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Perfluoroalkyl-Substituted Triazapentadienes and Their Metal Complexes

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Triazapentadienides, C_3F_7–C(=NR)–N=C(NHR)–C_3F_7, result from the reaction of primary amines RNH_2 with the fluorinated imine C_3F_7–CF=N–C_4F_9. The aniline derivative (R = Ph) is a weak monoprotic acid in dmso. Its conjugate base exhibits an extensive coordination chemistry. It acts as a bidentate ligand toward the molecular fragments $Pd(C_3H_5)$, $Rh(c\text{-}C_8H_{12})$, $Ir(c\text{-}C_8H_{12})$, and $Rh(CO)_2$. The chelates $[C_3F_7–C(NPh)–N–C(NPh)–C_3F_7]_2M$, M = Mg, Mn, Fe, Co, Ni, Cu, Zn, and Pd, were prepared. In the crystallographically characterized Co complex, the metal is $3d^7$, $S = {}^3/_2$ and tetrahedrally coordinated. Spin densities at carbon in the C_6H_5 and C_3F_7 groups were estimated from the ^1H and ^{19}F contact shifts. Spin delocalization onto phenyl sp^2 carbons is ∼10 times greater than onto the fluorinated sp^3 carbons.

Organic ligands form the cornerstone of a broad field of inorganic chemistry, that of coordination compounds. For example, *O*,*O*-*β*-diketone complexes, [R−C(O)−CH−C(O)−R]M, are one of the largest classes of transition metal and main group chelates; examples containing a substantial fraction of the elements in the periodic table are known.[1] Diaza analogues, in which the ligating oxygen atoms are replaced by isoelectronic NR groups, *β*-ketimine complexes, [R−C(NR)−CH−C(NR)−R]M, show chemical similarities and have recently been investigated as polymerization catalysts as well as models for copper metalloproteins[2,3] We present a survey of a broad, new class of ligands, perfluoroalkyl-substituted triazapentadienes of the type R_fC(=NR)−N=C(HNR)R_f (R_f = perfluoroalkyl). They exhibit substantial scope and diversity in their chemistry that we believe may rival that of diketones and diketimines.[4]

When $(C_4F_9)_3N$ and SbF_5 are heated to ∼140 °C, loss of C_4F_{10} occurs and the imine C_3F_7−CF=NC_4F_9, **1**, distills from the reaction mixture.[5] This acid-catalyzed α-elimination reaction is generally applicable to linear, cyclic, and heteroatom-substituted[6] perfluoroalkylamines. Addition of **1** to

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(4) Trifluoroacetamidine, HN=C(CF_3)−NH_2, undergoes a condensation reaction in the presence of platinum hydrides to liberate NH_3 and form compounds containing the HN−C(CF_3)−N−C(CF_3)−NH ligand among which the $RuH(CO)(PPh_3)_2$ complex was characterized crystallographically. Hursthouse, M. B.; Mazid, M. A.; Robinson, S. D.; Sahajpal, A. *J. Chem. Soc., Dalton Trans*. **1994**, 3615. We thank a reviewer for drawing notice to these ingenious syntheses.

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aniline in diethyl ether at 25 °C results in a series of addition−HF elimination steps, and $C_3F_7-C(=NPh)-N=C(PhNH)-C_3F_7$, **2** (65% yield), and insoluble $PhNH_2 \cdot 3HF$ are produced. Pale yellow **2** may be readily purified by evaporation of the solvent and recrystallization from heptane or vacuum sublimation.[7,8] This quite general synthesis of triazapentadienes succeeds with a wide variety of primary amines of diverse functionality so long as they do not contain other acidic groups (NH_2, CO_2H, OH, SH).[9] Chiral amines can be employed as well. Anilines containing electron-releasing groups such as *p*-OMe undergo instead intramolecular cyclization to give benzopyrimidines. Monosubstituted hydrazines, RN_2H_3, yield the corresponding 1-R-3,5-$(C_3F_7)_2$-1,2,4-triazoles.

Perfluoroalkyltriazapentadienes are weak monoprotic acids: **2** and $C_3F_7-C(=NR)-N=C(NRH)-C_3F_7$ ($R = C_6H_4-N=N-C_6H_5$), **3**, have pK_a's of 14.3 and 13.8, respectively, in dimethyl sulfoxide, cf. 13.3 for $(MeCO)_2CH_2$.[10] Salts of $[C_3F_7-C(NPh)-N-C(NPh)-C_3F_7]^-$ may be obtained using a wide variety of onium hydroxides in methanol. Treatment of **2** with *n*-BuLi in ether or THF affords $Li[C_3F_7-C(NPh)-N-C(NPh)-C_3F_7]$, **4**. This reacts with MeI, Me_3SiCl, Ph_3PAuCl, and MeHgCl and to give $C_3F_7-C(=NPh)-N=C(NPhR)-C_3F_7$, $R = CH_3$ (**5**), $SiMe_3$ (**6**), $AuPPh_3$ (**7**), and HgMe (**8**), respectively. **5**−**7** contain C_3F_7 groups that are inequivalent by ^{19}F NMR, which indicates that the conjugate base of **2** acts as a monodentate ligand in these compounds. In solution, **8** comprises a mixture of two isomeric η^1 compounds in which the MeHg moiety is attached to either the central or terminal nitrogen positions. These interconvert slowly on the NMR time scale, but only the former isomer is observed in crystals.

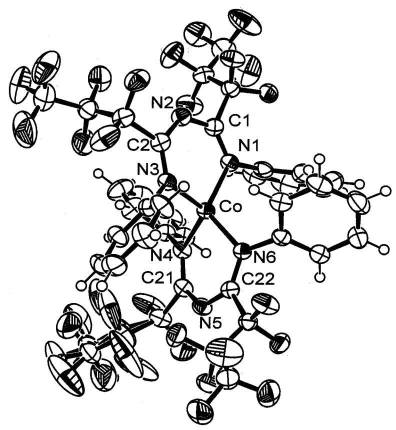

Figure 1. ORTEP drawing of $[C_3F_7-C(NPh)-N-C(NPh)-C_3F_7]_2Co$, **17**.

Most useful for the synthesis of transition metal derivatives are $Ag[C_3F_7-C(NPh)-N-C(NPh)-C_3F_7]$, **9**, $K[C_3F_7-C(NPh)-N-C(NPh)-C_3F_7)]$, **10**, and $Mg[C_3F_7-C(NPh)-N-C(NPh)-C_3F_7]_2$, **11**, prepared from **2** and Ag_2O in refluxing CH_3CN, KH in THF, and $(C_5H_5)_2Mg$ in toluene at 25 °C, respectively.

Reaction of **9** with $[(C_3H_5)PdCl]_2$, $[Rh(CO)_2Cl]_2$, and $(COD)MCl_2$ (M = Rh, Ir) in CH_3CN at room temperature affords $[C_3F_7-C(NPh)-N-C(NPh)-C_3F_7]E$, E = $Pd(C_3H_5)$, **12**, $Rh(CO)_2$, **13**, Rh(COD), **14**, and Ir(COD), **15**, respectively (COD = c-C_8H_{12}). Treatment of **10** with FeI_2, CoI_2, $CuCl_2$, and $Pd(CF_3CO-CH-COCF_3)_2$ in THF produces the symmetrical bis(chelates) $[C_3F_7-C(NPh)-N-C(NPh)-C_3F_7]_2M$ where M = Fe (**16**), Co (**17**), Cu (**18**), and Pd (**19**). The nickel complex, M= Ni (**20**), was obtained from **11** and $NiBr_2$(dimethoxyethane) in toluene at 70 °C.

Advantage can be taken of the acidic proton in **2** to prepare additional members of the symmetrical chelate set through reactions with compounds having polar metal−carbon bonds. The compounds $[C_3F_7-C(NPh)-N-C(NPh)\text{-}C_3F_7]_2M$, M = Mn (**21**) and Zn (**22**), were obtained upon treatment with $(C_5H_5)_2Mn$ and Me_2Zn, respectively. With the exception of **6**, **7**, and **11** (water reactive) and **21** (O_2 reactive), the new compounds reported here are air-stable. They have the useful property of being soluble in *both* hydrocarbon (C_6H_{14}) and fluorous (C_6F_{14}) solvents.

An ORTEP view of $[C_3F_7-C(NPh)-N-C(NPh)-C_3F_7]_2Co$ (**17**) is shown in Figure 1.[11] In it, cobalt is tetrahedrally coordinated, with the angle between the two CoN_2 planes being 92°; $d(Co-N)_{av}$ is 1.968(2) Å. This geometry helps to minimize nonbonded repulsion among the C_6H_5 rings. The CoN_3C_2 ring is asymmetric: $d(C-N)_{av}$ to N(1,3,4,6) is 1.307(4) Å but $d(C-N)_{av}$ to N(2,5) is much longer, 1.338(4) Å. The bite distance of the ligand is 2.870 Å.

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(7) A closely related compound, the C_7F_{15} analogue of **2**, was observed by GC/MS (but not isolated) among the five products of the reaction of $C_7F_{15}CN$ with aniline: Paciorek, K. J. L.; Nakahara, J. H.; Kratzer, R. H. *J. Fluorine Chem.* **1985**, *30*, 241.

(8) **2**: Mp 87.8 °C, ΔH_{fus} 31.3 kJ mol^{-1}. Molar conductance: 15.8 ohm^{-1} cm^2 mol^{-1} (2.2×10^{-3} M in $MeNO_2$). HRMS: *m/z* 559.0728 (M^+, calcd 559.0724), 390.0834 ($M^+ - C_3F_7$). IR (Nujol) (Raman, neat): 3200, 1682 (1691) 1633 (1625), 1593 (1590) cm^{-1}. UV (isooctane): λ_{max} 207 (log ϵ 4.34), 266 (3.87) nm. ^{15}N NMR (60.8 MHz, 1,2-$C_2D_2Cl_4$, 300 K, with respect to external NH_3, indirectly observed via a ^1H GHMBC pulse sequence): δ 288.4 (s, N_1), 226.3 (s, N_3), 113.7 (d, J_{NH} 93 Hz, N_5). Assignments were confirmed by ^{15}N labeling at terminal $N_{1,5}$ through synthesis of **2** from $Ph^{15}NH_2$. ^{19}F NMR (376.2 MHz, dmso, 300 K): the spectra disclose two inequivalent C_3F_7 groups in which the two different α-CF_2 groups show geminal inequivalence; but only one of the two inequivalent β-CF_2 groups shows geminal inequivalence [δ −126.39 (2F, β-CF_2), −125.69 and −125.28 (2F, β-CF_2, AB multiplet, J_{AB} 291 Hz), −118.76 and −114.46 (2F, α-CF_2, AB multiplet, J_{AB} 268 Hz), −116.13 and −114.50 (2F, α-CF_2, AB multiplet, J_{AB} 270 Hz), −80.14 and −79.90 (6F, CF_3)]. The ^{19}F resonances are broad ($w/2$ ∼10−20 Hz). NMR spectra are field, temperature, and solvent dependent on account of both a 1−5 prototropic shift and at least one additional, low-temperature process. Dynamics in **2** have been explored by crystallographic, DNMR, and computational methods. The results will be reported elsewhere.

(9) This is not a severe limitation because such groups can often be masked or protected. For example, $(p\text{-}NO_2Ph)_2N_3C_2(C_3F_7)_2H$, prepared from **1** and *p*-nitroaniline, can be reduced (H_2, Pd/C) to $(p\text{-}NH_2Ph)_2N_3C_2(C_3F_7)_2H$, which is unobtainable directly from *p*-phenylenediamine. Subsequent diazotization with $[NO][BF_4]$ in CH_3CN yields $[(p-N_2\text{-}Ph)_2N_3C_2(C_3F_7)_2H](BF_4)_2$, coupling of which with 2-naphthol (Py, CH_3CN) affords $[4\text{-}(2\text{-}HO-C_{10}H_8N=N)Ph]_2N_3C_2(C_3F_7)_2H$. Coupling with $p\text{-}Me_2NC_6H_4CH=CH-CHO$ and elimination of water yields the Schiff base $(p\text{-}Me_2NC_6H_4CH=CH-CH=N-C_6H_4)_2N_3C_2(C_3F_7)_2H$.

(10) By potentiometric titration with methanolic $[Bu_4N]OH$; cf.: Bordwell, F. G. *Acc. Chem. Res.* **1988**, *21*, 456.

(11) Crystal data: red-orange plates from C_6H_{14}, $P\bar{1}$ (triclinic), a = 11.706(2) Å, b = 12.112(2) Å, c = 17.756(4) Å, α = 102.939(3)°, β = 102.498(4)°, γ = 106.230(3)° at 173 K with Mo Kα radiation, V = 2248.7(3) Å^3, Z = 2, FW = 1175.55, d(calcd) = 1.736 g cm^{-3}, abs coeff = 0.537 mm^{-1}, max/min transmission = 1.000/0.908. Final R [$I > 2\sigma(I)$]: R1 = 0.04399, wR2 = 0.1083. R indices (all data): R1 = 0.0657, wR2 = 0.1233. X-ray crystallographic files (CIF) are available as Supporting Information.

Cobalt in **17** is high spin $3d^7$, $S = {}^3/_2$ ($\mu_{\mathrm{eff}} = 4.05\ \mu_B$ in CD_2Cl_2 at 300 K by NMR methods). Even so, well-resolved ^1H, ^{13}C, and ^{19}F NMR spectra were obtained and assigned with the aid of $^1H-^{13}C$ 2D HMQC spectroscopy.[12] Chemical shifts in **17** relative to the diamagnetic Zn complex **22**[13] comprise contact shifts,[14] and, following Eaton et al.,[15] they were used to calculate spin densities at the *o*-, *m*-, and *p*-carbon positions in the ligand phenyl rings: 13.3, −2.0, and 9.6 e $\times 10^{-3}$ respectively. Spin densities in the C_3F_7 moieties are much lower: −17, −6, and 8 e $\times 10^{-4}$ for the α- and β-CF_2 and CF_3 carbon nuclei, respectively. Spin delocalization through π bonds in the C_6H_5 rings is thus much more effective than through σ bonds in the C_3F_7 groups despite the strong electron-withdrawing effect of fluorine.

Supporting Information Available: Crystallographic data in CIF format and experimental details for the collection of crystallographic data. Experimental details for the synthesis of **1**, **2**, and **17**. This information is available free of charge via the Internet at http://pubs.acs.org.

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(12) **17**: ^1H NMR (599.7 MHz, CD_2Cl_2, 300 K): δ 15.3 (s, 8H, *w*/2 46 Hz, H_{meta}), −32.2 (s, 4H, *w*/2 57 Hz, H_{para}), −48.0 (s, 8H, *w*/2 720 Hz, H_{ortho}). ^{13}C (150.8 MHz): δ 534.3 (s, 8C, *w*/2 155 Hz, C_{ortho}), 320.2 (s, 4C, *w*/2 219 Hz, C_{para}), 155.1 (q, 4C, J_{CF} 289 Hz, *w*/2 108 Hz, CF_3), 135.6 (t, 4C, J_{CF} 256 Hz, *w*/2 186 Hz, CF_3CF_2), 106.6 (br s, 4C, *w*/2 334 Hz, $CF_3CF_2CF_2$), 42.9 (br s, 2C, *w*/2 204 Hz, $C_{\mathrm{ring\ ipso}}$), −24.8 (br s, 8C, *w*/2 59 Hz, C_{meta}). ^{19}F (564.2 MHz): δ −74.2 (s, 12F, *w*/2 39 Hz, CF_3), −117.61 (s, 8F, *w*/2 106 Hz, CF_3CF_2), −127.8 (s, 8F, *w*/2 205 Hz, NCF_2). Chemical shifts are in ppm relative to internal $(CH_3)_4Si$ (^1H and ^{13}C) and CCl_3F (^{19}F). Mp: 130.5−131 °C. HRMS: *m*/*z* 1175.0612 (M^+), 1006.1220 ($M^+ - C_3F_7$). UV (isooctane): λ_{max} 321 nm (log ϵ 4.29). IR: 1546, 1480 cm^{-1}. Raman: 1530, 1464 cm^{-1}. Anal.: Calcd (found) for $C_{40}H_{20}CoF_{28}N_6$: C, 40.8 (41.0); H, 1.7 (1.7); Co, 5.0 (4.9); N, 7.1 (7.1). Crystals suitable for X-ray diffraction studies were grown by slow evaporation of a heptane solution.

(13) **22**: ^1H NMR (599.7 MHz, CD_2Cl_2, 300 K) δ 7.29 (m, 8H, H_{meta}), 7.25 (m, 4H, H_{para}), 6.64 (m, 8H, H_{ortho}); ^{13}C (150.8 MHz) δ 158.9 (t, $^2J_{\mathrm{CF}}$ 23 Hz, NCN), 142.9 (4C, C_{ipso}), 129.7 (8C, C_{meta}), 126.9 (4C, J_{CF} 272 Hz, CF_3CF_2); ^{19}F (564.2 MHz) δ −80.5 (CF_3), −104.5 (CF_2N), −123.4 (CF_3CF_2). The ^1H spectrum shows more than the expected number of lines. We believe that the pairwise degeneracy of H_o and H_m is lifted due to restricted rotation of the phenyl rings. Assignments were confirmed by a 2D $^1H-^{13}C$ experiment. Mp: 130−131 °C. HRMS: *m*/*z* 1180.0749 (M^+). IR: 1558 cm^{-1}. UV (isooctane) λ_{max} (log ϵ): 253 (3.74), 337 (4.32). IR: 1580, 1507, 1489 cm^{-1}. Raman: 1647, 1581, 1560 cm^{-1}. Anal.: Calcd (found) for $C_{40}H_{20}F_{28}N_6Zn$: C, 40.6 (40.8); H, 1.7 (1.6); N, 7.1 (7.0); Zn, 5.5 (5.5).

(14) ^1H NMR for the *p*-tolyl analogue of **18**: δ 33.8 (CH_3), 15.0 (H_{meta}), −47.4 (H_{ortho}). That the *p*-CH_3 and H_{para} ^1H shifts are of opposite sign indicates that the paramagnetic shifts are primarily contact in origin.

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