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Reactions of the Perfluoroalkyltriazapentadiene $Ph_2N_3C_2(C_3F_7)_2H$ with Acids, Bases, and Water

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Treatment of the bis(perfluoroalkyl)triazapentadiene $PhN{=}C(C_3F_7){-}N{=}C(C_3F_7){-}NHPh$, **2**, with bases affords salts of the conjugate base. Alkylation of the Na^+ salt with CH_3I yields $PhN{=}C(C_3F_7){-}N{=}C(C_3F_7){-}NMePh$. The crystal structure of $[Bu_4N][Ph_2N_3C_2(C_3F_7)_2]$ demonstrates a twisted, zigzag geometry for the anion in the solid state, but in solution, it is conformationally unstable. Both compounds are stable in aqueous methanol, but hydrolysis occurs under acidic conditions. Protonation with CF_3SO_3H acid occurs at the sp^2 nitrogen to give $[PhN\underset{H}{\overset{\cdot\cdot}{-}}HC(C_3F_7)\overset{\cdot\cdot}{-}N\overset{\cdot\cdot}{-}C(C_3F_7)\overset{\cdot\cdot}{-}NHPh][CF_3SO_3]$. Heating **2** in CF_3SO_3H produces 2,4-bis(heptafluoropropyl)-1,3-quinazoline.

Introduction

Pentadienyl anions, the acyclic analogues of $C_5H_5^-$, that contain heteroatoms as part of the five-atom conjugated π system have attracted attention because of their synthetic utility and theoretical interest.[1] The reaction of perfluoro-5-aza-4-nonene, $C_3F_7{-}CF{=}N{-}C_4F_9$, **1**, with primary amines yields triazapentadienes, $RN(3){=}C(2)(C_3F_7){-}N(1){=}C(1)(C_3F_7){-}N(2)HR$ (the skeletal atom numbering scheme is designed for easy reference to that in the crystal structure of the derived anion, vide infra), whose chemistry has recently been outlined.[2] This paper reports some fundamental chemistry of **2** ($R = Ph$), an exemplary member of this broad class of compounds, which is obtained from **1** and aniline. Triazapentadienes are amphoteric because they contain an ionizable NH hydrogen atom and two potentially basic sp^2 nitrogen atoms. We describe here the synthesis, structure, and reactivity (including hydrolysis) of the conjugate base and conjugate acid of **2**. The alkali metal and silver salts of **2** reported here are useful in preparing inorganic and organometallic coordination complexes through metathetic reactions.

Results and Discussion

Triazapentadiene **2** is a weak monoprotic acid. Its pK_a in dimethyl sulfoxide is 14.3. Salts of the conjugate base of **2**, $[C_3F_7{-}C({=}NPh){-}N{-}C({=}NPh){-}C_3F_7]^-$, were obtained from onium (e.g., Bu_4N^+, Bu_4P^+, Me_3S^+) or metal (e.g., K^+, Cs^+) hydroxides in aqueous methanol, from metal hydrides (NaH, KH) in tetrahydrofuran, or from alkyllithium reagents in hydrocarbon solvents. Thus, for example, $Li[Ph_2N_3C_2(C_3F_7)_2]$, **3**, was obtained from **2** and *n*-butyllithium in hexane; $[Bu_4N][Ph_2N_3C_2(C_3F_7)_2]$, **4**, using $[Bu_4N]OH$ in methanol−water; and $K[Ph_2N_3C_2(C_3F_7)_2]$, **5**, from **2** and KH in THF.

A survey of reactions of **2** with various metal oxides and carbonates (e.g., HgO, $CoCO_3$) uncovered only one example of a salt (or complex) that could be prepared in organic solvents. Refluxing **2** with a suspension of Ag_2O in acetonitrile gave, after evaporation of the solvent, $Ag[Ph_2N_3C_2(C_3F_7)_2]$, **6**. This compound behaved as a 1:1 electrolyte in CH_3CN, the only solvent found in which it did not decompose. Reaction with $Ph_2PC_2H_4PPh_2$ afforded $[(diphos)Ag][Ph_2N_3C_2(C_3F_7)_2]$, **7**. This compound also behaved as a 1:1 electrolyte in CH_3CN although NMR experiments with more concentrated solutions were suggestive of cation−anion interaction.

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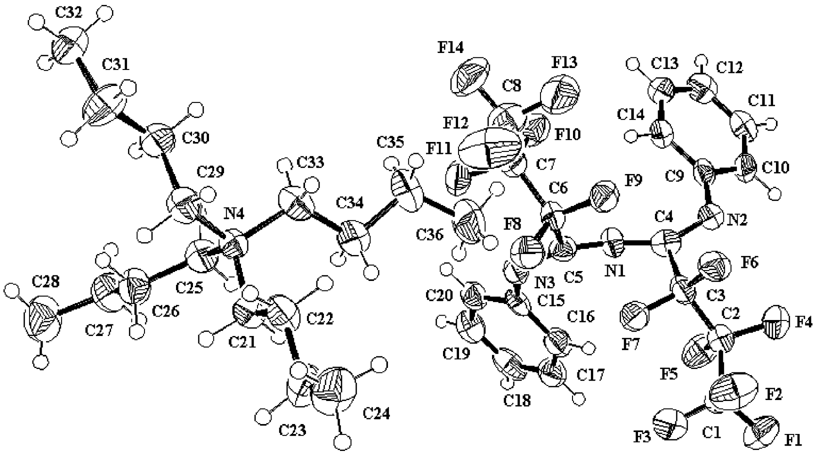

Figure 1. ORTEP drawing of the cation and anion components of **4** showing the numbering scheme.

Thus, in $CDCl_3$, the ^{19}F spectrum comprises three broad resonances at −81, −115, and −126 ppm; the ^{31}P NMR spectrum is a doublet $\delta = 0.77$ with $J(^{107,109}AgP) = 201$ Hz, whereas, in CD_3CN, the ^{19}F resonances are sharper but the ^{31}P signal is a broad hump. The infrared spectra of both silver complexes as Nujol mulls show C−N bands in the same positions as the alkali metal and quaternary ammonium salts of **2**, substantiating their formulation as ionic materials.

For the tetrabutylammonium salt **4**, the C═N stretching bands in the infrared [Raman] spectrum occur at 1606 (m) [1615 (s)] and 1551 (s) [1587 (m)] cm^{-1}. Corresponding bands in the Li^+ salt are at 1616 (s) and 1579 (s) cm^{-1}. The higher frequency band is attributed to the symmetric combination mode, and the lower frequency band to the asymmetric combination. This accounts for the interchange of intensities in these two bands in the infrared and Raman spectra. The lower C−N stretching frequencies (vs 1682 (s) [1691] and 1633 (m) [1625] cm^{-1}) in **2** indicate a reduction in C−N bond order upon deprotonation of **2**. The small separation between $\nu(CN)_{sym,asym}$, 55 and 49 cm^{-1} in **4** and **2**, respectively, indicates little stretch−stretch interaction between the intervening N atom.[3] A similar conclusion follows from the ^{15}N NMR chemical shifts of the terminal nitrogen atoms. In **2**, $\delta^{15}N$ for *N*Ph and *N*(Ph)H are 288.4 and 113.7 ppm (NH_3 reference), and for **3** in acetone, $\delta^{15}N$ for these (now equivalent) nitrogen atoms is 234.5 ppm and $J^{15}{}_{N}{}^{13}{}_{C}$ is 7 Hz.[2] Thus, deprotonation causes the sp nitrogen to shift to higher field, and the sp^2 nitrogen moves to lower field reflecting the changes in hybridization at these atoms. There is little concomitant change in $\delta^{13}C$, 147.3 ppm, compared with 145.2 (C(2)) and 139.9 ppm (C(1)) in **2**.

In chloroform solution, **4** exhibits interesting dynamic behavior. The fluorine nuclei in both CF_2 groups are geminally inequivalent and show exchange broadened pairs of AB doublet ^{19}F resonances in which the weaker, outer lines are significantly broader than the inner ones. Further analysis of the spectra showed that the free energy of activation for the process that averages the pairs of geminally inequivalent fluorine atoms is 14.8 kcal mol^{-1} at 296 K. We suggest that this process corresponds to generation of different conformations of the $Ph_2N_3C_2(C_3F_7)_2^-$ ion by rotation about one of the C−N bonds (vide infra). It could, for example, involve conversion of the W-shaped anion into an energetically similar S-shaped conformer. Solvent and cation effects for the rearrangement are small. ^{19}F DNMR spectra of the lithium salt **3** in acetone disclose a rearrangement process analogous to that just described for the Bu_4N^+ salt. The activation energy, 14.7 kcal mol^{-1} at 295 K, is the same within experimental error. The close similarity in activation energies and the narrow ^7Li resonance (*w*/2 16 Hz, δ −3.66) indicate the absence of a chemically significant cation−anion interaction in **3** in solution.

Table 1. Bond Distances (Å) and Angles (deg) in **4**

N3-C5	1.288(5)	C5−N3−C15	119.3(4)
N1−C5	1.336(5)	N3−C5−N1	129.6(4)
N1−C4	1.337(6)	C5−N1−C4	129.4(4)
N2−C4	1.297(6)	N2−C4−N1	130.0(4)
N2−C9	1.415(6)	C4−N2−C9	119.7(4)
N3−C15	1.411(6)	N2−C4−C3	110.9(4)
		N3−C5−C6	110.9(4)
		N1−C5−C6	118.5(4)

The conjugate base of **2** behaves as a nucleophile and can readily be alkylated. For example, $Na[Ph_2N_3C_2(C_3F_7)_2]$, prepared from **2** and NaH in THF, reacted with methyl iodide to give C_3F_7−C(═NPh)−N═C(NMePh)−C_3F_7, **8**, the *N*-methyl analogue of **2**. Electrophilic substitution occurs exclusively at the terminal nitrogen atom(s), suggesting (but not proving) that these are the sites of highest charge density in the anion.

Structure of $[Bu_4N][Ph_2N_3C_2(C_3F_7)_2]$. The crystal structure of **4** consists of well separated cations and anions. An ORTEP view of the complete ion pair is shown in Figure 1, and important bond distances and angles are collected in Table 1. If the N,C skeleton of the anion in **4** is represented as N(2)−C(4)−N(1)−C(5)−N(3) (the numbering is that used in Figure 1), a short−long−long−short pattern of C−N bond lengths can be seen: *d*(N(2)−C(4)) and *d*(C(5)−N(3)) are 1.297(6) and 1.288(5) Å, respectively, while *d*(C(4)−N(1)) and *d*(C(5)−N(1)) are 1.337(6) and 1.336(5) Å, respectively. The short bonds correspond, formally, to C═N fragments, and the long bonds to C−N moieties with a bond order

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[3] Cf. 33 cm^{-1} in ZrH_2D_2: Chertihin, G. V.; Andrews, L. *J. Am. Chem. Soc.* **1995**, *117*, 5402.

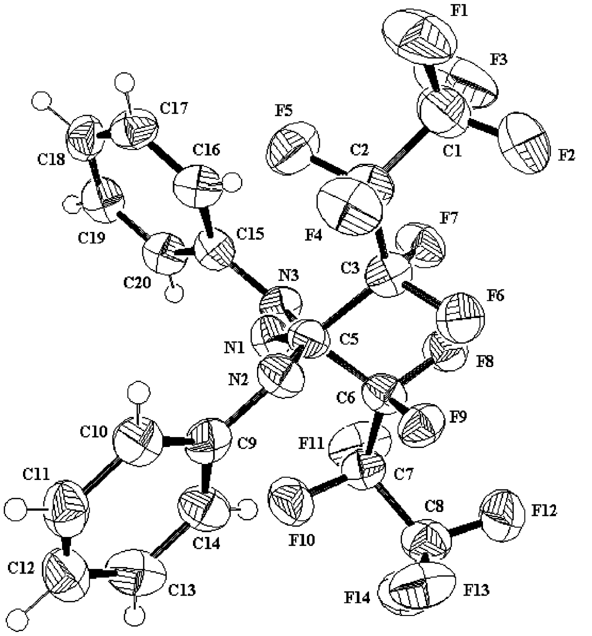

Figure 2. View of the $Ph_2N_3C_2(C_3F_7)_2(-)$ anion looking down the C(4)−C(5) vector.

between 1 and 2. This pattern indicates that the C═N units in $Ph_2N_3C_2(C_3F_7)_2^-$ are weakly interacting (conjugated), in contrast with those in **2** (vide infra). The N_3C_2 framework is not planar (even though the largest displacement from its least-squares plane is 0.23 Å at C(5)). It has instead a distinct helical twist such that the dihedral angle between the N(3)−C(5)−N(1) and N(1)−C(4)−N(2) planes is 55.8°. This framework describes a twisted zigzag trace or a W-shaped anion. This description is supported by noting that the N(2)−C(4)−N(1), C(4)−N(1)−C(5), and N(1)−C(5)−N(3) bond angles are 130.0(4), 129.4(4), and 129.6(6)°, respectively. Figure 2 shows a view of the $Ph_2N_3C_2(C_3F_7)_2$ anion looking down the C(4)−C(5) vector. N(1,2,3) and the two N-terminal phenyl groups are clustered to one side. N(1,2,3) atoms are seen not to be collinear in this projection because of the twist already noted. The two C_3F_7 groups are on the other side, and the anion has an *endo* structure. The terminal C−N bonds, N(2)−C(9) (phenyl) and N(3)−C(15)(phenyl), are 1.411(6) and 1.415(6) Å, comparable to the 1.402 Å C−N distance in aniline.[4] The dihedral angle between the two C_6H_5 planes is 73.65°.

The compounds 1,7-bis(trimethylsilyl)-1,3,5,7-tetraazaheptatrienylsodium[5] and -lithium[6] provide useful structural paradigms for **4** despite the complex interactions of the electropositive alkali metals with the several nitrogen atoms in the anion. In the former, C−N distances of 1.25 Å were considered to correspond to double bonds between carbon and nitrogen, 1.38 Å to short single bonds, and 1.33 Å to distances characteristic of a delocalized system.

The geometrical structure of $Ph_2N_3C_2(C_3F_7)_2^-$ in the crystal lattice is grossly different from that of its conjugate acid $Ph_2N_3C_2(C_3F_7)_2H$, and it is evident that substantial rearrangement attends seemingly simple detachment of a proton. Using the same HN(2)−C(4)−N(1)−C(5)−N(3) representation of the N_3C_2 skeleton in **2**, the pattern of C−N bond lengths is instead long−short−long−short, implying conjugation of the C═N units. The N(2)−C(4), C(4)−N(1), N(1)−C(5), and C(5)−N3 distances are 1.345(11), 1.258(10), 1,377(9), and 1.259(9) Å, respectively. The angles centered at N(1), C(4), and C(5) are similar, 131.8(6)°, 132.7(7)°, and 131.6(7)°, respectively. However, relative to $Ph_2N_3C_2(C_3F_7)_2H$, the N_3C_2 skeleton in the anion is rotated 180° about C(4)−N(1) so that the former is U-shaped whereas the latter is W-shaped. It is possible that both conformers are present in solution, and that their interconversion leads to permutation of geminally inequivalent CF_2 fluorine atoms as already described. There is abundant precedent for such rotational processes in homoatomic pentadienyl anions (and also enamines, for which the barrier to torsional isomerization is ca. 10 kcal mol^{-1}) that interconvert U- and W-shaped anions.[7] In pentadienyllithium itself, the carbon framework in the ground state structure is thought to be W-shaped, an arrangement that minimizes steric strain and permits electron delocalization over the greater distance than U- or S-shaped structures. However, NMR studies have shown that this compound is conformationally dynamic in solution[8] as is the case for its triaza congener **4** already described.

Hydrolysis of $Ph_2N_3C_2(C_3F_7)_2H$. Solutions of **2** in neutral methanol−water showed no change by ^{19}F NMR after heating for 4 h at 65°. Similar solutions of $Na[Ph_2N_3C_2(C_3F_7)]$, produced by adding 1 equiv of NaOH, were stable under the same conditions. In contrast, heating solutions of **2** in aqueous methanol containing ≥1 equiv of HCl produced a complex mixture of products. Analysis by GC/MS and infrared and NMR spectroscopy showed that it contained $[PhNH_3]Cl$, $(C_3F_7CO)_2NH$, $C_3F_7CONH_2$, $C_3F_7CO_2H$, and a bis(perfluoropropyl)quinazoline that will be described in detail. Thus, **2** and its conjugate base exhibit substantial hydrolytic stability, but gross degradation occurs under acidic conditions. Because it seemed likely that acid-catalyzed hydrolysis might involve protonation, reactions of **2** with acids under anhydrous conditions were studied.

Protonation of $Ph_2N_3C_2(C_3F_7)_2H$. Dissolution of **2** in trifluoromethanesulfonic (triflic) acid was mildly exothermic. Conversion to the triflate salt of its conjugate acid, $[Ph_2N_3C_2(C_3F_7)_2H_2][CF_3SO_3]$, **9**, was quantitative. Quenching with water at this point regenerated **2**, and so, the structure of **9** was deduced from solution-phase experiments. The conclusion from many NMR experiments is that the cation in **9** has a static C_{2v} structure and may be represented as PhN(1)1H−C(C_3F_7)−N(2)−C(C_3F_7)−N(3)HPh$^+$ for which numerous resonance structures can be written. Importantly, the ^{15}N NMR spectrum of the analogue of **9** in which N(1,3)

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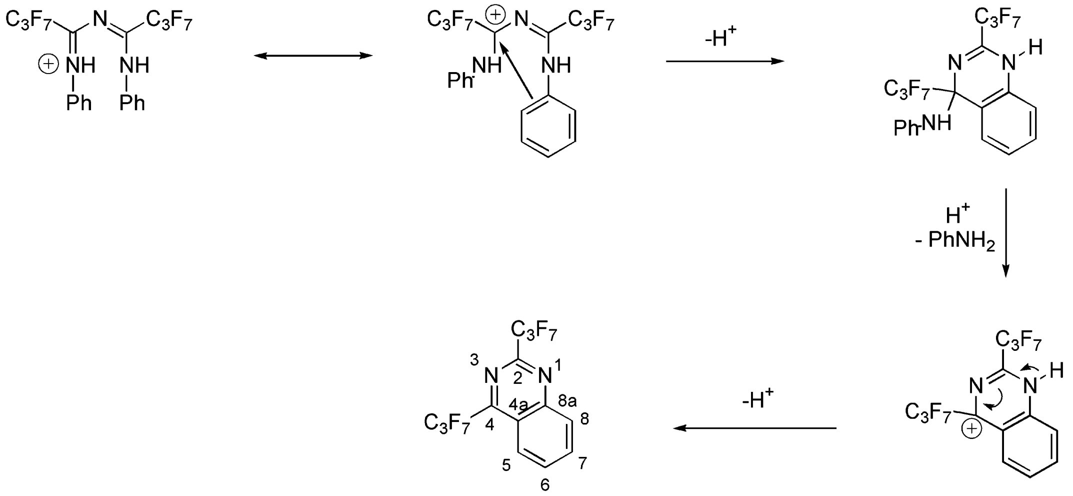
Scheme 1



atoms were labeled with ^{15}N, shows a doublet at 151 ppm with J_{NH} being 95 Hz. This indicates that **9** has a static structure on the NMR time scale and that it is not undergoing rapid loss and reaccession of its proton. ^{1}H and ^{13}C NMR indicated that both phenyl rings were equivalent; the C_3F_7 groups are equivalent as well by ^{19}F NMR, but as is often the case in **2** and its derivatives, the α- and *β*-CF_2 fluorine nuclei are geminally inequivalent. A detailed assignment of the NMR spectra is given in the Experimental Section. In **9**, δ^{13}C, 150.6 ppm, is only 3.3 ppm deshielded relative to the skeletal carbon atoms in the anion in **4**. The Raman spectrum of **9** in CF_3SO_3H in the C−N stretching region shows bands at 1633(m) and 1586(s) cm^{-1} compared with 1625(s) and 1591(m) cm^{-1} in **2**. This suggests that the C−N bond order is not greatly affected by protonation notwithstanding that these frequencies may not represent pure modes.

Atomic charges at N(1,2,3) in $PhN(3){=}C(C_3F_7){-}N(1){=}C(C_3F_7){-}N(2)HPh$ were calculated by DFT methods to be −0.17, −0.18, and −0.49 e, respectively. The sp^2 nitrogen atom, N(2), is thus expected to be the most basic of the three and to be the site of protonation. It is clear, however, that the observed product, **9**, results from protonation at N(3). We believe that although $PhN{=}C(C_3F_7){-}N{=}C(C_3F_7){-}NH_2Ph^+$ may be the kinetically preferred product, $PhNH{=}C(C_3F_7){-}N{=}C(C_3F_7){-}NHPh^+$ is the thermodynamically preferred product. This is because the latter has multiple resonance forms that, collectively, lead to charge delocalization over both the two carbon atoms and the two terminal nitrogen atoms in the N_3C_2 fragment. Extensive charge delocalization is consistent with the NMR and vibrational spectroscopic data, and some positive charge at carbon is consistent with the chemical reactivity now to be related.

Solutions of **9** in triflic acid were stable for several hours at room temperature, but then, NMR signals arising from a reaction product slowly grew in. When such solutions were heated at 80° and quenched with ice, 2,4-bis(heptafluoropropyl)-1,3-quinazoline, **10**, was isolated in 82% yield. The numbering scheme for this compound and a proposed mechanism for its formation are shown in Scheme 1. The structure of **10** was deduced from 1-D NMR spectra and 2-D gCOSY, DEPT, and HMQC NMR spectra (cf. Experimental Section). The ^{1}H NMR spectrum shows a typical *o*-disubstituted ring pattern, but in addition, H^5, *δ* 8.42, is broadened due to a 1.5 Hz five bond coupling to the α-fluorine in the nearby $CF_2CF_2CF_3$ group that is clearly resolved in the ^{19}F spectrum.

We suggest that the quinazoline ring is formed by nucleophilic attack by a formal carbocationic center in $PhNH{-}C^+(C_3F_7){-}N{=}C(C_3F_7){-}NHPh$ at the ortho carbon atom in one of the phenyl rings to form a new C−C bond. Protonation at the exocyclic nitrogen and loss of aniline and then of H$^+$ generates **10**.

Experimental Section

Reactions with metal alkyls and hydrides were conduced under dry nitrogen. Hexane and THF were distilled from NaK alloy and sodium-benzophenone, respectively. Reactions in triflic acid were also conducted under nitrogen with the intent of excluding water from this very hygroscopic liquid. NMR spectra were obtained on Varian instruments having ^{1}H operating frequencies of 500 or 600 MHz. Chemical shifts are expressed in ppm (coupling constants in Hz) relative to internal $(CH_3)_4Si$ (^{1}H and ^{13}C), and $CFCl_3$ (^{19}F). ^{15}N spectra were referenced to external CH_3NO_2 and the chemical shifts converted to the NH_3 scale to obtain the reported values. Raman spectra were recorded with 782 nm laser excitation. Infrared spectra were obtained on Nujol mulls unless otherwise noted. Experimental details for synthesis of **2** are given in ref 2.

$Li[Ph_2N_2C_2(C_3F_7)_2]$, 3. *n*-Buyllithium, 0.4 mL of a 2.5 M solution in hexane, was added under nitrogen with stirring to 0.56 g (1 mmol) of **2** in 5 mL of hexane. The product separated as a white solid that was collected on a Schlenk filter washed with toluene and then vacuum-dried. The yield was 0.38 g (67%). Anal. Calcd (Found) for $C_{20}H_{10}LiF_{14}N_3$: C, 42.5 (42.7); H, 1.8 (1.8); Li, 1.2 (1.3); N, 7.4 (7.3). NMR (acetone-d_6): ^{1}H: *δ* 6.99 (t, 8, H_{meta}), 6.7 (overlapping triplet and doublet, $H_{para,\ ortho}$). ^{7}Li: *δ* −3.66 (s, w/2 16 Hz) wrt LiCl in D_2O. ^{13}C: *δ* 150.0 (C_{ipso}), 146.9 (t, 23, *C*CF_2), 127.3 (C_{meta}), 123.3 (C_{ortho}), 120.9 (C_{para}). ^{19}F: *δ* −80.92 (t, $^4J_{FF}$ = 9, C*F*$_3$), −115.37 and −113.51 (AB, J_{AB} 260, C*F*$_2$CN), −125.87 and −125.67 (AB, J_{AB} 286, C*F*$_2$CF$_3$). IR: 1680, 1617, 1579, 1351, 1234, 1210, 1180, 1117, 1104, 909, 865 and 694 cm^{-1}.

$[Bu_4N][Ph_2N_3C_2(C_3F_7)_2]$, 4. Compound **2**, 1.12 g (2 mmol), was dissolved in 4 mL of 1 M $[Bu_4N]OH$ in methanol. Water was added to the cloud point. Slow rotary evaporation gave 1.35 g (87%) of product. Recrystallization from diethyl ether gave colorless rods, mp 102−103°, suitable for X-ray crystallography. Anal. Calcd (Found) for $C_{36}H_{39}F_{14}N_3$: C, 54.5 (54.2); H, 4.9 (4.9), N, 7.1 (7.0). NMR ($CDCl_3$). ^{1}H: δ 7.05 (dd, 8,7, H_{meta}), 6.78 (tt, 7, 2, H_{para}), 6.75 (dd, 8, 1, H_{ortho}), 2.69 (m, CH_2N), 1.23−1.15 (m, CH_2CH_2), 0.88 (t, 7, CH_3). ^{13}C: δ 149.7 (C_{ipso}), 147.3 (t, 23, CCF_2), 127.5 (C_{meta}), 123.3 (C_{ortho}), 121.1 (C_{para}), 58.1 (CH_2N), 23.5 (CH_2CH_2N), 19.3 (CH_2CH_3), 13.3 (CH_3). ^{15}N: δ 235.5 (N_1). ^{19}F: δ −80.9 (t, $^{4}J_{FF}$ = 9, CF_3), −114.04 and −115.23 (AB, J_{AB} = 261 Hz, CF_2-CN), −126.05 and −125.48 (AB, J_{AB} 284, CF_2CF_3). UV λ_{max} (CH_3CN, log ϵ): 203 (4.40), 327 (3.97) nm. IR: 1605, 1551, 1225, 1200, 1117, and 843 cm^{-1}. Raman: 1691, 1625, 1590, 1350, 1372, 1225, 1006, 756, 726, 623, and 303 cm^{-1}. Molar conductance: 96 Ω^{-1} cm^2 mol^{-1} (9.2×10^{-4} M in CH_3NO_2).

^{19}F spectra of **4** were calculated using the equations of Kaplan[9] for dynamic NMR analysis of a pair of coupled spin $^{1}/_{2}$ nuclei. The center CF_2 group (i.e., $CF_2CF_2CF_3$) displays inner and outer resonances for the AB quartet having line widths of 7.7 and 41.4 Hz, respectively, determined from a resolution enhanced spectrum in which the line width of the $CFCl_3$ reference was 1.0 Hz. Activation energies were 14.72 and 14.81 kcal mol^{-1} for the inner and outer resonances, respectively. The CF_2N resonances also show exchange broadening, but accurate measurements of line widths would have required simultaneous decoupling of the 9 Hz FF interaction with CF_3.

K[Ph$_2$N$_3$C$_2$(C$_3$F$_7$)$_2$], 5. Solid **2**, 0.84 g (1.5 mmol), was added to a stirred suspension of (excess) KH in THF. After gas evolution had ceased, the reaction mixture was allowed to settle. The supernatant was withdrawn and clarified by centrifugation. Solvent was removed under vacuum. After 16 h of pumping, the solid was washed with hexane and dried. The yield of **5**, a pale yellow powder, was 0.75 g (83%). Anal. Calcd (Found) for $C_{20}H_{10}F_{14}KN_3$: C, 40.2 (40.0); H, 1.7 (1.8); N, 7.0 (7.1). IR: 1607, 1584, 1379, 1344, 1231, 1113, 910, 853, 758, and 701 cm^{-1}.

Ag[Ph$_2$N$_3$C$_2$(C$_3$F$_7$)$_2$], 6. Compound **2**, 0.56 g (1 mmol), and a suspension of 0.13 g (1 mmol, 50% excess) of Ag_2O were refluxed and stirred for 12 h. A silver mirror lined the reaction vessel. The cooled reaction mixture was filtered through Celite. Evaporation of the solvent under vacuum left 0.56 g (84%) of **6** as a yellow powder. It was stored in an amber bottle. The compound decomposed without melting on heating. DSC analysis (under N_2) revealed three exothermic events at 210°, 240°, and 275° with that at 240° being the most highly exothermic. The residue after heating consisted of Ag metal (XRD). In the mass spectrum, the positive-ion thermal desorption electron impact spectrum showed no silver-containing species. However, the laser desorption positive-ion spectrum was more informative: *m*/*z* 666, 668 (**6**·H^+); 772, 774, and 776 (**6**·Ag^+). In addition, Ag_n^+ clusters were seen up to n = 17 and, at longer trapping times, up to n = 25.[16] Anal. Calcd (Found) for $C_{20}H_{10}AgN_3F_{14}$: C, 36.1 (36.2); H, 1.5 (1.5); Ag, 16.2 (16.0); N, 6.3 (6.5). IR: 1693, 1612, 1566, 1377, 1231 (br), 1122, 911, 874, 748, and 693 cm^{-1}. Molar conductance: 85 Ω^{-1} cm^2 mol^{-1} (8.6×10^{-4} M in CH_3CN).

[(diphos)Ag][Ph$_2$N$_3$C$_2$(C$_3$F$_7$)$_2$], 7. Diphos (1,2-bis(diphenylphosphino)ethane), 0.24 g (0.6 mmol), and compound **6**, 0.4 g (0.6 mmol), in 5 mL of CH_3CN were stirred for 30 min. The solution was centrifuged to remove a small amount of dark solid and then evaporated under vacuum. The residue was recrystallized by slow evaporation of a CH_2Cl_2−hexane solution to give 0.58 g (90%) of **7** as a light yellow powder that decomposed on heating. Anal. Calcd (Found) for $C_{46}H_{34}AgF_{14}N_3P_2$: C, 51.9 (52.6); H, 3.2 (3.3); N, 4.0 (3.9). In the laser desorption mass spectrum, no molecular ion was observed. Instead, clusters of peaks due to isotopomers of Ag_n^+ (n = 3,5,7,9) and *m*/*z* 558 due to the triazapentadiene ligand were observed. IR: 1610, 1570, 1523, 1371, 1344, 1229, 1199, 1113, 743, 694, and 510 cm^{-1}. Molar conductance: 61 and 27 Ω^{-1} cm^2 mol^{-1} (1.6×10^{-3} M in CH_3CN and 1.3×10^{-3} M in CH_3NO_2, respectively). NMR. ^{19}F: δ −78.7, −112.5, and −123.2; −80.8, −115, and −126; −83.0, −116, and −128 in CD_3CN, $CDCl_3$, and toluene-d_8, respectively. ^{31}P: δ 4.8 (hump), 0.77 (d, 201 Hz), and −0.1 (broad doublet, ca. 200 Hz) in CD_3CN, $CDCl_3$, and toluene-d_8, respectively. The ^{31}P and ^{19}F line widths appear, approximately, to be inversely related. The 201 Hz $^{31}P-^{107,109}Ag$ coupling is suggestive of 4-coordinate silver.[17] In the final analysis, none of the characterization data obtained in fluid solution are adequate to differentiate between free (or paired) ions, structures with different silver coordination numbers, or equilibria between all of these.

C$_3$F$_7$−C(=NPh)−N=C(NMePh)−C$_3$F$_7$, 8. A solution of 1.2 g (2 mmol) of **2** in 20 mL of THF was stirred with excess NaH until gas evolution ceased. The unreacted NaH was allowed to settle and the supernatant solution of $Na[Ph_2N_3C_2(C_3F_7)_2]$ removed by cannula and treated with 0.43 gm (3 mmol) methyl iodide. After 16 h, the THF was stripped and the oily residue sublimed under vacuum. The sublimate was recrystallized from hexane to give 0.81 g (71%) of colorless product, mp 60−61°. Anal. Calcd (Found) for $C_{21}H_{13}F_{14}N_3$: C, 44.0 (44.1); H, 2.3 (2.3); N, 7.3 (7.3). Mass spectrum: *m*/*z* 573.0877 (M^+, calcd 573.0886), 404.0927 ($M^+ - C_3F_7$). NMR ($CDCl_3$). ^{1}H: δ 7.38 (dd, 8, 8, H_{meta}[B]), 7.25 m, H_{para}[A]), ~7.23 (m, H_{para}[B]), 7.20 (m, H_{meta}[A]), 7.04 (dd, 9, 1, H_{ortho}[B]), 6.39 (d, ~6, H_{ortho}[A]), 3.14 (CH_3). A and B refer to the C_6H_5 rings that are respectively proximal and distal to the NCH_3 group. ^{13}C: δ 147.16 (dd, $^{3}J_{CF}$ 31, 24, C=NPh), 145.96 (C_{ipso}[B]), 144.78 (t, $^{3}J_{CF}$ 27, C-NMePh), 141.86 (C_{ipso}[A]), 129.37 (C_{meta}[B]), 129.22 (C_{meta}[A]), 128.31 (C_{para}[A]), 126.22 (C_{ortho}[A]), 125.10 (C_{para}[B]), 121.51 (C_{ortho}[B]), 42.71 (CH_3). ^{19}F: δ −127.30 and −126.97 (AB, J_{AB} 287, CF_2CF_3 [B]), −124.95 and −123.96 (AB, J_{AB} 288, CF_2-CF_3 [A]), −117.6 and −116.37 (AB, J_{AB} 268, $NCCF_2$ [B]), −108.30 and −104.31 (AB, J_{AB} 289, $NCCF_2$ [A]), −81.3 (t, 8, CF_3 [B]), −81.6 (t, 10, CF_3 [A]). IR (KBr): 1651 (br), 1590, 1492, 1353, 1222 (br), 1123, 826, 752, and 699 cm^{-1}.

[Ph$_2$N$_3$C$_2$(C$_3$F$_7$)$_2$H$_2$][CF$_3$SO$_3$], 9. This compound was characterized in situ using ca. 0.1 M solutions of **2** in CF_3SO_3H or CF_3SO_3D that were prepared in a drybox using freshly opened ampules of the acids (Aldrich). Samples were contained in 5 mm NMR tubes sealed with J. Young Teflon in-line valves. After NMR spectra had been collected, they were reacquired in rapid survey scans after adding small amounts of $CFCl_3$ and $(CH_3)_4Si$ to serve as internal ^{19}F, ^{1}H, and ^{13}C references, thus defining the chemical shift scale. Only a short time was available for this purpose because $(CH_3)_4Si$

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reacts with triflic acid to form CH_4 and silicon triflates. [$^{15}NH_4$]Cl in triflic acid was used as an external ^{15}N chemical shift reference.

NMR. ^1H: δ 9.64 (d, J_{NH} 94), 7.89 (t, 7, H_{para}), 7.85 (t, 8, H_{meta}), 7.50 (d, 8, H_{ortho}). ^{13}C: δ 152.0 (N*C*, $^2J_{CF}$ 31), 133.61 (C_{para}), 133.46 (C_{ipso}), 132.56 (C_{meta}), 126.15 (C_{ortho}). ^{15}N: δ 151.1 (d, J_{NH} 95, N_1). ^{19}F: δ −80.2 (t, 10, CF_3), −122.6 and −122.0 (AB pattern, J_{AB} 275, $NCCF_2$), −129.7 and −129.5 (AB pattern, J_{AB} 296, CF_3CF_2). $J_{^{15}N^{13}C}$, determined from the ^{13}C spectrum of a terminally ^{15}N labeled sample, was 9 Hz. UV λ_{max} (CF_3SO_3H, log ϵ): 231 (4.19), 315 (3.94) nm.

2,4-Bis(heptafluoropropyl)-1,3-quinazoline, 10. A solution of 0.8 g (1.4 mmol) of **2** in 1 mL of triflic acid was heated at 80° in a Schlenk tube for 16 h. The cooled reaction mixture was poured onto ice. The solid phase was collected on a filter, washed with ice water, and purified by vacuum sublimation onto a probe cooled to 0°. The yield of clear, colorless prisms was 0.55 g (82%), mp 30.5−31.5°. Anal. Calcd (Found) for $C_{14}H_4F_{14}N_2$: C, 36.1 (36.1); H, 0.9 (0.9); N, 6.0 (6.2). Mass spectrum: *m/z* 466.0145 (M^+, calcd 466.0170). NMR ($CDCl_3$). ^1H: δ 8.42 (br d, 9, H_5), 8.30 (d, 9, H_8), 8.18 (dt, 8, 1, H_7), 7.96 (dt, 8, 1, H_6). ^{13}C: δ 156.3 (t, $^3J_{CF}$ 26, C_4), 152.0 (t, $^3J_{CF}$ 26, C_2), 151.5 (s, C_{8a}), 136.0 (C_7), 131.5 (C_6), 130.4 (C_8), 124.8 (t, $^4J_{CF}$ 7, C_5), 122.0 (s, C_{4a}). ^{19}F: δ −80.27, −80.92 (t, 9, CF_3), −109.14 (qd, 9, $^5J_{H(5)F}$ 1.5, C_4CF_2), −115.65 (q, 9, C_2CF_2), −125.8 (s, $C_4CF_2CF_2$), −126.42 (s, $C_2CF_2CF_2$). IR: 1615, 1563, 1497, 1466, 1004, 952, 899, 844, 825, 799, 749, 725, 675, 660, 596, and 510 cm^{-1}.

Crystal Structure Determination. A crystal of **4** was attached to a glass fiber and mounted on the Siemens SMART system. An initial set of cell constants was calculated from reflections harvested from three sets of 20 frames. The initial sets of frames were oriented so that orthogonal wedges of reciprocal space were surveyed. Final cell constants were calculated from a set of 6846 strong reflections.

Hemisphere data collection was used. A randomly oriented region of reciprocal space was surveyed to 1.3 hemispheres and a resolution of 0.84 Å. Three major swaths of frames were collected with 0.30° steps in ω. The space group $Pna2_1$was determined on the basis of systematic absences and intensity statistics. A successful direct-methods solution provided most non-hydrogen atoms from the E-map. Several full-matrix least-squares difference Fourier cycles located the remainder of them. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in ideal positions and refined as riding atoms with individual displacement parameters. Crystallographic data are summarized in Table 2.

Table 2. Crystallographic Data for 4

	$C_{36}H_{46}N_4F_{14}$
cryst size	0.4 × 0.2 × 0.08 mm^3
cryst syst	orthorhombic
space group	$Pna2_1$
a	16.8541(6) Å
b	14.2085(6) Å
c	17.0180(6) Å
V	4075.3(3) $Å^3$
Z	4
λ	0.71073 Å
fw	800.77 g mol^{-1}
D_{calcd}	1.305 g cm^{-1}
μ	0.122 mm^{-1}
T	173(2) K
$F(000)$	1664
θ range for data collection	1.87−25.06°
reflns collected	21184
indep reflns	7077 (R_{int} = 0.0747)
R indices[a] ($I > 2\sigma(I) = 4084$)	R1 = 0.0622; wR2 = 0.0951
R indices (all data)	R1 = 0.133; wR2 = 0.1135
GOF on F^2	1.050
largest diff peak and hole	0.176 and −0.223 e $Å^{-3}$

[a] $R_{int} = \sum|F_o^2 - \langle F_o^2\rangle|/\sum|F_o^2|$, $R1 = \sum||F_o| - |F_c||/\sum|F_o|$, $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum w(F_o^2)^2]^{1/2}$ where $w = q/\sigma^2(F_o^2) + (ap)^2 + bp$. $GOF = S = [\sum[w(F_o^2 - F_c^2)^2]/(n - p)^{1/2}$.

Computational Studies. The structure of **2** was determined by a geometry optimization calculation using density functional theory (DFT)[10] code Dgauss 4.1 (CAChe/Fujitsu)[11] using the B88-LYP[12,13] GGA functional with polarized double ζ split valence DZVP[14] basis sets. The charge distributions correspond to Mulliken net atomic charges.[15]

Supporting Information Available: X-ray file in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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