Å, respectively. Such a difference between the two $C_2{-}F$ distances seemed unrealistic, especially when compared to the theoretical computations which consistently predicted the value of p_4 to be ca. −0.01 Å. This parameter was refined subsequently, subject to a flexible restraint.[43]

Flexible restraints may allow the refinement of parameters which would otherwise have to be fixed.[43] Estimates of the values of these restrained quantities and their uncertainties are used as additional observations in a combined analysis similar to those routinely carried out for electron-diffraction data combined with rotation constants and/or dipolar coupling constants.[44] The values and uncertainties for the extra observations are derived from another method such as X-ray diffraction or theoretical computations. *All* geometrical parameters are then included in the refinements. In cases where a restrained parameter is also a refinable parameter, if the intensity pattern contains useful information concerning the parameter, it will refine with an esd less than the uncertainty in the corresponding

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[40] This arises as a consequence of the large phase shift in molecules containing heavy atoms. See, for example: Bartell, L. S. In *Stereochemical Applications of Gas Phase Electron Diffraction*; Hargittai, I., Hargittai, M., Eds.; VCH: New York, 1988; Vol. I, Chapter 2, p 77.

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Table 5. Interatomic Distances and Amplitudes of Vibration for the GED Study (r_a/pm, u/pm)[a,b]

no.	atom pair	dist (r_a)	amplitude (u)	restraint
r_1	$C_2{-}F_2$	1.321(7)	0.051(3)	
r_2	$C_1{=}C_2$	1.326(8)	0.049(4)	$u_1/u_2 = 1.040 \pm 0.052$
r_3	$C_2{-}F_3$	1.332(7)	0.052(4)	$u_1/u_3 = 0.986 \pm 0.049$
r_4	$C_1{-}F_1$	1.357(13)	0.053(4)	$u_1/u_4 = 0.944 \pm 0.047$
r_5	$Hg{-}C_1$	2.054(3)	0.058(2)	
r_6	$F_2{\cdots}F_3$	2.178(7)	0.066(7)	$u_7/u_6 = 1.063 \pm 0.053$
r_7	$C_2{\cdots}F_1$	2.301(15)	0.067(7)	$u_7/u_8 = 1.055 \pm 0.053$
r_8	$C_1{\cdots}F_3$	2.332(12)	0.062(7)	$u_7/u_9 = 1.050 \pm 0.053$
r_9	$C_1{\cdots}F_2$	2.368(8)	0.063(7)	
r_{10}	$F_1{\cdots}F_2$	2.764(13)	0.104(12)	
r_{11}	$Hg{\cdots}F_1$	2.945(10)	0.098(6)	$u_{11}/u_{12} = 1.069 \pm 0.053$
r_{12}	$Hg{\cdots}C_2$	3.003(10)	0.090(5)	
r_{13}	$Hg{\cdots}F_3$	3.243(8)	0.111(12)	
r_{14}	$F_1{\cdots}F_3$	3.547(7)	0.063(9)	
r_{15}	$C_1{\cdots}C_{1A}$	4.108(6)	0.080[c]	
r_{16}	$Hg{\cdots}F_2$	4.276(4)	0.079(4)	
r_{17}	$C_1{\cdots}F_{1A}$	4.893(14)	0.124(15)	$u_{17}/u_{19} = 1.083 \pm 0.054$
r_{18}	$C_1{\cdots}F_{3A}$	4.903(13)	0.259(26)	$u_{18} = 1.270 \pm 0.027$
r_{19}	$C_1{\cdots}C_{2A}$	4.971(11)	0.115(15)	
r_{20}	$C_1{\cdots}F_{2A}$	6.277(5)	0.121(25)	

[a] For atom-numbering scheme, see Figure 2. [b] Figures in parentheses are the estimated standard deviations (1σ). [c] Fixed.

additional observation. However, if there is essentially no relevant experimental information, the parameter will refine with an esd approximately equal to the uncertainty of the extra observation and its refined value will equal that of the restraint. In this case, if the correlation matrix also shows no correlation with other refining parameters, the parameter can simply be fixed, in the knowledge that doing this does not influence either the magnitudes or the esds of other parameters. In some cases, because increasing the number of refining parameters allows all effects of correlation to be considered, some esds may increase. Overall, this approach utilizes all available data as fully as possible and returns more realistic esds for refining parameters; the unknown effects of correlation with otherwise fixed parameters are revealed and included.[45]

Using a flexible restraint of -0.011 ± 0.001 Å, based upon the MP2/DZP value and the variation shown across other computations, the value of p_4 refined to $-0.011(1)$, i.e. precisely the value and uncertainty of the restraint. Thus, the GED intensity data does not contain any information pertinent to this parameter. Further, since p_4 was not found to be correlated with the other refining parameters, its value was fixed thereafter at the MP2/DZP value.

It was possible to refine the amplitudes of vibration for the 19 distances contributing more than 2% of the scattering relative to the principal scattering pair ($Hg{-}F_1$). However, it was necessary to restrain the value of $u_{18}(C_1{\cdots}F_{3A})$ to 0.270 ± 0.027 Å and the ratios of eight pairs of refining amplitudes, the values being derived from the MP2/DZP force field (see Table 5).

Since $Hg(CF{=}CF_2)_2$ has been shown to yield trifluoroethene, $CF_2{=}CHF$, as a volatile decomposition compound, a further refinement was undertaken in which the model described a mixture of the two compounds. With the parameters for $CF_2{=}CHF$ fixed at the values reported by Huisman et al.,[46] the R_G factor was found to be consistently worse for a mixture as compared to that for a vapor consisting of $Hg(CF{=}CF_2)_2$ alone.

Table 6. Comparison of Geometrical Parameters (r/Å, ∠/deg)[a,b]

param	X-ray	GED (r_a)	theoretical (r_e)[c]
$r(Hg{-}C_1)$	1.998(5)	2.054(3)	2.066
$r(C_1{=}C_2)$	1.312(6)	1.326(8)	1.343
$r(C_1{-}F_1)$	1.362(6)	1.357(13)	1.373
$r(C_2{-}F_2)$	1.286(6)	1.321(7)	1.327
$r(C_2{-}F_3)$	1.324(6)	1.332(7)	1.338
$\angle C_2C_1Hg$	125.4(4)	123.9(7)	126.2
$\angle F_1C_1Hg$	118.4(3)	117.9(11)	117.6
$\angle C_2C_1F_1$	116.3(4)	118.2(6)	116.2
$\angle C_1C_2F_2$	125.4(5)	127.0(5)	126.5
$\angle C_1C_2F_3$	124.2(5)	122.7(7)	122.2
$\angle F_2C_2F_3$	110.4(4)	110.4(10)	111.3
$\Phi(C{=}C{\cdots}C{=}C)$	180	free rotation	98.2

[a] For atom-numbering scheme, see Figure 2. [b] Figures in parentheses are the estimated standard deviations (1σ). [c] MP2/DZP level parameters optimized for the C_{2h} geometry; Φ obtained from a rigid potential-energy scan as detailed in the Experimental Section.

The success of the final GED refinement, for which $R_G = 0.080$ ($R_D = 0.068$), may be assessed on the basis of the difference between the experimental and calculated radial-distribution curves (Figure 3). The interatomic distances and vibrational amplitudes (and restraints) of the optimum refinement are listed in Table 5. The least-squares correlation matrix is available as part of the Supporting Information together with the experimental molecular-scattering intensity curves and Cartesian coordinates.

Ab Initio Calculations. At the SCF/DZP level, the planar C_{2h} form is not a minimum but has one very small imaginary frequency (6i cm^{-1}) corresponding to the rotation of the vinyl moieties about the Hg−C bonds. The true minimum, with C_2 symmetry and essentially perpendicular vinyl groups ($\Phi = 89°$) is 0.9 kJ mol^{-1} lower in energy, a situation similar to that found for $Hg(CH{=}CH_2)_2$ at the SCF/LANL1DZ level.[11] At the MP2/DZP level, the minimum for $Hg(CF{=}CF_2)_2$ has a $C{=}C{\cdots}C{=}C$ torsion near 98° and a rotational barrier via the C_{2h} form of ca. 1.0 kJ mol^{-1}. At this level, the C_{2v} conformer with synperiplanar vinyl groups is 1.6 kJ mol^{-1} above the C_2 form, consistent with the observation of free rotation of the vinyl groups at the temperature of the GED experiment ($RT = 3.0$ kJ mol^{-1}, $T = 361$ K).

The slight preference of a perpendicular over a planar arrangement of the vinyl groups is also apparent when two C_2F_3H molecules are aligned along the $C{-}H{\cdots}H{-}C$ axis (employing fixed SCF/DZP monomer geometries and a fixed $C{\cdots}C$ distance of 4.13 Å, corresponding to the MP2/DZP value in the Hg compound); the SCF/DZP energies of the planar anti and syn orientations are calculated to be 0.1 and 0.3 kJ mol^{-1} higher in energy, respectively, than that of a perpendicular arrangement. However, the larger barriers for $Hg(CF{=}CF_2)_2$ clearly indicate that this preference is somewhat reinforced by bonding to mercury.

Discussion

A comparison of the geometrical parameters refined experimentally and optimized ab initio is given in Table 6. The agreement between the electron-diffraction and theoretical values is good, with the largest differences being 0.017(8) Å for bond distances [$r(C{=}C)$] and 2.3(7)° for bond angles [$\angle C_2C_1Hg$]. In making such a comparison, it should be borne in mind that the electron-diffraction r_a refinements define a structure averaged over all vibrational motions; although the $C{=}C{\cdots}C{=}C$ torsional motion has been modeled explicitly, no other allowance for the effects of shrinkage has been undertaken for a comparison with

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the ab initio equilibrium (r_e) structure. The most significant differences are associated with an angle involving Hg and the C=C double-bonded distance; it is possible that these differences would become smaller with a larger basis set, especially for Hg, and at higher levels of electron correlation. Unfortunately, computational resources were not available to us to explore this further. The calculations support the experimental finding that, in the gas phase, $r(C_1-F_1)$ is longer than $r(C_2-F_2)$ and $r(C_2-F_3)$ and that there is a marked difference between the two C_1C_2F bond angles.

In the solid state, the geometry is planar, in keeping with the theoretical prediction of a low torsional barrier about the Hg−C bonds. There are significant differences in a number of geometrical parameters as compared to the gas-phase structure (Table 6). Thus, while the C_2-F bond distances are similar in the gas phase [$\Delta = 0.011(10)$ Å], in the solid $r(C_2-F_2)$ is 0.038(8) Å shorter than $r(C_2-F_3)$, i.e. more than a factor of 3 increase on condensation. This is accompanied by a marked decrease in the difference between the C_1C_2F bond angles, which, at 4.3(9)°, is significant in the gas phase but, at 1.2(7)°, hardly so in the solid phase. Further, the solid-state structure is characterized by an Hg−C bond distance 0.056(6) Å shorter than that determined experimentally for the gas phase. Such variations arise presumably as a consequence of intermolecular forces on packing the molecules together in the crystalline phase. Nonbonded interactions of the type C−F···Hg are evident from the X-ray data, shown schematically in Figure 3; as a result of changes in dipole moment and a larger ionic contribution to bonding, these result in the shorter Hg−C and C_2-F_2 bond distances relative to the gas-phase structure.

There has been much interest in the bonding of fluoroalkyl fragments to metals. The results of early studies by Cotton and others[47] suggested that the small fluorocarbon ligands, such as CF_3, are good π-acceptors and that back-bonding from the metal to low-energy π-acceptor levels occurs. More recent interpretations are based on the influence that the electronegative fluorine atoms have on the charges, and s- and p-character of the orbitals, within the ligand.[48] To date there has not been any interpretation of the bonding of perfluorovinyl moieties to metals, although there have been speculations about a “conjugative interaction” between a filled mercury 5d-orbital and the π*-orbital of the C=C bond in vinylmercury compounds. This “double-bond character” has been taken as a rationale for the observed Hg−C bond contraction on going from $Hg(CH_3)_2$ to $Hg(CH=CH_2)_2$.[11] However, natural population and natural bond orbital (NBO) analysis has indicated highly ionic bonding in $Hg(CH_3)_2$, best described in terms of mesomeric structures [$H_3CHg^+\ CH_3 \leftrightarrow H_3C\ M^+CH_3$].[49]

Essentially the same picture emerges from an NBO analysis of $Hg(CF=CF_2)_2$, i.e. only one Hg−C bond orbital, with a natural charge of +1.3 on Hg and a Wiberg bond order between Hg and each associated C atom of 0.46. In the Hg−C natural bond orbital, which is strongly polarized toward C, Hg uses predominantly the 6s orbital for bonding, with a minor admixture (ca. 9%) of the 5d orbital. From the second-order perturbation analysis of the NBO donor−acceptor interactions, no significant evidence for the proposed $d(Hg) \rightarrow \pi^*(C=C)$ interaction could be found. Instead, the longer Hg−C bond in saturated compounds, for instance in $Hg(CF_3)_2$ relative to $Hg(CF=CF_2)_2$, is found to result from the different overlaps of the formally sp^3- and sp^2-hybridized orbitals on carbon; NBO analysis affords $sp^{2.4}$ and $sp^{2.0}$, respectively.

In conclusion, this work provides a detailed description of the synthesis and characterization of bis(perfluorovinyl)mercury and the determination of the structure and bonding in the solid and gaseous phases. This is the first such analysis for any perfluorovinyl-containing compound. In the solid state the compound exhibits a planar geometry with stacking of the perfluorovinyl groups. Weak interactions between the fluorine atoms and mercury atoms in adjacent molecules occur. By comparison, in the gas phase there is essentially free rotation about the Hg−C bond; calculations at the MP2/DZP level predict that an energy minimum exists where the C=C···C=C torsion angle is 98.2° with barriers to rotation of ca. 1.6 kJ mol^{-1} (C_{2v}) and 1.0 kJ mol^{-1} (C_{2h}).

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Supporting Information Available: For the single-crystal structure determination, tables of crystal data and structure refinement, atomic coordinates, and anisotropic displacement parameters, for the gas-phase electron-diffraction study, plots of the separate and combined molecular intensity scattering curves, the coordinates for the final geometry, and the experimental molecular scattering intensities, and for the ab initio study, the atomic coordinates optimized in the MP2/DZP calculations and scaled frequencies and an X-ray crystallographic file, in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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