

Structure and Dynamics in a Bis(perfluoroalkyl)triazapentadiene Methylmercury Compound

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The compound $[\text{Ph}_2\text{N}_3\text{C}_2(\text{C}_3\text{F}_7)_2]\text{HgCH}_3$ was synthesized from $\text{Na}[\text{Ph}_2\text{N}_3\text{C}_2(\text{C}_3\text{F}_7)_2]$ and CH_3HgCl . In solution, it exists as a mixture of two isomers that interconvert slowly on the NMR time scale. Both isomers feature a $\eta^1\text{-Ph}_2\text{N}_3\text{C}_2(\text{C}_3\text{F}_7)_2$ ligand. In the asymmetrical one, the CH_3Hg group is bonded to one of the two terminal nitrogen atoms. In the more stable symmetrical isomer, $[\text{PhN}=\text{C}(\text{C}_3\text{F}_7)]_2\text{NHgCH}_3$, mercury is attached to the central nitrogen atom. It is this isomer that crystallizes and that was characterized by X-ray diffraction. Thermodynamic parameters for the CH_3Hg shift reaction were obtained by DNMR spectroscopy. ^{19}F NMR spectra were analyzed. A metallotropic rearrangement was not observed in $[\text{Ph}_2\text{N}_3\text{C}_2(\text{C}_3\text{F}_7)_2]\text{AuPPh}_3$.

Introduction

Reaction of perfluoro-5-aza-4-nonene, $\text{C}_3\text{F}_7\text{—CF}=\text{N—C}_4\text{F}_9$, with primary amines, exemplified by aniline, proceeds by a series of addition–HF elimination processes and yields the triazapentadiene $\text{Ph}_2\text{N}_3\text{C}_2(\text{C}_3\text{F}_7)_2\text{H}$, **1**, a triaza analogue of the much studied diimines. This compound is a weak acid that can be readily deprotonated to form $\text{Ph}_2\text{N}_3\text{C}_2(\text{C}_3\text{F}_7)_2^{(-)}$, **2**, which has a rich and diverse coordination chemistry.^{1,2} Alkylation of **2** with CH_3I affords $\text{Ph}_2\text{N}_3\text{C}_2(\text{C}_3\text{F}_7)_2\text{CH}_3$, **3**, in which the methyl group is attached to a terminal nitrogen atom. A similar reaction with CH_3HgCl was carried out to obtain the N-HgCH₃ analogue. The reaction was successful, but the product has an unanticipated structure with mercury being bonded to the central rather than the terminal nitrogen atom. This diimine complex exists in solution in equilibrium with another isomer in which mercury is bonded to the terminal nitrogen atom.

Results

Synthetic Chemistry and Dynamic Properties.

Reaction of **1** with NaH in THF produced $\text{Na}[\text{Ph}_2\text{N}_3\text{C}_2(\text{C}_3\text{F}_7)_2]$, treatment of which with 1 equiv of CH_3HgCl yielded $[\text{Ph}_2\text{N}_3\text{C}_2(\text{C}_3\text{F}_7)_2]\text{HgCH}_3$, **4**. Analytical and mass spectral data were wholly consistent with a single species of this composition. The ^1H NMR spectrum of **4** revealed two broad HgCH_3 signals in a 1:1 ratio at δ

1.0 (w/2 20 Hz) and -0.13 (w/2 14 Hz). These two peaks persisted unchanged after repeated recrystallizations from hexane, casting doubt on the initial hypothesis that the product was merely impure.

On cooling, both ^1H signals sharpen; the lower field one decreases in intensity, while that at $\delta -0.13$ increases. Conversely, upon heating, both resonances broaden and then coalesce. Exemplary variable-temperature ^1H NMR spectra (1,2- $\text{C}_2\text{D}_2\text{Cl}_4$ solvent) are shown in Figure 1. They indicate that **4** is actually a mixture of two slowly interconverting isomers, **4a** and **4b**, with the latter being more stable. Analysis of the DNMR data indicates that ΔH° and ΔS° are 10.5 kJ mol⁻¹ and 35 J K⁻¹ mol⁻¹, respectively, and that the barrier connecting the two isomers is 69 kJ mol⁻¹. The **4a:4b** ratio is little affected by solvent, being 1:1.1 in $\text{c-C}_6\text{D}_{12}$ at 30°. The structures of the two isomers were inferred from ^{19}F NMR spectra at -25°C . At this temperature, **4b** is more abundant, and so assignments to the two species present can be made on the basis of relative peak intensities. The minor isomer **4a** (at this temperature) has inequivalent C_3F_7 groups. By analogy to **3**, it is considered to be $[\eta^1\text{-1-Ph}_2\text{N}_3\text{C}_2(\text{C}_3\text{F}_7)_2]\text{HgCH}_3$, in which the HgCH_3 group is attached to one of the terminal nitrogen atoms. In contrast, isomer **4b** has equivalent C_3F_7 groups. Although several structures having this feature can be imagined, we believe that the correct one is $[\eta^1\text{-2-Ph}_2\text{N}_3\text{C}_2(\text{C}_3\text{F}_7)_2]\text{HgCH}_3$, in which the CH_3Hg group is attached to the central nitrogen atom. Although such a bonding mode has not been observed before in triazapentadienide chemistry, it is the one that occurs in the crystalline state (vide infra).

NMR Spectra. Data for **4a** and **4b** are collected in Table 1. The CH_3 protons in both are in a normal position for alkylmercury compounds.³ The CH_3 shifts

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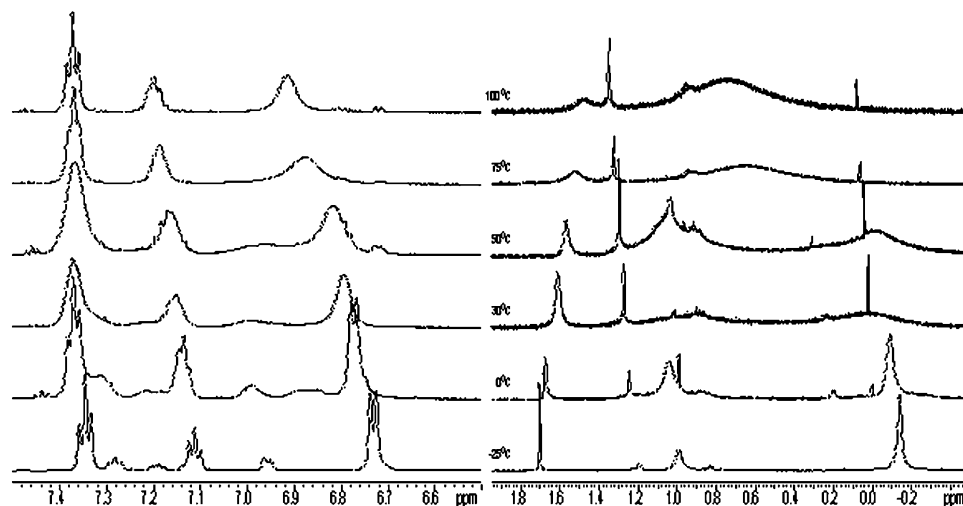


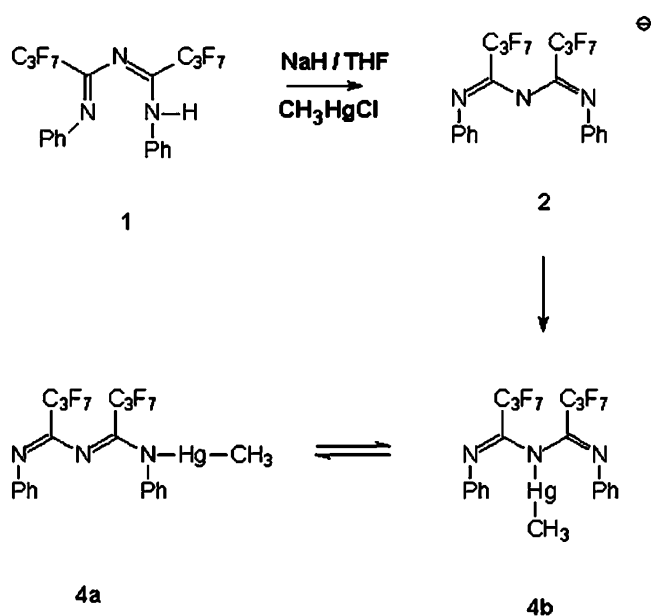
Figure 1. Variable-temperature ^1H NMR spectra of **4a** and **4b** in 1,2- $\text{C}_2\text{D}_4\text{Cl}_2$. The δ 1.7 peak at -25°C is attributed to adventitious water. Temperatures (top to bottom, $^\circ\text{C}$) are 100, 75, 50, 30, 0, and -25 .

Table 1. NMR Data for **4a** and **4b**^a

| 4a | | 4b | |
|-------------------|---|-------------------|---|
| ^1H | 1.0 ($w/2 = 20$, $^2J_{\text{HCHg}} = 191$) CH_3 | ^1H | -0.13 ($w/2 = 14$, $^2J_{\text{HCHg}} = 202$), CH_3 |
| ^{13}C | 147.6, 147.4 (t , $^2J_{\text{CF}} \sim 25$) CCF_2 145.7, 142.7 (Ph C_{ipso}) 129.6, 128.3 (Ph C_{meta}) 126.3, 124.69 (Ph C_{para}) 124.75, 122.6 (Ph C_{ortho}) 1.87 ($w/2 = 34$), CH_3 | ^{13}C | 151.8 (dd, $^2J_{\text{CF}} = 32, 21$), CCF_2 145.9 (Ph C_{ipso}) 129.9 (Ph C_{meta}) 126.2 (Ph C_{para}) 121.3 (Ph C_{ortho}) 1.64 ($w/2 = 16$, $J_{\text{CHg}} = 754$), CH_3 |
| ^{19}F | -80.42 (t , $^4J_{\text{FF}} = 11$), CF_3 -81.11 (t , $^4J_{\text{FF}} = 9$), CF_3 AB quartet, $\delta_{\text{A}} = -112.3$, $\delta_{\text{B}} = -113.8$, $J_{\text{AB}} = 270$, CF_2C AB quartet, $\delta_{\text{A}} = -115.7$, $\delta_{\text{B}} = -121.5$, $J_{\text{AB}} = 262$, CF_2C AB quartet, $\delta_{\text{A}} = -125.0$, $\delta_{\text{B}} = -125.8$, $J_{\text{AB}} = 289$, CF_3CF_2 AB quartet, $\delta_{\text{A}} = -127.8$, $\delta_{\text{B}} = -128.0$, $J_{\text{AB}} = 286$, CF_3CF_2 | ^{19}F | -80.21 (dd, $^4J_{\text{FF}} = 12, 7$), CF_3 -108.25 (d of heptets, 269, 8), $\text{CF}_2(\text{a})\text{C}$ -117.21 (d, 270), $\text{CF}_2(\text{b})\text{C}$ -124.17 (dt, 290, 12), $\text{CF}_3\text{CF}_2(\text{a})$ -126.83 (dd, 290, 5), $\text{CF}_3\text{CF}_2(\text{b})$ |
| ^{199}Hg | -926 ($w/2 = 429$) | ^{199}Hg | -770 ($w/2 = 103$) |

^a In 1,2- $\text{C}_2\text{D}_4\text{Cl}_4$ at -25°C . Coupling constants and line widths at half-height are in Hz.

Scheme 1



are substantially upfield of the model compound $\text{CH}_3\text{-HgCl}$, δ 6.03, but the $^2J_{\text{H-C-Hg}}$ values are unremarkable.⁴ ^{199}Hg chemical shifts cover such a large range that

it is difficult to make correlations with structure. The problem is compounded by the dominant effect of the paramagnetic shielding term.⁵ Nevertheless, shifts for **4a,b**, -926 and -770 ppm, are in the range found for two-coordinate mercury in CH_3HgX ($\text{X} = \text{Cl}, \text{Br}, \text{I}$; -811 , -910 , -1085 ppm, respectively).⁶ Changes in metal coordination number from 2 to 3 or 4 are associated with substantially decreased ^{199}Hg shielding.⁷ Given that δ -770 represents two-coordinate mercury in **4b**, the upfield shift of only 156 ppm in **4a** appears to be small and inconsistent with three-coordinate mercury, as would occur in a $\eta^3\text{-NCN}$ diaza-allyl structure.

Some additional aspects of the NMR data warrant comment. First, the ^1H , ^{13}C , ^{19}F , and ^{199}Hg resonances for **4a** are broader than for **4b**. This effect is presumably due to migration of the HgCH_3 moiety from central to terminal positions, a process, which, at this temperature, is intermediate on the NMR time scale. Second, in **4a**, the geminally inequivalent CF_3CF_2 geminal AB doublets ($J \approx 280$ Hz) show very different line widths. Further, the two relatively sharp CF_3CF_2 resonances

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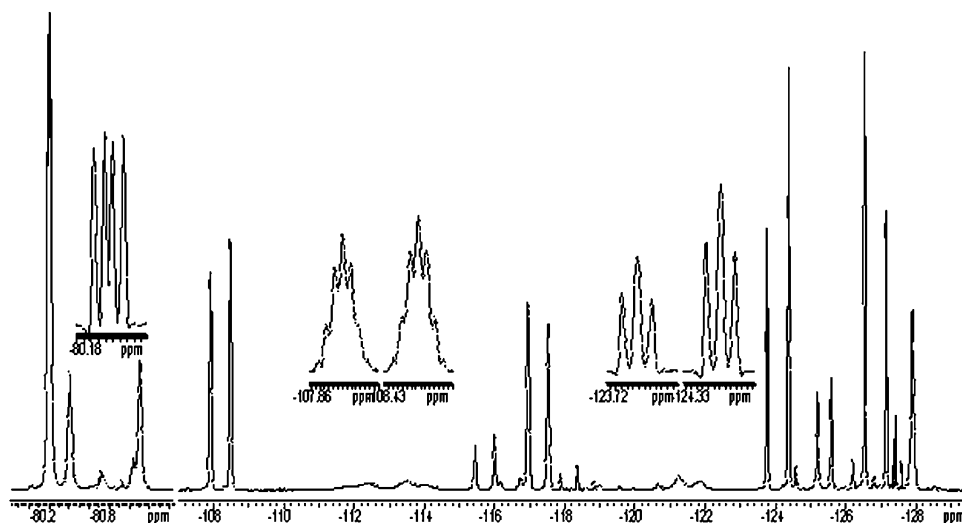


Figure 2. ^{19}F NMR spectrum of **4a** and **4b** in $1,2\text{-C}_2\text{D}_4\text{Cl}_2$ at -25°C . Insets of the resonances showing FF coupling are resolution enhanced. Other resonances of **4b** are exchange broadened.

Table 2. ^{19}F – ^{19}F NMR COSY Correlations in **4b**

| fluorine | δ (ppm) | J s (Hz) | COSY correlations |
|--|----------------|-------------------------|--|
| CF_3 | -80.21 | dd, 12.2, 6.9 | -108.25 , -117.21 |
| $\text{CF}_\text{A}\text{F}_\text{B}\text{N}$ | -108.25 | d of heptets, 270, 8 | -80.21 , -117.21 , -124.17 , -126.83 |
| $\text{CF}_\text{A}\text{F}_\text{B}\text{N}$ | -117.21 | d, 271 ^a | -80.21 , -108.25 , -124.17 |
| $\text{CF}_\text{A}\text{F}_\text{B}\text{CF}_3$ | -124.17 | dt, 289.4, 12.4 | -126.83 , -108.25 , -117.21 |
| $\text{CF}_\text{A}\text{F}_\text{B}\text{CF}_3$ | -126.83 | dd, 289, 5 ^b | -108.25 , -124.17 |

^a Broad resonances due to exchange; coupling under 10 Hz would not be resolved. ^b 5 Hz splitting is barely resolved.

in **4b** also show different line widths with resolved couplings in the downfield doublets but broader resonances without resolved coupling in the upfield doublets. We conclude that, at -25°C , both **4a** and **4b** are each involved in dynamic processes in addition to the equilibrium between the two. Similar effects have also been seen in **2**, and on the basis of DNMR studies of $[\text{Bu}_4\text{N}][\text{Ph}_2\text{N}_3\text{C}_2(\text{C}_3\text{F}_7)_2]$,⁸ we think that the process involves restricted rotation about the C–N bonds in the triazapentadiene ligand.

A ^{19}F NMR spectrum of **4a,b** at -25°C is shown in Figure 2; resolution-enhanced expansions of selected regions of the spectrum are displayed as insets and ^{19}F COSY correlations are listed in Table 2. A COSY spectrum is included in the Supporting Information. Scrutiny of the data in this figure for the $\eta^1\text{-N}(2)$ isomer **4b** reveals some unusual features. The CF_3 fluorines, $\delta -80.21$, appear as a double doublet, $J = 12$ and 7 Hz, due to four-bond coupling to the two inequivalent CF_2 fluorines, $\delta -108.25$ and -117.21 . The $^4J_{\text{FF}}$ values are within normal limits for such a spin–spin interaction, but it is remarkable that they are different. The ^{19}F resonance at $\delta -108.25$ is a symmetrical 270 Hz doublet of 8 Hz heptets. Large couplings to the $\delta -126.83$ fluorines are indicated by a COSY experiment, but only the $\delta -124.17$ resonance shows resolved $^3J_{\text{FF}}$ coupling (as a 12.4 Hz triplet). The COSY intensities for the correlations from the $\delta -80.21$ CF_3 to the geminally inequivalent fluorines at $\delta -108.25$ and -117.21 are identical despite the broadening present in the latter resonance (possibly due to additional dynamic processes

in **4b**). The broader $\delta -117.21$ resonance will exhibit attenuated COSY intensity, and so the larger coupling, 12.4 Hz, must be due to this fluorine. The COSY spectrum also indicates strong correlations between the 12.4 Hz triplet at $\delta -124.17$ and both the $\delta -108.25$ and -117.21 multiplets. The former correlation is 3-fold stronger, although both correlations must be from identical 12 Hz coupling constants, thus confirming the attenuation due to the greater line width of the latter.

There is also a strong correlation between the $\delta -108.25$ resonance and the poorly resolved 5 Hz multiplets in the AB pattern centered at $\delta -126.83$. We conclude that, to a first approximation, the multiplets for the fluorine at $\delta -108.25$ should be a 270 Hz doublet of 12.4 Hz doublets of 6.2 Hz quartets of 5 Hz doublets. Each half of the 270 Hz doublet is then approximately 12 Hz doublets of 6 Hz quintets, which gives an apparent 6 Hz heptet with calculated intensities of 1:4:7:8:7:4:1, in good agreement with experiment.

Vicinal $^3J_{\text{FF}}$ coupling constants in perfluoroalkyl groups are typically undetectable (<2 Hz). Larger values of $^3J_{\text{FF}}$ occur in $\text{XCF}_2\text{--CF}_2\text{Y}$ if X and Y have electronegativities different from that of carbon. They range from $+3.5$ Hz in $\text{CF}_3\text{--CF}_3$ to -23 Hz in $\text{CF}_2\text{Cl--CFCI}$.^{9,10} The $^3J_{\text{FF}}$ coupling constants are also a function of dihedral angle: they are -16.1 and -21.5 Hz in the asymmetrical and symmetrical isomers of $\text{CF}_2\text{Br--CFBr}_2$.¹¹ It is unclear how to assess the effect of the MeHgN substituent on the electron distribution in the C_3F_7 groups. It appears, however, that the conformations of the $\text{CF}_3\text{--CF}_2\text{Y}$ moieties are impacted because the two $^4J_{\text{FF}}$ couplings differ by 5.3 Hz in **4b** but are identical in **4a**.

Evidence for a second isomer of **4** in solution was also obtained using infrared spectroscopy. The solid in a Nujol mull shows two bands in the C–N stretching region at 1606 and 1588 cm^{-1} that are attributable to **4b**. In $1,2\text{-C}_2\text{D}_2\text{Cl}_4$ solution, the same two bands (at 1610 and 1587 cm^{-1}) are seen, but, in addition, there is an additional C–N stretching band appearing as a shoulder

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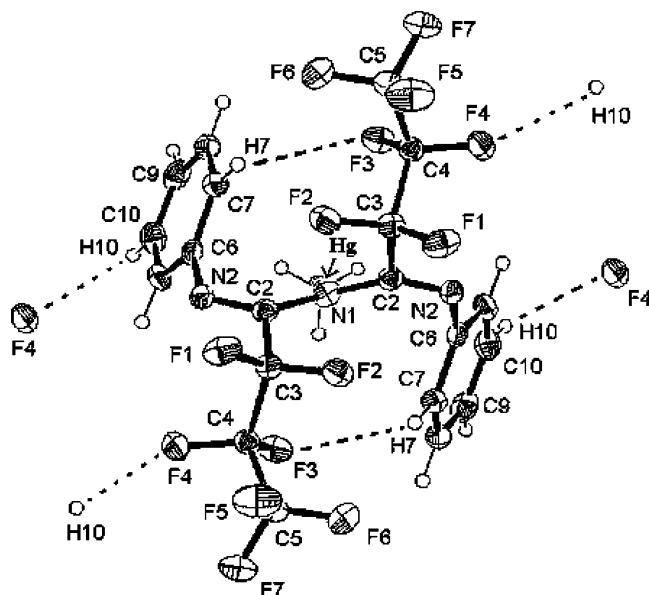


Figure 3. ORTEP drawing of η^1 -[PhN=C(C₃F₇)₂]NHgMe, **4b**. The Hg atom (arrow) lies between N1 and the CH₃ group behind it.

Table 3. Selected Bond Distances (Å) Angles (deg) in **4b**

| | |
|------------------|------------|
| C(1)–Hg(1) | 2.029(17) |
| Hg(1)–N(1) | 2.168(14) |
| N(1)–C(2) | 1.368(9) |
| C(2)–N(2) | 1.272(8) |
| N(2)–C(6) | 1.414(8) |
| C(1)–Hg(1)–N(1) | 180.000(2) |
| C(2)–N(2)–C(6) | 119.1(5) |
| N(1)–C(2)–N(2) | 129.6(7) |
| C(2)–N(1)–C(2)#1 | 127.3(12) |

at 1640 cm^{−1} that is attributed to **4a** (cf. 1645 and 1588 cm^{−1} for **3** in Nujol).

Molecular Structure of [Ph₂N₃C₂(C₃F₇)₂]HgCH₃. An ORTEP view of the structure and numbering scheme are shown in Figure 3. Intramolecular bond distances and angles are summarized in Table 3.² The N₃C₂ skeleton approximates a helix. The CH₃Hg moiety is bonded to the center nitrogen atom [N(1) in Figure 3] in it. C(1), Hg, and N(1) lie on a crystallographic 2-fold axis, and the N(1)–Hg–C(1) axis coincides with the crystallographic *c* axis. The CH₃ group is 2-fold rotationally disordered with equal populations of the two conformations. A packing diagram viewed along the crystallographic *c* axis is shown in Figure 4.

There is a short–long–short–long pattern in the C–N bond lengths: the C(2)–N(2) and N(1)–C(2) distances are 1.272(8) and 1.368(9) Å, respectively. This is consistent with localized C=N and C–N bonding, and in valence bond formalism, the structure can be written as PhN=C(C₃F₇)–N(HgCH₃)–C(C₃F₇)=NPh. For comparison, in a series of tri- and tetraaza-heptadienyl-lithium compounds, C(sp²)=N(sp²) and C(sp²)–N(sp²) bond distances of 1.28 and 1.37 Å, respectively, were reported.¹² The coordination geometry of mercury is precisely linear because of crystallographic constraints, in accord with the tendency for linear geometry in organomercury compounds. D(Hg–N), 2.168(14) Å, is

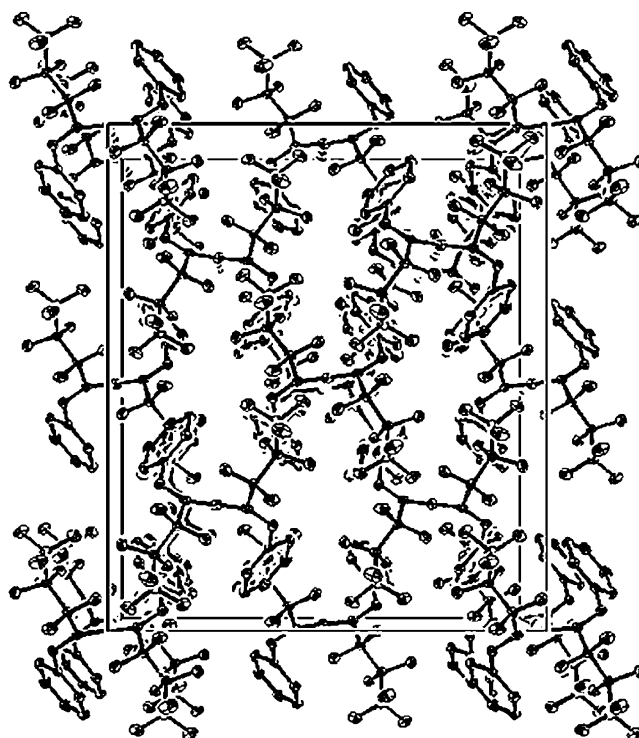


Figure 4. ORTEP drawing of η^1 -[PhN=C(C₃F₇)₂]NHgMe, **4b**; packing diagram along the *c*-axis.

rather long in comparison with, for example, [(7-methylguanidine)HgCH₃]·2H₂O, 2.101(5) Å, and [(7-methylguanidine·H)HgCH₃][NO₃], 2.111(4) Å.¹³ The intermolecular and intramolecular distances between the center of the phenyl rings to Hg are 4.78 and 3.20 Å, respectively.

Each molecule contains four equivalent 2.50 Å intermolecular contacts between H(10A), a meta hydrogen atom in a phenyl ring, and F4, located in the β-CF₂ group in the adjacent PhN=C(C₃F₇) group. The C(4)–F(4)–H(10A) and C(10)–H(10A)–F(4) angles, 127.5° and 164.9°, respectively, indicate a relatively strong interaction between F(4) and H(10A). The molecule contains two equivalent 2.74 Å intramolecular contacts between H(7A), an ortho hydrogen atom in a phenyl ring, and F(3), located in the β-CF₂ group in the adjacent PhN=C(C₃F₇) group. The C(4)–F(3)–H(7A) and C(7A)–H(7A)–F(3) angles, 115.3° and 124.8°, respectively, are so acute as to imply that this interaction is primarily electrostatic in nature.¹³ There are four layers of molecules in the unit cell, and the orientation of the molecules in a single layer is identical. Adjacent layers are related by a translation along the *c* axis by *d*/4 and molecules within a layer are rotated 90° about the *c* axis with respect to adjacent layers. Intramolecular contacts are between layers separated by *d*/2 and which have the same molecular orientation.

Discussion

Nucleophilic displacement of chloride from CH₃HgCl by the triazapentadienide anion Ph₂N₃C₂(C₃F₇)₂[−] affords

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[Ph₂N₃C₂(C₃F₇)₂][HgCH₃]. Variable-temperature ¹H and ¹⁹F NMR spectra showed that, in 1,2-C₂D₂Cl₄ or CDCl₃ solution, this compound exists as two slowly interconverting (at room temperature) isomers. The minor, less stable, and asymmetrical one, **4a**, is formulated as having the CH₃Hg group attached to a terminal nitrogen atom. The more abundant, more stable symmetrical isomer, **4b**, is considered to have the CH₃Hg moiety attached to the central nitrogen atom, and it is this bonding mode that was revealed by an X-ray diffraction study of crystals obtained from hexane.

As the temperature is increased, the CH₃Hg group moves increasingly rapidly among the two terminal and central nitrogen sites. Metallotropic rearrangements, in which a metal atom moves from one ligating site to another, are well known in organometallic and coordination chemistry. Pertinent examples are the 1,3-shifts of HgR groups in ArN(HgR)–N=NAr' and ArN(HgR)=CH–NAr'.¹⁵ Often, only one of several equilibrating structures is observed in solution, the other(s) being intermediates lying in shallow wells on the potential energy surface. It is therefore interesting that, in the case of **4**, the concentrations of the two isomers at 25 °C are instead approximately equal. The long Hg–N distance in **4b**, as well as the similarity of its ¹⁹⁹Hg chemical shift and ²J_{HCHg} coupling constant to the methylmercury halides, suggests that the [PhN=C(C₃F₇)₂]₂N group is electron-withdrawing, cf. (CF₃SO₂)₂N.¹⁶

The triazapentadienide ligand **2** bears comparison with β-diketones, which most often occur as η²-O,O structures.¹⁷ However, heavy metallic elements such as Pt and Hg give rise to η¹-C structures in which the metal is attached to the central carbon atom of the ligand. Bis(dipivaloylmethyl)mercury crystallizes as an isomer in which both ligands are C-bonded to the metal, but in solution, additional isomers in which one or both diketones are in a η¹-enol form were detected by NMR.¹⁸ This is analogous to the **4a**–**4b** rearrangement. However, with β-diketone ligands, the ligating atom changes from carbon to oxygen, whereas in the triazapentadienide complex, the ligating atom in both forms is nitrogen. Thus, at this point, it is not understood why **4b** is more stable than **4a**.

Similarly, it is not clear why only **4b** crystallizes from a solution containing both **4a** and **4b** except to note that, in solution, the latter is more stable. When **4b** is melted then cooled and allowed to crystallize, the melting point is unchanged. This indicates that only **4b** crystallizes from the melt.

To see if metallotropic rearrangements analogous to that seen for mercury would occur with other heavy metals, [Ph₂N₃C₂(C₃F₇)₂][AuPPh₃], **5**, was prepared from

Na[Ph₂N₃C₂(C₃F₇)₂] and Ph₃PAuCl. This compound has nonequivalent C₃F₇ groups, and so it is believed to contain a η¹-Ph₂N₃C₂(C₃F₇)₂ ligand as in **3** and **4a**. The ¹⁹F NMR spectra of this compound are both subtle and complex and have not been completely analyzed. The CF₂C fluorine resonances are broad. The broadening is not symmetric within either CF₂ group, suggestive of three dynamic processes: two averaging the inequivalent CF₂ fluorine nuclei in different CF₂ groups and another averaging the two different C₃F₇ groups. The latter process is somewhat slower on the NMR time scale because there is no line broadening evident in the resolution-enhanced ¹³C NMR of the N–C₆H₅ groups. We believe that the first two processes reflect restricted rotation about C–N bonds in the N₃C₂ skeleton. However, in the context of the isomeric pair of HgMe compounds **4a**, **b**, ¹⁹F spectra between +50 and –50 °C show no evidence of an additional, stable, symmetrical isomer corresponding to **4b**.

Experimental Section

General Procedures. NMR spectra were obtained on a Varian XL-600 instrument with a ¹H operating frequency of 600 MHz. Chemical shifts are expressed in ppm relative to internal (CH₃)₄Si (¹H and ¹³C) or CFCl₃ (¹⁹F); coupling constants and line widths at half-height are in Hz. {¹H}¹⁹⁹Hg spectra were referenced to external saturated aqueous Hg(NO₃)₂ (δ –2340 ppm) but are expressed relative to (CH₃)₂Hg (0.0 ppm).

[Ph₂N₃C₂(C₃F₇)₂][HgCH₃], **4.** A suspension of (excess) NaH in THF and 0.56 g of **1** (1 mmol) were stirred under N₂ until gas evolution ceased. The reaction mixture was allowed to settle and decanted by cannula into a clean Schlenk tube containing 0.25 g (1 mmol) of MeHgCl. After stirring for 16 h, the solvent was evaporated. The residue was sublimed at 100–120 °C onto a water-cooled probe to give 0.66 g of product. This was crystallized from hexane to give 0.51 g (66%) of colorless blocks, mp 88–89 °C. The compound developed a light pink color on standing in daylight and so was stored in a dark bottle. Anal. Calcd (found) for C₂₁H₁₃F₁₄HgN₃: C, 32.6 (32.5); H, 1.7 (1.7); Hg, 26.0 (25.8); N, 5.4 (5.5). MS: *m/z* 771.038 with Hg isotopomers; 606.057 (M⁺ – C₃F₇); 558.052 (M⁺ – HgCH₃). IR (Nujol): 1606, 1588, 1351, 1325, 1220, 1160, 1116, 847, 758, 743, 706, 698, 651 cm^{–1}. Raman (neat, λ_{ex} 782 nm): 1635, 1585, 1227, 1002 cm^{–1}. UV [isooctane, λ_{max} (log ε)]: 202 (3.97), 285 (sh) nm. Molar conductance (1.4 × 10^{–3} M in CH₃CN): 14 Ω^{–1} cm² mol^{–1}. Crystals for the X-ray study were grown from hexane solution.

[Ph₂N₃C₂(C₃F₇)₂][AuPPh₃], **5.** To a solution of 1 mmol of Na[Ph₂N₃C₂(C₃F₇)₂] in 15 mL of THF was added 0.495 g (1 mmol) of Ph₃PAuCl. After stirring for 16 h, solvent was evaporated. The residue was extracted with boiling heptane. Concentration and cooling of the filtered extract gave 0.60 g (54%) of a yellow solid that crystallized upon standing, mp 91–93 °C after vacuum-drying. Anal. Calcd (found) for C₃₈H₂₅AuF₁₄N₃P: C, 44.8 (44.8); H, 2.5 (2.6); N, 4.4 (4.1). MS: *m/z* 1017.1155 (M⁺, calcd 1017.1222), 848 (M⁺ – C₃F₇). IR (Nujol): 1606, 1569, 1236, 1207, 1121, 1104, 748, 594, 547, and 506 cm^{–1}. NMR (CDCl₃, 30 °C) ¹⁹F: –80.2 (t, ⁴J_{FF} = 7) and –81.1 (t, ⁴J_{FF} = 9) (CF₃), –111.3 and –111.8 (AB quartet, J_{AB} = 265, CF₂C), –116.1 and –122.0 (AB quartet, J_{AB} = 259, CF₂C), –126.6 and –125.7 (AB quartet, J_{AB} = 281, CF₃CF₂), –127.9 and –128.2 (AB quartet, J_{AB} = 283, CF₃CF₂). ³¹P: 26.8 (s). UV [CH₃CN, λ_{max} (log ε)]: 204 (4.90), 240 (sh), and 320 (sh) nm. Molar conductance (1.8 × 10^{–3} M in CH₃CN): 11 Ω^{–1} cm² mol^{–1}.

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Table 4. Crystal Data and Refinement for 4b

| | |
|--|---|
| formula | C ₂₁ H ₁₃ F ₁₄ HgN ₃ |
| fw | 773.93 |
| temp, K | 173(2) |
| cryst habit, color | block, colorless |
| cryst size, mm | 0.40 × 0.37 × 0.21 |
| cryst syst | orthorhombic |
| space group | <i>Fdd2</i> |
| unit cell dimens | <i>a</i> = 17.814(4) Å, α = 90° <i>b</i> = 20.590(4) Å, β = 90° <i>c</i> = 13.184(3) Å, γ = 90° |
| <i>V</i> , Å ³ | 4835.7(17) |
| <i>Z</i> | 8 |
| ρ_{calcd} , g cm ⁻³ | 2.126 |
| λ , Å | 0.71073 |
| abs coeff, mm ⁻¹ | 6.490 |
| θ range for data collection, deg | 2.16 to 27.57 |
| no. of reflns collected | 10 691 |
| no. of indep reflns | 2426 [<i>R</i> (int) = 0.0345] |
| max., min. transmn | 1.000000 and 0.599670 |
| no. of data/restraints/params | 2774/1/179 |
| GOF on <i>F</i> ² | 1.061 |
| final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)] | <i>R</i> 1 = 0.0282, <i>wR</i> 2 = 0.0694 |
| <i>R</i> indices (all data) | <i>R</i> 1 = 0.0356, <i>wR</i> 2 = 0.0729 |
| abs struct param | −0.025(11) |
| largest diff peak and hole, e Å ⁻³ | 1.103 and −0.653 |

A similar reaction with Et₃PAuCl produced metallic gold.

X-ray Crystallographic Analysis. A crystal was secured to a 0.1 mm glass fiber and mounted on a Bruker SMART system for data collection. A preliminary set of cell constants was calculated from reflections harvested from 3 sets of 20 frames. The initial sets of frames were oriented so that orthogonal wedges of reciprocal space were surveyed. This produced orientation matrixes determined from 180 reflec-

tions. Data collection was carried out with a frame time of 30 s and a detector distance of 4.9 cm. A randomly oriented region of reciprocal space was surveyed to the extent of 1.5 hemispheres and to a resolution of 0.77 Å. Three major sections of frames were collected with 0.50° steps in ω at three different ϕ settings and a detector position of −28° in 2θ . Intensity data were corrected for absorption and decay with SADABS.¹⁹ Final cell constants were calculated from 3800 strong reflections from the actual data collection after integration (SAINT 6.01).²⁰

The structure was solved using SHELXS-86²¹ and refined using SHELXL-97. The space group was determined on the basis of systematic absences and intensity statistics. A direct-methods solution was calculated that provided most non-hydrogen atoms from the E-map. Full-matrix least-squares/difference Fourier cycles were performed that located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters unless otherwise noted. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. No disorder or twinning was found in the structure. Crystallographic data are summarized in Table 4.

Supporting Information Available: ¹⁹F COSY spectrum of **4a,b** and X-ray file in CIF format. This information is available free of charge via the Internet at <http://pubs.acs.org>.

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(21) SHELXTL-Plus V5.10; Bruker Analytical X-Ray Systems: Madison, WI.