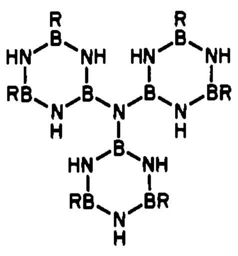


4

R = C_2H_5

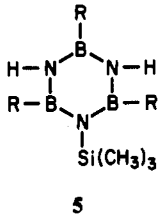
it converted to **4**, but adhering traces of **1b** were difficult to remove and the formation of an intractible material indicated additional decomposition processes.

Compound **4** is the first known tris(borazin-2-yl)amine and seems to offer great potential for the preparation of two-dimensional network structures of linked borazine rings. Ongoing studies are directed to explore this possibility.

It is of interest to note the distinct broadening of the ^{11}B NMR signals in the above series monoaminoborazine-bis(borazinyl)amine (**1b**)-tris(borazinyl)amine (**4**). It is definitely not due to an overlap of signals from mixtures of compounds of similar ^{11}B chemical shifts, but parallels the observations made in the series $(H_2N)(CH_3)_2B_3N_3(CH_3)_3$ (**2e**)-$HN[(CH_3)_2B_3N_3(CH_3)_3]_2$ (**1a**). It is possible that this indicates the overlap of signals, which would suggest that the borazine rings of individual poly(borazine) species are not coplanar. This has indeed been established by an X-ray structure determination of **1a**,[4] but variable-temperature NMR studies on **4** were inconclusive.

In summary, the current study clearly documents that unsymmetrically B-substituted borazines of types **2** and **3** are conveniently obtained originating from symmetrically substituted *B,B′,B″*-triorganylborazines. Thus, such compound are no longer laboratory curiosities but are readily available starting materials for molecular architecture, which opens the door for an extensive exploration of the chemistry of unsymmetrically B-substituted borazines. Most interesting seems to be the application of the species for the formation of poly(borazines), i.e., compounds in which individual borazine rings are linked to form polycyclic systems. The bis(borazin-2-yl)amines **1a** and **1b** and the tris(borazin-2-yl)amine $N[(C_2H_5)_2B_3N_3H_3]_3$ (**4**) are examples of such materials, and the synthesis of a variety of poly(borazine) structures is currently under investigation.

Finally, one other observation is worth mentioning. During the course of preparing the starting material $(C_2H_5BNH)_3$ by the reaction of $C_2H_5BCl_2$ with $HN[Si(CH_3)_3]_2$,[6] considerable variations in the yield were observed, even under apparently identical reaction conditions. Concurrently, the formation of variable amounts of a byproduct was noted, the amount of which increased when the yield of $(C_2H_5BNH)_3$ decreased. This (higher boiling) byproduct has now been identified as the unsymmetrically N-substituted borazine $(C_2H_5)_3B_3N_3H_2[Si(CH_3)_3]$ (**5**). Attempts to modify the reaction conditions in order to make **5** the main product did not yet lead to any reasonable conclusions. However, yields of $(C_2H_5)_3B_3N_3H_2[Si(CH_3)_3]$ (**5**) ranging from 10-40% were usually obtained, especially when the reaction was performed on a relatively large scale. Thus, it presents the possibility of studying N-unsymmetrically substituted borazines in more detail.



5

R = C_2H_5

Acknowledgment. This work was supported by the Office of Naval Research (K.N.).

Registry No. **1a**, 127232-88-6; **1b**, 136237-51-9; **2a**, 136237-52-0; **2b**, 136237-53-1; **2c**, 136237-54-2; **2d**, 136237-55-3; **2e**, 89417-01-6; **2f**, 136237-56-4; **2g**, 69562-24-9; **2h**, 98425-56-0; **3b**, 136237-57-5; **3c**, 136237-58-6; **3d**, 66535-66-8; **4**, 136237-59-7; **5**, 136237-60-0; $Cl(CH_3)_2B_3N_3(CH_3)_3$, 13058-05-4; $Pb(SCH_3)_2$, 35029-96-0; $O[(CH_3)_2B_3N_3(CH_3)_3]_2$, 15270-88-9; $NaN[Si(CH_3)_3]_2$, 1070-89-9; BCl_3, 10294-34-5; $(C_2H_5BNCH_3)_3$, 715-62-8; $(C_6H_5BNH)_3$, 976-28-3; $C_2H_5BCl_2$, 1739-53-3; $[(CH_3)_3Si]_2NH$, 999-97-3; BBr_3, 10294-33-4; $(C_2H_5BNH)_3$, 7443-22-3.

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Perfluorocarbon Phosphonic and Sulfonic Acids Containing Discretely Varying Terminal Functional Groups

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Several new per- and polyfluorocarbon phosphonic and sulfonic acids and their salts (or ethyl esters) $C_6F_5CH_2P(O)(OH)_2$, $(CF_3)_2CFP(O)(OH)_2$, $CF_3CH_2N(H)P(O)(OH)_2$, and $(CF_3)_3CCFHCF_2SO_3Na$ were prepared from the corresponding alkyl iodides or alkenes and tetraethyl pyrophosphite or sodium hydrogen sulfite, respectively. We have also prepared the previously reported acid $CF_3CFHCF_2SO_3H$ and completed the spectroscopic characterization of this material.

Introduction

Our continuing interest in the potential of per- and polyfluorocarbon sulfonic and phosphonic acids for use as catalytic additives or for replacement of phosphoric acid as the electrolyte of choice in fuel cells, as well as our interest in inert surfaces, has prompted us to synthesize perfluorocarbon phosphonic and/or sulfonic acids of discretely varying structure. It has been well established that the structure and composition of the terminal group of poly- and perfluorocarbon chains are largely responsible for their observed behavior on surfaces and in solution.[1,2] This is particularly important with respect to the behavior of these acids in fuel cells[3] and in coating applications. Within fuel cells, the degree and nature of the interactions of the electrolyte or additive with the Teflon surface of the electrodes have a dramatic impact on the operating efficiency of the fuel cell.

A large number of per- and polyfluorinated sulfonic and disulfonic acids,[4-7] phosphonic acids,[8-11] and mixed sulfonic/

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phosphonic and phosphonic/carboxylic acids[12,13] have been synthesized and made available for evaluation in fuel cells. However, very little attention has been paid to determining the effect of specific changes in structure of the electrolyte on its interaction with Teflon fuel cell electrodes and the resulting effect on fuel cell operating efficiency.[14] Consequently we have synthesized a series of sulfonic and/or phosphonic acids terminated with $C_6F_5CH_2$–, $(CF_3)_3C$–, $(CF_3)_2CF$–, CF_3CFH–, and CF_3CH_2– structural moieties. The discrete structural changes exhibited by these acids should provide valuable data regarding Teflon electrode/fluorinated electrolyte/additive interactions in fuel cells and any resulting changes in fuel cell operating efficiency as a function of electrolyte structure or composition.

Results and Discussion

The wetting properties or surface energies of a large number of halogenated and hydrocarbon coatings have been determined by Zisman and others.[15,16] The structure and wettability of polymeric and monolayer surfaces composed of fluorinated acid monolayers and polymeric surfaces of the type $CF_3(CF_2)_n(CH_2)_2$– (where $n = 4, 6, 8, 10$) have recently been compared via Zisman plots (contact angle versus surface tension) and plots of surface tension versus length and area of the perfluoroalkyl side chains.[17] Other researchers have quantified the effect of replacing single protons by fluorine on the wettability of ethylenic polymers, both in the polymer backbone and pendant chains terminated with trifluoromethyl groups or perfluorophenyl moieties. They found a decrease in the critical surface tension of 3 dyn/cm when a single proton in the polymer backbone was replaced with a fluorine atom.[18] Many of the literature reports correlate changes in surface energy as a function of perfluorocarbon chain structure.[19–22]

The surface energy of perfluorinated coatings has been known for some time to decrease in the order $CF_3 < CF_3/CF_2 < CF_2$.[19,20] Fowkes reported that the surface energy decrease, which occurs in the order $CF_3 < CF_2 < CH_3 < CH_2$, is primarily due to increasing group size. The larger volume occupied by CF_3, as compared to CF_2, results in fewer interactions per unit area and a lower surface energy.[23] The properties of these coatings have been found to be primarily a function of the composition of the material tested at the solid/substrate interface, i.e. the structure of the chemical functionality used to terminate the coating, with some additional effect attributable to chain length and chain composition. Within fuel cells, where electrolyte or catalysts for enhanced operation of these devices may act as monolayer coatings on the fuel cell electrodes, these surface/substrate interactions become extremely important. Furthermore, although the literature is replete with examples of fluorinated electrolytes for use in fuel cell applications, no correlations that relate electrolyte structure or size to fuel cell operating efficiency have appeared, principally because of the large differences in structure and composition of the electrolytes or catalysts previously made available for testing.

The synthesis of a discretely varying series of potential fuel cell electrolytes or catalytic additives is not a trivial task. The acids we report herein are such a series, however, and should provide some insight into the structure/fuel cell efficiency correlations mentioned above, when tested in model fuel cell systems.

The preparation of acids containing CF_3CH_2– and CF_3CFH– terminal groups was accomplished by the two routes given as follows:

$$CF_3CF{=}CF_2 + NaHSO_3 \xrightarrow[\substack{(C_6H_5CO)_2O_2 \\ H_2O}]{Na_2B_4O_7{\cdot}10H_2O} CF_3CFHCF_2SO_3Na$$

$$CF_3CFHCF_2SO_3Na + H_2SO_4 \rightarrow CF_3CFHCF_2SO_3H$$

and

$$(C_2H_5O)_2P(O)Cl + CF_3CH_2NH_2 \xrightarrow[\text{ether}]{\text{reflux}} CF_3CH_2N(H)P(O)(OC_2H_5)_2$$

$$CF_3CH_2N(H)P(O)(OC_2H_5)_2 \xrightarrow[\text{2. } H_2O]{\text{1. } Me_3SiBr} CF_3CH_2N(H)P(O)(OH)_2$$

Purification of both acids was extremely difficult and required repeated extraction from aqueous solution to remove inorganic impurities. In order to obtain pure $CF_3CH_2N(H)P(O)(OH)_2$, it was necessary to purify the precursor $CF_3CH_2N(H)P(O)(OC_2H_5)_2$ prior to conversion to the phosphonic acid. The synthesis of $CF_3CFHCF_2SO_3H$ has been reported previously;[24] however, the product was not completely characterized spectrally. The asymmetric carbon center present in this molecule results in a typical AB fluorine NMR spectrum. The theoretical spectrum was calculated and was found to match the observed spectrum.

The new sulfonic acid sodium salt, $(CF_3)_3CCFHCF_2SO_3Na$, was similarly synthesized from $(CF_3)_3CF{=}CF_2$.

$$(CF_3)_3CCF{=}CF_2 + NaHSO_3 \xrightarrow[\substack{H_2O \\ (C_6H_5CO)_2O_2}]{Na_2B_4O_7{\cdot}10H_2O} (CF_3)_3CCFHCF_2SO_3Na$$

The sodium salt product is an intractable hard white solid and is stable at temperatures exceeding 300 °C. The CF_2 fluorines, which are nonequivalent, are, as in the case of $CF_3CFHCF_2SO_3H$, found as an AB pattern between −100 and −120 ppm (calculated shifts are −107 and −113 ppm). Fast atom bombardment mass spectral data gives rise to a parent ion plus sodium, and infrared analysis shows the asymmetric S=O stretch around 1400 cm^{-1}.

Two additional phosphonic acids, containing $(CF_3)_2CF$– and $C_6F_5CH_2$– terminal functional groups, were also prepared from the corresponding perfluoro- and polyfluoroalkyl iodides by reaction with tetraethyl pyrophosphite.

$$R_fI + (EtO)_2POP(OEt)_2 \xrightarrow[\text{2. } Bu_3CO_2H]{\text{1. } (CH_3)_3COOC(CH_3)_3} R_fP(O)(OEt)_2$$

$$R_fP(O)(OEt)_2 + Me_3SiBr \xrightarrow{RT} R_fP(O)(OSiMe_3)_2$$

$$R_fP(O)(OSiMe_3)_2 + H_2O \rightarrow R_fP(O)(OH)_2$$

$$R_f = (CF_3)_2CF,\ C_6F_5CH_2$$

While $(CF_3)_2CFP(O)(OH)_2$ is only marginally stable at temperatures greater than approximately 50 °C, it may be useful as a catalytic electrode coating in fuel cell systems.

Pentafluorobenzylphosphonic acid is stable at least up to its melting point of 223 °C. Both of these compounds were char-

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acterized and identified by their fluorine, proton, and phosphorus NMR spectra, infrared spectra, and mass spectral analysis. They were purified by repetitive extraction and recrystallization as described in the Experimental Section.

This short series of phosphonic and sulfonic acids differs in size (CF_3, $(CF_3)_2CF$, and $(CF_3)_3C$), chemical composition (CF_3CFH and CF_3CH_2), and functionality (aromatic versus alkyl) of the terminal fluorocarbon group. Testing of these compounds in model fuel cells should provide the beginnings of a correlation between electrolyte or additive structure and fuel cell operating efficiency. Such information will aid in the rational design of future fuel cell electrolytes and allow the synthetic chemist to focus on the synthesis of those acids expected to exhibit the most useful properties for this application.

Experimental Section

Materials. The starting materials $CF_3CF{=}CF_2$, $(CF_3)_2CFI$, pentafluorobenzyl bromide, and $CF_3CH_2NH_2$ (PCR), $(C_2H_5O)_2P(O)Cl$, trimethylsilyl bromide, *tert*-butyl hydroperoxide, and sodium hydrogen sulfite (Aldrich) were purchased and used as received. Dr. James Adcock (University of Tennessee) generously supplied samples of $(CF_3)_3CF{=}CF_2$.

General Procedures. A Pyrex glass vacuum line equipped with a Heise Bourdon tube gauge and a Televac thermocouple gauge was used for the manipulation of gases and volatile liquids. Infrared spectra were obtained with a Perkin-Elmer Model 1710 Fourier transform infrared spectrometer. ^{19}F, ^{1}H, and ^{31}P NMR spectra were recorded on a JEOL FX-90Q Fourier transform nuclear magnetic resonance spectrometer with $CFCl_3$, $(CH_3)_4Si$, and H_3PO_4 as external references. Electron impact (17–70 eV) and chemical ionization mass spectral data were obtained with a VG 7070 mass spectrometer. The PMR program from Serena Software was used for the calculation of NMR shift values.

Preparation of $CF_3{}^{A}CF^{B}HCF_2{}^{C,D}SO_3Na$. Into a 75-mL stainless steel vessel were added 113 mmol of $CF_3CF{=}CF_2$, 100 mmol of $NaHSO_3$, 12.5 mmol of $Na_2B_4O_7\cdot 10H_2O$, 2.12 mmol of $(C_6H_5CO)_2O_2$, and 29 mL of distilled water. The contents of the vessel were heated with agitation for 10 h at 115 [illegible] 5 °C. The solvent was removed under vacuum, and the residue was extracted twice with hot ethanol. The extracts were combined and dried under vacuum. The resulting white solid, $CF_3CFHCF_2SO_3Na$, was formed in 59% yield. The compound was stable to 150 °C. Spectral data obtained were as follows. IR (solid): 3670 m, 3466 m, 3191 b, m, 1654 m, 1636 m, 1377 m, 1355 w, 1293 sh, 1273 s, 1242 vs, 1201 s, 1180 s, 1094 s, 1043 sh, 1002 m, 850 m, 827 m, 780 w, 709 w, 660 sh, 654 m, 644 m, 620 w, 597 w, 589 w, 556 m, 535 w, 527 m, 459 m, 450 sh, 441 sh, 430 m cm^{-1}. MS (FAB$^-$) [*m/e* (species), intensity]: 487 ($2M^- + Na + 2$), 12.4; 232 ($CF_3CFHCF_2SO_3H^-$), 100; 214 ($M^- - Na - OH$), 3.3; 185 ($CFHCF_2SO_3Na^-$), 3.8; 149 ($C_2F_2SO_2Na^-$), 9.1; 145 ($C_2F_3SO_2{}^-$), 13.6; 112 ($CFSO_3H^-$), 1.9; 81 (SO_3H^-), 8.1; 80 ($SO_3{}^-$), 5.2; 69 ($CF_3{}^-$), 1.6. ^{19}F NMR: ϕ −72.6 (A, d, d, d, d), −113.4 (C, d, d, d, q), −121.0 (D, d, d, q, d), −209.3 (B, d, d, q, d). ^{1}H NMR: δ 6.15 (d, d, q, d); $J_{A-B} = 6.0$ Hz, $J_{A-C} = 8.9$ Hz, $J_{A-D} = 11.7$ Hz, $J_{B-C} = 17.5$ Hz, $J_{B-D} = 3.4$ Hz, $J_{C-D} = 261$ Hz, $J_{A-H} = 11.3$ Hz, $J_{B-H} = 43.7$ Hz, $J_{C-H} = 13.5$ Hz, $J_{D-H} = 10.6$ Hz.

Preparation of $CF_3{}^{A}CF^{B}HCF_2{}^{C,D}SO_3H\cdot 1.5H_2O$. Into a 100-mL Pyrex glass round-bottomed flask equipped with a Teflon stirring bar were added 64.8 mmol of $CF_3CFHCF_2SO_3Na$ and 170 mmol of 100% H_2SO_4. The mixture was slowly distilled under reduced pressure, giving 30.3 mmol (46.8% yield) of $CF_3CFHCF_2SO_3H\cdot 1.5H_2O$. The boiling point was found to be 100–111 °C at 20 mm pressure. Spectral data obtained were as follows. IR (liquid): 2985 s, 2213 m, s, 1714 s, 1384 s, 1351 m, s, 1343 vs, 1261 vs, 1181 s, 1085 s, 1053 sh, 1029 sh, 992 s, 885 w, 851 m, 744 w, 727 w, 718 w, 646 vs, 620 m, 562 s, 542 sh, 533 sh, 525 m, 475 m, 403 m cm^{-1}. MS (CI$^+$) [*m/e* (species), intensity]: 151 ($CF_3CFHCF_2{}^+$), 80; 150 ($CF_3CFCF_2{}^+$), 10; 131 ($CF_2SO_3H^+$), 4.0; 100 (CF_3CF^+), 3.5; 69 ($CF_3{}^+$), 30; 65 (SO_2H^+), 4.1; 64 ($SO_2{}^+$), 5.0. ^{19}F NMR: ϕ −75.2 (A, d, d, d, d), −113.2 (C, d, d, d, d), −118.5 (D, d, d, q, d), −210.5 (B, d, d, q, d). ^{1}H NMR: δ 5.6 (CH, d, d, q, d), 10.65 (SO_3H, s); $J_{A-B} = 6.0$ Hz, $J_{A-C} = 8.6$ Hz, $J_{A-D} = 12.8$ Hz, $J_{B-C} = 17.5$ Hz, $J_{B-D} = 3.5$ Hz, $J_{C-D} = 262$ Hz, $J_{A-H} = 10.8$ Hz, $J_{B-H} = 42.6$ Hz, $J_{C-H} = 12.8$ Hz, $J_{D-H} = 10.7$ Hz.

Preparation of $(CF_3)_3{}^{A}CCF^{B}HCF_2{}^{C,D}SO_3Na$. A 10-mmol sample of $(CF_3)_3CCF{=}CF_2$ was condensed into a 25-mL stainless steel vessel containing 10.3 mmol of $NaHSO_3$, 2.6 mmol of $Na_2B_4O_7\cdot 10H_2O$, 0.22 mmol of $(C_6H_5CO)_2O_2$, and 6.0 mL of water. The mixture was heated at 115 °C for 10 h and cooled to room temperature, and the solvent was removed under vacuum. The residue was extracted with three 15-mL portions of hot ethanol and water (75:25), and the extracts were combined and dried under vacuum. The solid product, $(CF_3)_3CCFHCF_2SO_3Na$, was obtained in 50% yield. This compound is stable to 320 °C. Spectral data obtained were as follows. IR (solid): 3480 m, b, 1650 w, b, 1490 m, b, 1400 m, b, 1260 m, 1210 s, sh, 1190 s, 1120 w, 1070 s, 985 s, 910 w, sh, 821 m, 712 w, 720 m, 710 m, sh, 698 w, sh, 670 w, sh, 610 m, 593 w, 572 m, 540 m, sh, 520 m, 452 m cm^{-1}. MS (FAB$^+$) [*m/e* (species), intensity]: 427 ($M^+ + Na$), 17.2; 407 ($M^+ + Na - HF$), 14.6; 389 ($M^+ + Na - 2F$), 4.1; 337 ($C_5F_{10}SO_2Na^+$), 5.3; 237 ($C_3H_6SO_2Na^+$), 48.8; 215 ($C_3F_6SO_2H^+$), 32.0; 163 ($CF_3CCFHCF_2{}^+$), 25.6; (CSO_3Na^+), 21.5; 69 ($CF_3{}^+$), 28.0. ^{19}F NMR: ϕ −62.84 (A, m), −107 (C, m), −113 (D, m), −200.2 (B, m). ^{1}H NMR: δ 6.73 (m); $J_{C-D} = 244$ Hz.

Preparation of $(CF_3)_2CFP(O)(OH)_2$. Into a 160-mL stainless steel vessel were added 25 mmol of $(CF_3)_2CFI$, 37.5 mmol of tetraethyl pyrophosphite, 12.5 mmol of di-*tert*-butyl peroxide, and 35 mL of Freon 113. The reaction mixture was evacuated at −196 °C, warmed to room temperature, and finally heated at 110–115 °C for 3 h. After cooling to room temperature, the reaction mixture was transferred to a 250-mL three-necked round-bottomed Pyrex flask equipped with a dropping funnel, a Teflon-coated magnetic stirring bar, and a nitrogen line. The apparatus was purged with nitrogen, and a solution of 90 mmol of *tert*-butyl hydroperoxide and 30 mL of methanol was added slowly from the dropping funnel at 0 °C with stirring. After complete addition of the *tert*-butyl hydroperoxide solution, the mixture was allowed to stir at 0 °C for an additional 1 h. The mixture was then warmed to room temperature and washed with three 30-mL portions of water. Solvent was then removed under vacuum, and the liquid product, $(CF_3)_2CFP(O)(OC_2H_5)_2$, was obtained in 85% yield. It was identified by comparison to data given in the literature.[25] Spectral data obtained for $(CF_3)_2CFP(O)(OC_2H_5)_2$ were as follows. ^{19}F NMR: ϕ −73.8 (CF_3, d, d), −192.8 (CF, d, sep). $^{31}P\{H\}$ NMR: δ 0.52 (d, sep); $J_{CF_3-P} = 1.98$ Hz, $J_{CF_3-CF} = 9.28$ Hz, $J_{CF-P} = 67.2$ Hz. A 21.1-mmol sample of $(CF_3)_2CFP(O)(OC_2H_5)_2$ was then placed into a 50-mL round-bottomed Pyrex flask, and 31.7 mmol of $(CH_3)_3SiBr$ was added. The reaction mixture was stirred at room temperature for 48 h. Excess $(CH_3)_3SiBr$ was then removed under vacuum, 40 mL of water was added to the flask, and the solution was again stirred for 48 h at room temperature. Water was removed under vacuum to leave a 51% yield of the desired liquid product $(CF_3)_2CFP(O)(OH)_2$. The compound was partially purified by stirring with charcoal in 3 mL of water followed by filtration and drying under vacuum. Spectral data obtained were as follows. MS (CI$^+$) [*m/e* (species), intensity]: 281 ($M^+ + 2CH_3 + 1$), 29.1; 249 ($M^+ - 1$), 1.9; 216 ($(CF_3)_2CFP(O)^+$), 5.1; 169 ($(CF_3)_2CF^+$), 1.9; 81 ($P(O)(OH)_2{}^+$), 56.9; 69 ($CF_3{}^+$), 10.0. ^{19}F NMR: ϕ −73.0 (CF_3, d, d), −192 (CF, d, sep). $^{31}P\{H\}$ NMR: δ −3.33 (d, sep). ^{1}H NMR: δ 9.13 (s, bd); $J_{CF_3-P} = 2.1$ Hz, $J_{CF_3-CF} = 9.5$ Hz, $J_{CF-P} = 65.1$ Hz.

Preparation of $C_6F_5CH_2P(O)(OC_2H_5)_2$. Into a 60-mL stainless steel vessel were added 3.0 mmol of $C_6F_5CH_2Br$ and 4.5 mmol of triethyl phosphite. The mixture was heated at 125–130 °C for 10 h. The desired product, $C_6F_5CH_2P(O)(OC_2H_5)_2$, was separated and purified by distillation and was obtained as a colorless liquid (bp = 108 °C/0.3 mm) in 30% yield. Spectral data obtained were as follows. MS (EI$^+$) [*m/e* (species), intensity]: 318 (M^+), 10.0; 291 ($M^+ + H_2O - OC_2H_5$), 2.0; 181 ($C_6F_5CH_2{}^+$), 53.0; 137 ($P(O)(OC_2H_5)_2{}^+$), 32; 109 ($P(O)(OC_2H_5)OH$), 100; 81 ($P(O)(OH)_2$), 49. ^{19}F NMR: ϕ −142.7, −159.4, −165.5 (C_6F_5, m). $^{31}P\{H\}$ NMR: δ 21.1 (s). ^{1}H NMR: δ 1.24 (q), 3.16 (d), 4.06 (m).

Preparation of $C_6F_5CH_2P(O)(OH)_2$. A 3-mmol sample of $C_6F_5CH_2P(O)(OC_2H_5)_2$ was combined with 9 mmol of $(CH_3)_3SiBr$ in a round-bottomed Pyrex vessel equipped with a Teflon stopcock, and the mixture was stirred at room temperature for 30 h. Excess $(CH_3)_3SiBr$ was removed under vacuum, and 20 mL of water was added. Stirring was initiated at room temperature for 2 h, followed by stirring for 2 h at 50 °C. After cooling to room temperature, the solvent was removed under vacuum, and the remaining solid was recrystallized from a mixture of acetone and chloroform (5:1) to give a 45% yield of white crystalline $C_6F_5CH_2P(O)(OH)_2$ (mp 223 °C). Spectral data obtained were as follows. MS (EI$^+$) [*m/e* (species), intensity]: 262 (M^+), 3.0; 242 ($M^+ - HF$), 100; 181 ($C_6F_5CH_2{}^+$), 52.0; 161 ($C_6F_4CH^+$), 4.0; 81 ($P(O)(OH)_2{}^+$), 6.1. ^{19}F NMR: ϕ −141.1, −157.7, −163.4 (C_6F_5, m). $^{31}P\{H\}$ NMR: δ 16.0 (s). ^{1}H NMR: δ 3.05 (d), 5.04 (s, b).

Preparation of $CF_3CH_2N(H)P(O)(OC_2H_5)_2$. Into a round-bottomed Pyrex vessel containing 30 mL of ether were combined 2.18 g (12.7 mmol) of $(C_2H_5O)_2P(O)Cl$ and 2.17 g (21.9 mmol) of $CF_3CN_2NH_2$. The mixture was refluxed for 3 h after stirring for 3 h at 5 °C. The product solution was washed with three 25-mL portions of water or additionally with water until the water wash was neutral. The ether layer was evaporated to give 1.81 g (7.7 mmol, 61% yield), of a white solid product $CF_3CH_2N(H)P(O)(OC_2H_5)_2$. Spectral data obtained were as follows. IR (solid): 3203 vs, b, 3000 s, 2955 s, 2925 s, 2060 w, b, 1846

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w, 1489 s, 1453 s, 1404 s, 1380 m, sh, 1310 m, sh, 1310 s, 1290 s, 1240 vs, 1163 vs, 1109 m, 1070 s, 1040 vs, 982 vs, 877 s, 838 s, 810 s, 760 m, 670 s, 627 w, 571 m, sh, 550 s, 528 s, b, 490 s, 429 w cm^{-1}. MS (EI$^+$) [*m/e* (species), intensity]: 235 (M$^+$), 5.2; 216 (M$^+$ − F), 13.0; 162 ($CF_3CH_2N(H)PO_2H^+$), 51.5; 110 ($C_2H_5OPO_2H_2^+$), 100; 92 ($P(O)OC_2H_5^+$), 22.5; 81 ($P(O)(OH)_2^+$), 28.0; 69 (CF_3^+), 38.0. ^{19}F NMR: ϕ −75.1 (t). ^{31}P{H} NMR: δ 6.8 (s). ^{1}H NMR: δ 1.2 (t), 3.5 (q, b), 4.33 (p), 5.1 (b); $J_{CF_3CH_2} = 8.2$ Hz, $J_{CH_3-CH_2} = 7.1$ Hz.

Preparation of $CF_3CH_2N(H)P(O)(OH)_2$. A 1.87-mmol sample of pure $CF_3CH_2N(H)P(O)(OC_2H_5)_2$ was combined with 3.9 mmol of $(CH_3)_3SiBr$ in a round-bottomed Pyrex vessel equipped with a Teflon stopcock. The mixture was stirred at 40 °C for 12 h and at 45 °C for 18 h, after which excess $(CH_3)_3SiBr$ was removed under vacuum. Water (20 mL) was then added, and stirring at room temperature was continued for 24 h. The solvent was then removed under vacuum to leave the white solid product $CF_3CH_2N(H)P(O)(OH)_2$ in approximately 20% yield. Spectral data obtained were as follows. IR (KBr): 3460 b (OH), 3200 cm^{-1} vb (NH). MS (CI$^+$) [*m/e* (species), intensity]: 180 (M$^+$ + 1), 72.0; 160 (M$^+$ − F), 30.4; 138 (M$^+$ − F − 2H), 29.6; 110 (M$^+$ − CF_3), 33.6; 80 ($P(O)_2OH^+$), 14.0; 69 (CF_3^+), 1.2. ^{19}F NMR: ϕ −73.6 (t). ^{31}P{H} NMR: δ −10.9 (s). ^{1}H NMR: δ 3.66 (b), 5.87 (b), 4.2 (q); $J_{CF_3-CH_2} = 7.9$ Hz.

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Synthesis and Structural Characterization of Trimethylphosphine Complexes of Technetium(III)

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The first structurally characterized technetium(III) complexes containing trimethylphosphine as a ligand are reported. A novel cationic technetium(III) phosphine hydride complex was prepared by reaction of $[Tc(S\text{-tu})_6][PF_6]_3$ (tu = η^1-S=C(NH$_2$)$_2$) with excess trimethylphosphine in methanol. The complex, $[TcH\{\eta^2\text{-}N,S\text{-}NHC(NH_2)S\}(PMe_3)_4][PF_6]$ (**1**) was characterized spectroscopically and crystallographically, and shown to contain the unusual bidentate ligand $[\eta^2\text{-}N,S\text{-}NHC(NH_2)S]^-$ and a hydride ligand. Stirring **1** in methanol-d_4 led to formation of a spectroscopically identified technetium(III) deuteride, $[TcD\{\eta^2\text{-}N,S\text{-}NDC(ND_2)S\}(PMe_3)_4][PF_6]$. Crystallographic data for **1** are as follows: monoclinic, *Cc*, $a = 9.305$ (2) Å, $b = 16.726$ (2) Å, $c = 19.951$ (3) Å, $\beta = 91.24°$, $V = 3104.4$ Å^3, $Z = 4$, $R = 0.062$ ($R_2 = 0.060$) for 2043 observed reflections having $F_o > 3\sigma(F_o)$. Reaction of a Tc(V) substrate, $[NBu_4][TcOCl_4]$, with excess trimethylphosphine yielded *mer*-$TcCl_3(PMe_3)_3$ (**2**). Crystals of **2** suitable for X-ray analysis were obtained by cocrystallizing **2** with triphenyl isocyanurate, $[(PhNCO)_3]$. The resulting material, [*mer*-$TcCl_3(PMe_3)_3$]$[(PhNCO)_3]$, crystallized in the orthorhombic space group *Pnma* in a unit cell of dimensions $a = 18.461$ (1) Å, $b = 13.934$ (2) Å, $c = 14.035$ (1) Å, $V = 3610.3$ Å^3, and $Z = 4$, with $R = 0.044$ ($R_w = 0.039$) for 3699 observed reflections having $F_o > 3\sigma(F_o)$. The closest intermolecular distances revealed no bonding between the two components in the crystal, **2** and $[(PhNCO)_3]$.

Introduction

The increased use of radiodiagnostic compounds labeled with the metastable isotope ^{99m}Tc (γ = 140 keV, $t_{1/2}$ = 6 h) has led to numerous studies exploring the basic coordination chemistry of technetium. Technetium compounds containing tertiary phosphine ligands have been studied extensively.[2-5] However, the reports of technetium compounds containing trimethylphosphine as a ligand are limited. Deutsch[6] reported the preparation of a cationic Tc(III) complex containing a tetradentate Schiff-base ligand and trans trimethylphosphine ligands. The reaction of sodium pertechnetate and excess trimethylphosphine was claimed[7] to yield the cationic Tc(I) species $[Tc(PMe_3)_6]^+$, which was not isolated. Neither of these compounds has been structurally identified. We now report the synthesis and structural characterization of two trimethylphosphine complexes of technetium, as well as their spectroscopic and electrochemical properties.

Experimental Section

Materials. Technetium-99, as $NH_4{}^{99}TcO_4$, was purchased from Oak Ridge National Laboratories, Oak Ridge, TN. *Caution*! ^{99}Tc is a weak β-emitter with a half-life of 2.12×10^5 years, and a particle energy of 0.292 MeV. When handled in milligram amounts, ^{99}Tc does not present a significant health hazard since common laboratory materials (glass, Lucite) provide adequate shielding. Bremsstrahlung is not a significant problem due to the low energy of the β-particle emission. All manipulations were carried out in a fume hood, on a conventional vacuum line, as appropriate, or in a drybox under dinitrogen. Standard techniques for handling air-sensitive compounds were employed throughout. The work area was routinely monitored for residual radiation by using a calibrated Technical Associates Model TBM-3 contamination meter. All solvents were water and dioxygen free. Methanol, acetonitrile, and methylene chloride (Baker, Reagent Grade) were purged with dinitrogen, dried twice over activated molecular sieves (3 Å), and filtered through $^1/_4$-in. of activated alumina prior to use. Diethyl ether and tetrahydrofuran (THF; Baker, Reagent Grade) were distilled under dinitrogen from the sodium ketyl of benzophenone, stored over activated molecular sieves (3 Å), and filtered through $^1/_4$-in. of activated alumina prior to use. Trimethylphosphine and thallium hexafluorophosphate was purchased from Strem Chemicals Inc. All other chemicals were purchased from Aldrich Chemical Co. All reagents were used as received. $[NBu_4][TcOCl_4]$[8] and $[Tc(S\text{-tu})_6][Cl]_3$[9] were prepared by standard methods (tu = thiourea, i.e., S=C(NH$_2$)$_2$).

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