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Application of *n*-Bu_4NHF_2 as a Fluorinating Agent for the Preparation of Fluoroanions: Synthesis and Crystal Structure of the Anions $[t\text{-}BuPO_3AlF_2]_2^{2-}$, $[PhPO_3AlF_2]_2^{2-}$, and $[(O\text{-}i\text{-}Pr)_3Ti(\mu\text{-}F)_2(\mu\text{-}O\text{-}i\text{-}Pr)Ti(O\text{-}i\text{-}Pr)_3]^-$

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The first phosphonate anions of aluminum-containing fluorine and an anionic bridged fluoroalkoxy derivative of titanium have been realized using *n*-Bu_4NHF_2 as a fluorinating agent in organometallic synthesis. Reactions of $[RPO_3AlMe]_4$ [R = Ph (**1**), *t*-Bu] with *n*-Bu_4NHF_2 yield organic-soluble compounds of the type $[n\text{-}Bu_4N]_2[RPO_3\text{-}AlF_2]_2$ [R = Ph (**2**), *t*-Bu (**3**)], whereas the reaction of $Ti(O\text{-}i\text{-}Pr)_4$ with *n*-Bu_4NHF_2 results in the formation of $[n\text{-}Bu_4N][(O\text{-}i\text{-}Pr)_3Ti(\mu\text{-}F)_2(\mu\text{-}O\text{-}i\text{-}Pr)Ti(O\text{-}i\text{-}Pr)_3]$ (**4**). These compounds have been obtained in high yields and have been adequately characterized through spectroscopic techniques and X-ray diffraction studies.

Introduction

Zeolites, aluminophosphates, and their transition-metal analogues have gained significant attention as size- and shape-selective catalysts, molecular sieves, ion exchangers, and fabricators of reactors of molecular dimensions.[1−5] We were interested in developing synthetic routes to microporous materials via nonaqueous routes, and consequently, we used the building block strategy to pursue this goal. To the previously known models of single four-ring (4R) and double four-ring (D4R) compounds were added a double six ring (D6R), a single six ring (6R), and a tricyclic unit ($6\equiv1$).[6−10] In the recent years, the areas of organic-soluble phosphonates and fluorides have been at the forefront of our diversified facets of research.[11] Very recently, we developed new synthetic routes for the production of neutral phosphonate assemblies containing fluorine, which resemble the structural motifs of zeolite frameworks and elucidate the mineralizing and structure-directing properties of fluoride in such systems.[10] In the past, weakly coordinating fluoro anions such as BF_4^-, PF_6^-, AsF_6^-, and SbF_6^- have been studied in detail for their importance in synthesis and catalysis.[12] These anions could be easily replaced by more powerful donor ligands or reacting substrates. The first example of weak coordination behavior was the synthesis of $Ag[\{((Me_3Si)_3C)_2\text{-}Al_2F_5\}Li]$ starting from $[(Me_3Si)_3CAlF_2]_3$, LiCl, and AgF.[13] In past years, one of the primary objectives for fluoride-based research in our laboratory had been the development of new fluorinating agents.[14] In the past, we have investigated the effects of alkali and alkaline earth fluorides (NaF, KF, CaF_2) on titanium−fluoro complexes resulting in tetranuclear bridged fluoro compounds, which effectively demonstrate molecular recognition through the nucleophilic host molecules formed in a template-controlled manner.[15] Moreover, we have found a new synthetic route for the generation of the anionic difluoro group-13-metal-containing compounds of the type $[n\text{-}Bu_4N][Me_2MF_2]$

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[M = Al, Ga, In] using the title compound as the fluorinating agent.[16] Hence, our objective was to extend these principles to transition metals and also to explore the possibility of the derivation of the several phosphonate cages that we have successfully synthesized in recent years.

Results and Discussion

The reaction of $[RPO_3AlMe]_4$ [R = Ph (**1**), *t*-Bu] with *n*-Bu_4NHF_2 in a 1:4 molar ratio in THF at 0 °C results in the formation of organic-soluble aluminophosphonate anions of the type $[n\text{-}Bu_4N]_2[RPO_3AlF_2]_2$ [R = Ph (**2**), *t*-Bu (**3**)] in high yields as colorless crystalline solids along with the evolution of methane.

$$\underset{(R = Ph\ (\mathbf{1}),\ t\text{-}Bu)}{[RPO_3AlMe]_4} + 4n\text{-}Bu_4NHF_2 \xrightarrow[-4MeH]{THF,\ 0\ °C} \underset{(R = Ph\ (\mathbf{2}),\ t\text{-}Bu\ (\mathbf{3}))}{2[n\text{-}Bu_4N]_2[RPO_3AlF_2]_2} \quad (1)$$

Compound **1** was synthesized according to the literature procedure.[7a] The $Al_2O_4P_2$ core formation in **2** and **3** via $[RPO_3AlMe]_4$ precursors with $Al_4O_8P_4$ core structures could be attributed to the highly negative charge of −4 that would have resulted if $[RPO_3AlMe]_4$ had retained the core structure during fluorination, bearing eight fluorine atoms.

The ^1H NMR of **2** and **3** in CD_3CN revealed the signals corresponding to the various moieties in the required area ratios. In **2**, the phenyl groups on the phosphorus centers were observed as two sets of multiplets in the aromatic range (7.32 and 7.73 ppm), whereas in compound **3**, the *t*-Bu groups appeared as doublets centered at 1.03 ppm ($^3J_{P-H}$ = 15 Hz). The analysis of the ^{31}P NMR spectra for the above compounds revealed a strong dependence of the chemical shift on the adjacent substituent environment. For compound **2**, a sharp signal was observed at −2.3 ppm, while for **3**, a broad signal appeared at 15.2 ppm. In the ^{19}F NMR spectra of **2** and **3**, signals were observed at −180 and −179.5 ppm, respectively. The ^{27}Al NMR spectra of the compounds revealed the presence of a signal at 47.4 ppm for **2** and at 46.8 ppm for **3**. In the IR spectra of the compounds, sharp bands were observed in the range of 1210−1240 cm^{-1}, which is characteristic for metallophosphonate assemblies.[6,7]

The NMR (^1H, ^{31}P) and IR data are consistent with the dimeric structure of $[RPO_3AlF_2]_2^{2-}$.[6a−e] The preference of Al to achieve a coordination number of 4 and the absence of coordinated THF, as indicated by ^1H NMR spectroscopy, support a dimeric or tetrameric structure. Compounds **2** and **3** cannot be redissolved completely in the mother liquor or MeCN after having been isolated in the solid state; as a result, molecular weight determination analysis was not possible, and an unambiguous structural assignment could not be made. The spectroscopic conclusions, however, were corroborated through single-crystal X-ray diffraction studies on **2** and **3**.

The molecular structures of the anions of **2** and **3** are depicted in Figures 1 and 2. Suitable crystals for X-ray diffraction studies were obtained by layering hexane onto saturated solutions of these compounds in THF at room temperature. Compounds **2** and **3** crystallize in the monoclinic space group $P2_1/c$. The eight-membered $[RPO_3AlF_2]_2^{2-}$ anion is a dimer possessing distorted four-coordinate tetrahedral aluminum centers. The $Al_2O_4P_2$ core in **2** and **3** assumes a chair conformation, which is consistent with the 4R-type aluminum phosphonates that have been structurally characterized.[6e,j,17] However, in compound **2**, the eight-membered $Al_2P_2O_4$ core consists of two $PhPO_3$ bridges between distorted tetrahedral Al centers related by a crystallographically imposed inversion center. The average intra-ring Al−O bond distance (1.722 Å for **2** and 1.733 Å for **3**) is slightly shorter than those found for the neutral rings, whereas the average O−P bond length (1.540 Å for **2** and 1.549 Å for **3**) is slightly longer.[6j,17] The P=O bond distances for **2** and **3** were found in the range of 1.474−1.482 Å. The average Al−F bond lengths (1.659 Å for **2** and 1.666 Å for **3**) are in agreement with the literature precedents.[18] The *n*-Bu_4N^+ cations are positioned at an average distance of 4.651 Å from the anionic moiety for **2** and 4.720 Å for **3**.

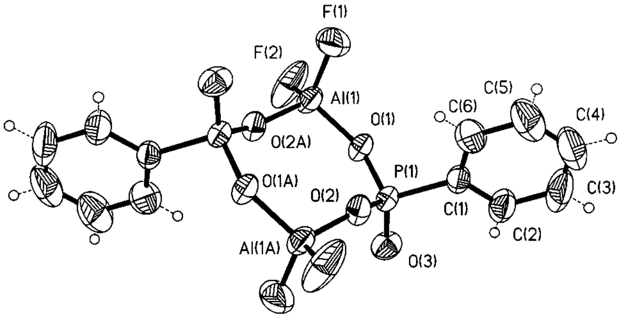

Figure 1. Molecular structure of $[PhPO_3AlF_2]_2^{2-}$.

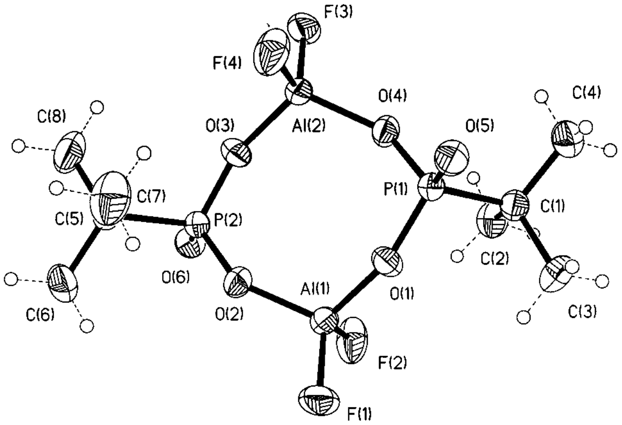

Figure 2. Molecular structure of $[t\text{-}BuPO_3AlF_2]_2^{2-}$.

Recently, we have shown the applications of titanium alkoxides as alternative synthons to titanium alkyls in the preparation of ring systems and aggregates of phosphonates and silicates, which signifies the importance of metal alkoxides as an emerging class of compounds in organometallic chemistry.[19] To test the feasibility of *n*-Bu_4NHF_2 as a fluorinating agent for transition metals, we conducted a 2:1 reaction between $Ti(O\text{-}i\text{-}Pr)_4$ and *n*-Bu_4NHF_2 at 0 °C to obtain $[n\text{-}Bu_4N][(O\text{-}i\text{-}Pr)_3Ti(\mu\text{-}F)_2(\mu\text{-}O\text{-}i\text{-}Pr)Ti(O\text{-}i\text{-}Pr)_3]$ (**4**) in high yield after

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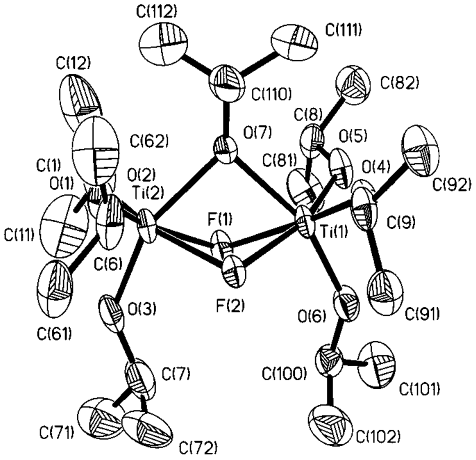

Figure 3. Molecular structure of $[(O\text{-}i\text{-}Pr)_3Ti(\mu\text{-}F)_2(\mu\text{-}O\text{-}i\text{-}Pr)Ti(O\text{-}i\text{-}Pr)_3]^-$.

subsequent workup.

$$2Ti(O\text{-}i\text{-}Pr)_4 + n\text{-}Bu_4NHF_2 \xrightarrow[-i\text{-}PrOH]{\text{hexane, } 0\ °C} [n\text{-}Bu_4N][(O\text{-}i\text{-}Pr)_3Ti(\mu\text{-}F)_2(\mu\text{-}O\text{-}i\text{-}Pr)Ti(O\text{-}i\text{-}Pr)_3] \quad (2)$$

4

A 1:1 reaction between the corresponding starting materials yielded **4** with an excess of n-Bu$_4$NHF$_2$, indicating that **4** is the most favorable product under the reaction conditions. The composition of the anion is consistent with the known behavior of titanium fluorides as dimers.[14]

Compound **4** was found to have a low melting point (58−59 °C) and a high degree of solubility in toluene and polar solvents (THF, MeCN, and CH$_2$Cl$_2$). In the ^{1}H NMR spectrum of **4** (benzene-d_6), two distinct sets of signals for the O-i-Pr groups at 1.12 and 4.79 ppm (bridged O-i-Pr) and at 1.20 and 4.46 ppm (terminal O-i-Pr) with the appropriate area ratios were observed in addition to the signals for the cation. The ^{19}F NMR spectrum revealed a broad signal at 65 ppm, which is characteristic for bridged titanium fluorides.[14] In the FAB-MS spectrum of **4**, the cationic moiety n-Bu$_4$N$^+$ was observed (at m/z 242) with 100% intensity, whereas the molecular ion corresponding to the anion was observed (at m/z 547) with 40% intensity. In the IR spectrum, the band at 568 cm^{-1} provides additional evidence for the Ti−F bond.[14]

Single crystals of **4** were obtained from a saturated solution of toluene at −30 °C over a period of 3 days. $[n\text{-}Bu_4N][(O\text{-}i\text{-}Pr)_3Ti(\mu\text{-}F)_2(\mu\text{-}O\text{-}i\text{-}Pr)Ti(O\text{-}i\text{-}Pr)_3]$ crystallizes as a dimer (in the monoclinic space group $P2_1/c$) with two titanium centers. Its anion molecular structure is depicted in Figure 3. The metal centers are bridged by two fluorine atoms and an O-i-Pr moiety, resulting in a hexacoordinate environment around each titanium. The Ti−F bond distance (mean 2.051 Å) and the Ti−O bond lengths (mean 2.063 Å) for the bridging O-i-Pr group are in accord with the previously observed values.[20] The terminal Ti−O bond lengths (mean 1.830 Å) were found to be shorter than the corresponding bridged distance. The n-Bu$_4$N$^+$ cation is located at a distance of 6.406 Å from the mean plane of the anion.

In summary, we have effectively demonstrated the use of n-Bu$_4$NHF$_2$ as a fluorinating agent which possesses the capability to functionalize D4R-type phosphonates and form fluorinated metal alkoxides. The facile access to this type of compounds opens up an attractive field to material science and catalysis.

Experimental Section

General Information. All manipulations were carried out under a dry, prepurified argon atmosphere, using Schlenk techniques and rigorously excluding moisture and air.[21] The samples for spectral measurements were prepared in a drybox. Solvents were dried over a Na/K alloy and freshly distilled prior to use. ^{1}H, ^{31}P, ^{19}F, and ^{27}Al NMR spectra were measured on Bruker MSL-400, AM-250, and AM-200 instruments. The chemical shifts are reported in parts per million with reference to SiMe$_4$ (external) for ^{1}H, 85% H$_3$PO$_4$ (external) for ^{31}P, CFCl$_3$ (external) for ^{19}F, and AlCl$_3$ (external) for ^{27}Al nuclei. IR spectra were recorded on a Bio-Rad Digilab FTS 7 spectrometer. Mass spectra were obtained on a Finnigan MAT 8230 or a Varian MAT CH 5 spectrometer. Elemental analyses were performed at the Analytical Laboratory of the Institute of Inorganic Chemistry, University of Göttingen.

Starting Materials. t-BuP(O)(OH)$_2$ and [t-BuPO$_3$AlMe]$_4$ were prepared using the literature procedures.[8,22] PhP(O)(OH)$_2$ (Aldrich) was dried in high vacuum prior to use. Trimethylaluminum (Witco), titanium isopropoxide (Aldrich), and n-Bu$_4$NHF$_2$ (Fluka) were used as received.

Preparation of [PhPO$_3$AlMe]$_4$ (1). To a stirred solution of PhP(O)(OH)$_2$ (0.631 g, 4.02 mmol) in THF (50 mL) was added a solution of AlMe$_3$ (2.9 mL, 4.02 mmol, 15% hexane) at 0 °C. The reaction mixture was allowed to warm to ambient conditions and subsequently heated under reflux for 2 h. The solvent was removed in vacuo to yield 5.43 g (6.85 mmol, 85%) of **1**. Mp: >350 °C. Anal. Calcd for $C_{28}H_{32}Al_4O_{12}P_4$: C, 42.44; H, 4.07. Found: C, 42.4; H, 4.3. ^{1}H NMR (200 MHz, THF-d_8): δ 7.8, 7.5 (m, broad, 20 H, C$_6$H$_5$), −0.79 (s, 12 H, AlCH$_3$). MS (EI, 70 eV): m/z 777 [M$^+$ − Me]. IR (KBr, Nujol, cm^{-1}): 3079 (m), 3046 (s), 1957 (m), 1892 (m), 1816 (m), 1771 (m), 1597 (s), 1464 (vs), 1206 (vs), 1150 (w), 1084 (m), 999 (w), 754 (w).

Preparation of [n-Bu$_4$N]$_2$[PhPO$_3$AlF$_2$]$_2$ (2). To a stirred solution of [PhPO$_3$AlMe]$_4$ (1.03 g, 1.3 mmol) in THF (40 mL) was added a solution of n-Bu$_4$NHF$_2$ (2.6 mL, 5.2 mmol, 50% in CH$_2$Cl$_2$) via a syringe at 0 °C. The reaction mixture was allowed to warm to room temperature and stirred for 2 h. Subsequently, hexane (40 mL) was layered onto the reaction mixture. Colorless cubic crystals of **2** (1.7 g, 62%), which were suitable for X-ray crystal structure analysis, were obtained at room temperature. Mp: 177 °C dec. Anal. Calcd for $C_{44}H_{82}Al_2F_4N_2O_6P_2$: C, 57.01; H, 8.92; N, 3.02; P, 6.68. Found: C, 57.2; H, 8.6; N, 3.1; P, 6.8. ^{1}H NMR (500 MHz, CD$_3$CN): δ 7.73, 7.32 (m, broad, 10 H, C$_6$H$_5$), 3.08 (m, 16 H, NCH$_2$), 1.58 (m, 16 H, CH$_2$), 1.32 (m, 16 H, CH$_2$), 0.93 (t, 24 H, CH$_3$). ^{19}F NMR (188 MHz, CD$_3$CN): δ −180 (s). ^{31}P NMR (202 MHz, CD$_3$CN): δ −2.3 (s). ^{27}Al NMR (65 MHz, CD$_3$CN): δ 47.4 (s). IR (KBr, Nujol, cm^{-1}): 3077 (s), 1956 (w), 1891 (w), 1815 (m), 1773 (w), 1596 (m), 1492 (vs), 1440 (vs), 1214 (s), 1135 (s), 1054 (vs), 1027 (vs), 885 (s), 788 (m), 763 (m), 737 (w), 696 (vs), 617 (w), 603 (w), 556 (w), 491 (s), 452 (s), 386 (sh), 367 (s).

Preparation of [n-Bu$_4$N]$_2$[t-BuPO$_3$AlF$_2$]$_2$ (3). The method of preparation is identical to that used for **2**. Mp: 206 °C dec. Anal. Calcd for $C_{40}H_{90}Al_2F_4N_2O_6P_2$: C, 54.16; H, 10.23; N, 3.16; P, 6.98. Found: C, 54.5; H, 9.8; N, 3.2; P, 7.1. ^{1}H NMR (200 MHz, CD$_3$CN): δ 3.08 (m, 16 H, NCH$_2$), 1.58 (m, 16 H, CH$_2$), 1.32 (m, 16 H, CH$_2$), 1.03 (d, $^3J_{P-H}$ = 15 Hz, 9 H, t-Bu), 0.93 (t, 24 H, CH$_3$). ^{19}F NMR (188 MHz, CD$_3$CN): δ −179.5 (s). ^{31}P NMR (202 MHz, CD$_3$CN): δ 15.2 (br, s). ^{27}Al NMR (65 MHz, CD$_3$CN): δ 46.8. IR (KBr, Nujol, cm^{-1}): 2725 (s), 1236 (s), 1197 (sh), 1152 (s), 1110 (vs), 1050 (vs), 976 (sh), 944 (m), 888 (s), 838 (s), 788 (vs), 738 (vs), 685 (m), 610 (m), 580 (m), 508 (sh), 482 (s), 403 (s).

Preparation of [n-Bu$_4$N][(O-i-Pr)$_3$Ti(μ-F)$_2$(μ-O-i-Pr)Ti(O-i-Pr)$_3$] (4). To a stirred solution of Ti(O-i-Pr)$_4$ (1.14 g, 4 mmol) in hexane (20 mL) at 0 °C was added n-Bu$_4$NHF$_2$ (1.0 mL, 2.0 mmol, 50% in CH$_2$-

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Table 1. Crystal Data and Structure Refinement Details for **2**, **3** and **4**

	2	**3**	**4**
empirical formula	$C_{44}H_{82}Al_2F_4N_2O_6P_2$	$C_{40}H_{90}Al_2F_4N_2O_6P_2$	$C_{37}H_{85}F_2NO_7Ti_2$
fw	927.02	887.04	789.86
cryst syst	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$	$P2_1/c$
a (Å)	10.634(11)	15.530(15)	10.210(2)
b (Å)	17.081(2)	17.093(2)	18.167(4)
c (Å)	14.698(2)	19.721(3)	25.330(5)
α (deg)	90	90	90
β (deg)	92.040(15)	100.210(13)	100.46(3)
γ (deg)	90	90	90
V (Å^3)	2668.1	5152.3	4619.9
T (°C)	−73	−123	−140
λ (Å)	0.71073	0.71073	0.71073
D_{calcd} (g cm^{-3})	1.154	1.144	1.136
μ (mm^{-1})	0.171	0.173	0.394
F(000)	1000	1936	1728
cryst size (mm)	1.00 × 0.80 × 0.80	1.00 × 0.60 × 0.20	0.30 × 0.30 × 0.30
θ range (deg)	3.52−25.03	3.58−25.17	1.98−21.97
index range	$-12 \le h \le 12$	$-18 \le h \le 18$	$-10 \le h \le 10$
	$0 \le k \le 20$	$-20 \le k \le 20$	$0 \le k \le 19$
	$-16 \le l \le 17$	$-23 \le l \le 23$	$0 \le l \le 26$
reflns colld	4757	13415	56260
indep reflns	4697	9207	5628
R (int)	0.0383	0.0509	0.0622
no. of data	4673	9181	5628
no. of params	275	519	502
no. of restraints	0	0	0
goodness-of-fit on F^2	1.057	1.048	1.073
R1 [$I > 2\sigma(I)$][a]	0.0592	0.0533	0.0613
wR2 (all data)	0.1761	0.1653	0.1514
largest diff peak and hole (e Å^{-3})	0.473, −0.306	0.340, −0.352	1.061, −0.345

[a] $R1 = \sum||F_o| - |F_c||/\Sigma|F_o|$. $wR2 = [\sum w(|F_o^2| - |F_c^2|)^2/\sum w|F_o^2|^2]^{1/2}$.

Cl_2) diluted in CH_2Cl_2 (5 mL). The reaction mixture was allowed to attain ambient conditions. All volatiles were removed in vacuo, and the residue obtained was crystallized from toluene (5 mL) at −30 °C over a period of 2 days to yield 1.35 g (85.4%) of **4**. Mp: 58−59 °C. Anal. Calcd for $C_{37}H_{85}F_2NO_7Ti_2$: C, 56.27; H, 10.85; N, 1.77. Found: C, 56.2; H, 10.8; N, 1.7. ^{1}H NMR (200 MHz, benzene-d_6): δ 0.96 (t, 12 H, NCH_2), 1.12 (d, 6 H, $OCH(CH_3)_2$), 1.20 (d, 36 H, $OCH(CH_3)_2$), 1.41 (m, 8 H, CH_2), 1.62(m, 8 H, CH_2), 3.31 (m, 8 H, CH_2), 4.46 (m, 6 H, $OCH(CH_3)_2$), 4.79 (m, 1 H, $OCH(CH_3)_2$). ^{19}F NMR (188 MHz, benzene-d_6): δ 65 (s). MS (FAB): m/z (%)$^+$ 242($C_{16}H_{36}N$, 100); m/z (%)$^-$ 547 ($C_{21}H_{49}F_2O_7Ti_2$, 40). IR (CsI, Nujol, cm^{-1}): 2617 (m), 1586 (m), 1371 (vs), 1329 (s), 1261 (w), 1161 (vs), 1127 (s), 1005 (w), 980 (s), 880 (m), 845 (s), 737 (m), 614 (s), 568 (vs), 467 (s), 423 (w), 390 (w), 357 (w), 341 (w).

X-ray Structure Determination. Crystal data for **2** and **3** were collected on a Stoe-Siemens-AED four-circle diffractometer using the learnt-profile method.[23] The data for **4** were collected on a Stoe-Siemens-Huber four-circle diffractometer equipped with a Siemens CCD area detector using the ψ-scan mode. The structures were solved by direct methods (SHELXS-90/96)[24] and refined on all data by full-matrix least-squares on F^2.[25] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were added in idealized positions and refined using a riding model. The crystal data and structure refinement details for **2**, **3**, and **4** are given in Table 1.

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Supporting Information Available: Tables listing detailed crystallographic data, atomic positional parameters, and bond lengths and angles This material is available free of charge via the Internet at http://pubs.acs.org.

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