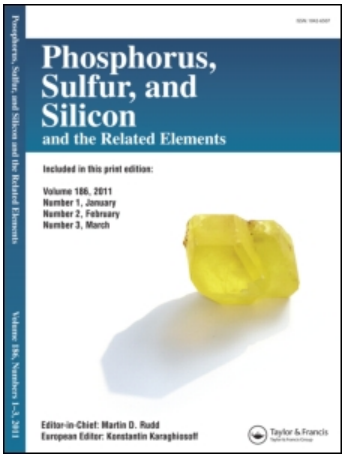


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Synthesis and Characterization of Monohaloalkoxyarsoranes Bearing a Novel Tridentate Ligand Occupying One Apical and Two Equatorial Sites

Hideaki Yamamichi[a]; Shiro Matsukawa[a]; Yohsuke Yamamoto[a]
[a] Department of Chemistry, Graduate School of Science, Hiroshima University, Higashi-Hiroshima, Japan

Online publication date: 27 May 2010

To cite this Article Yamamichi, Hideaki , Matsukawa, Shiro and Yamamoto, Yohsuke(2010) 'Synthesis and Characterization of Monohaloalkoxyarsoranes Bearing a Novel Tridentate Ligand Occupying One Apical and Two Equatorial Sites', Phosphorus, Sulfur, and Silicon and the Related Elements, 185: 5, 974 — 982
To link to this Article: DOI: 10.1080/10426501003772003
URL: http://dx.doi.org/10.1080/10426501003772003

Phosphorus, Sulfur, and Silicon, 185:974–982, 2010

ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426501003772003

Taylor & Francis
Taylor & Francis Group

SYNTHESIS AND CHARACTERIZATION OF MONOHALOALKOXYARSORANES BEARING A NOVEL TRIDENTATE LIGAND OCCUPYING ONE APICAL AND TWO EQUATORIAL SITES

Hideaki Yamamichi, Shiro Matsukawa, and Yohsuke Yamamoto
Department of Chemistry, Graduate School of Science, Hiroshima University, Higashi-Hiroshima, Japan

A series of pentavalent organoarsenic monohalides (F, Cl, and Br) were synthesized using a rigid tridentate ligand with a 2,2,2-trifluoro-1,1-diphenylethanol skeleton. The chloro derivative (4) could not be isolated due to its sensitivity to air, whereas the fluoro (5) and bromo derivatives (6) were isolated as crystalline solids. The X-ray crystallography of 5 and 6 revealed that both compounds adopted a pentacoordination at the arsenic atom with a covalent arsenic-halogen bond rather than the tetracoordinated ionic form. The solid state structures around the arsenic atom of 5 and 6 were almost ideal trigonal bipyramidal (TBP) geometries. The NMR measurements implied that 4, 5, and 6 were in the pentacoordinated state even in solution.

Keywords Arsenic; hypervalent; NMR study; pentacoordinate; X-ray analysis

INTRODUCTION

Hypervalent[1] group 15 element compounds, especially the phosphorus compounds, have attracted significant interests and have been widely investigated because such species are assumed to be involved as intermediates (or transition states) in the biological phosphoryl transfer reaction[2] as well as in synthetic reactions such as the Wittig olefination.[3] Pentacoordinate hypervalent group 15 element compounds generally adopt a trigonal bipyramidal (TBP) geometry, which has two different types of bonds, i.e., apical and equatorial bonds. Since the apical (hypervalent) bond is weaker and longer than the equatorial bond, the former is considered to be involved in the bond formation/cleavage reaction with the pentacoordinate species. Thus, understanding the bonding nature of hypervalent compounds is very important in order to appreciate the reactions involving such species as intermediates.

Received 18 November 2008; accepted 19 December 2008.
Dedicated to Professor Naomichi Furukawa on the occasion of his 70th birthday.
This work was supported by a Grant-in-Aid for Scientific Research on Priority Areas (No. 18064013) from the Ministry of Education, Culture, Sports, Science, and Technology, Japan.
Address correspondence to Yohsuke Yamamoto, Department of Chemistry, Graduate School of Science, Hiroshima University, 1-3-1 Kagamiyama, Higashi-Hiroshima 739-8526, Japan. E-mail: yyama@sci.hiroshima-u.ac.jp

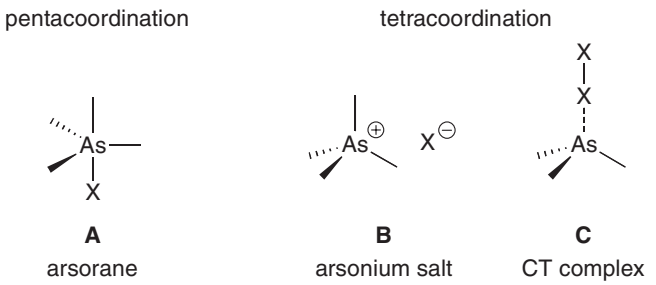


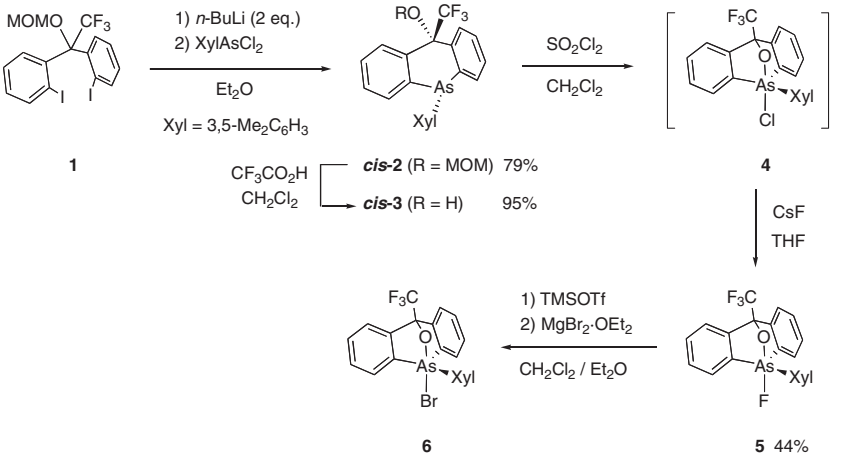
Figure 1 Possible structure forms for pentavalent arsenic compounds having halogen atoms.

A pentavalent arsenic compound having one or more halogen atoms can adopt the following forms: a pentacoordinate arsenic (arsorane) with a covalent arsenic–halogen bond (**A**), a tetracoordinate arsonium salt (**B**), and a charge-transfer (CT) complex (**C**) (Figure 1). The arsoranes (**A**) generally assume a trigonal bipyramidal (TBP) geometry, whereas the tetracoordinated arsenic compounds (**B** and **C**) adopt a tetrahedral geometry at the arsenic atom. Such structural diversity is found in the crystal structures of the triorganoarsenic dihalides. For example, in the solid state Ph_3AsF_2,[4] Me_3AsCl_2,[5a] and Ph_3AsBr_2[5b] are TBP molecules (**A**), whereas Me_3AsBr_2[5] exists as the CT complex, i.e., $Me_3As\cdots Br—Br$ (**C**). In contrast, the tetraorganoarsenic monohalides, Ph_4AsI,[6] Me_4AsBr,[7] and Me_4AsI[8] exclusively adopt the ionic form (**B**) in both the solid state and in solution. Furthermore, no structural insights regarding the haloalkoxyarsoranes ($R_3As(OR')X$) have been reported.[9] In this article, we report the first synthesis of monohalo-alkoxyarsoranes using a novel tridentate ligand, which occupies one apical and two equatorial sites in a TBP geometry. The single crystal X-ray analysis of the fluoro and bromo derivatives revealed that both compounds have TBP structure.

RESULTS AND DISCUSSION

Synthesis

Monohalogenated arsoranes **4**, **5**, and **6** were synthesized as shown in Scheme 1. The diiodide **1**[10] was first dilithiated with 2 equivalents of *n*-BuLi, and then treated with dichloro(3,5-dimethylphenyl)arsine ($XylAsCl_2$; Xyl = 3,5-$Me_2C_6H_3$) to afford the triarylarsine ***cis*-2** in 79% yield as a single stereoisomer. The deprotection of ***cis*-2** with trifluoroacetic acid gave the alcohol ***cis*-3** in 95% yield. The oxidative chlorination of ***cis*-3** using SO_2Cl_2 gave the moisture-sentitive chloroarsorane **4**, which was easily hydrolyzed upon exposure to air. Thus, in-situ generated **4** was treated with CsF to afford the fluoroarsorane **5** as an air- and moisture-stable crystalline solid in 44% yield (two steps from ***cis*-3**) as a single isomer. Abstraction of the fluorine atom of **5** with trimethylsilyl trifluoromethanesulfonate (TMSOTf), followed by bromination with $MgBr_2\cdot OEt_2$, then afforded the bromoarsorane **6** as a single isomer. Compound **6** was slightly unstable to moisture and contained a small amount of hydrolyzed compounds.



Scheme 1

Crystal Structures

Single crystals of fluoroarsorane **5** and bromoarsorane **6** were obtained by recrystallization from CH_3CN and CH_2Cl_2/*n*-hexane, respectively, and were then subjected to an X-ray crystallographic analysis. The ORTEP drawings of the molecular structures of these compounds are shown in Figure 2. Selected bond lengths and angles are contained in Table I. In both cases, the geometry at the arsenic atom is regarded as TBP, and the halogen atoms are covalently bonded to the corresponding arsenic atom. According to the apicophilicity rule,[11] it is reasonable that the electronegative fluorine and bromine atoms occupy the apical sites of **5** and **6**, respectively. The As–F distance in **5** (1.8099(10) Å) is close to that of the pentacoordinated Ph_3AsF_2 (1.834(3) Å for both fluorine atoms).[4] Similarly, the As–Br distance in **6** (2.4788(6) Å) is close to those of pentacoordinated Ph_3AsBr_2 (2.552(5), 2.441(5) Å),[5b] and much shorter than that observed in the arsonium salt $Me_4As^+Br^-$ (4.01(2) Å).[7]

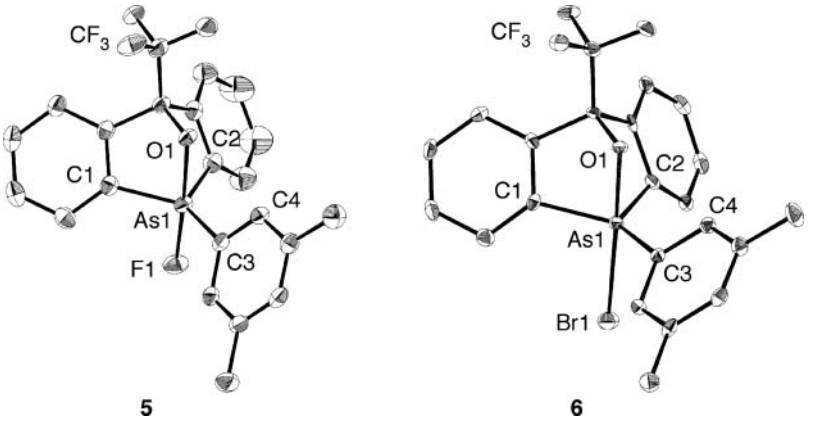


Figure 2 ORTEP drawings of the structures of compounds **5** and **6** with the thermal ellipsoids shown at the 50% probability level. All hydrogen atoms are omitted for clarity.

Table I Selected bond lengths and angles for compounds **5** and **6**

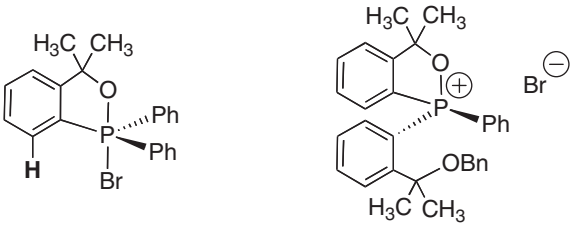
	5 (X = F)	**6** (X = Br)
Bond length (Å)		
As1–O1	1.9249 (11)	1.889 (2)
As1–C1	1.9182 (16)	1.931 (4)
As1–C2	1.9182 (17)	1.926 (4)
As1–C3	1.9087 (16)	1.909 (4)
As1–X1	1.8099 (10)	2.4788 (6)
Bond angles (deg)		
O1–As1–C1	82.64 (6)	83.23 (13)
O1–As1–C2	82.44 (6)	83.26 (13)
O1–As1–C3	93.27 (6)	89.34 (13)
O1–As1–X1	174.76 (5)	177.67 (8)
C1–As1–C2	101.02 (7)	100.87 (16)
C1–As1–C3	130.26 (7)	132.14 (15)
C1–As1–X1	93.80 (6)	94.83 (11)
C2–As1–C3	127.69 (7)	125.15 (16)
C2–As1–X1	94.52 (6)	95.86 (11)
C3–As1–X1	91.97 (6)	92.93 (11)

To evaluate the pentacoordination character, the $\%TBP_e$ values were calculated.[12] The $\%TBP_e$ values of **5** and **6** are 97% and 94%, respectively. Furthermore, the apical bond angles (O1–As1–X1, 174.76(5)° for **5** and 177.67(8)° for **6**) are close to the ideal value of 180°. These values apparently indicate that the compounds adopt the TBP structure. The reason for adoption of the TBP geometry in **5** and **6** is that the well-designed tridentate ligand prefers to occupy one apical and two equatorial sites of the TBP geometry rather than three apices of tetrahedral geometry.

The As1–O1 distance of the fluoro derivative **5** (1.9249(11) Å) is 0.03 Å longer than that of the bromo derivative **6** (1.889(2) Å). This difference could originate from the degree of tilt of the monodentate Xyl group, probably due to the difference in the crystal packing force. The dihedral angle O1–As1–C3–C4 of **5** (31.2°) is significantly smaller than that of **6** (47.0°). Therefore, steric repulsion between the oxygen atom (O1) and the ortho proton at C4 should be greater in **5** than in **6**, giving rise to the longer As1–O1 distance in **5**. The fact that the O1–As1–C3 angle of **5** (93.3°) is larger than that of **6** (89.4°) is also pertinent to the greater steric repulsion in **5**.

Structure in Solution

It is interesting whether the haloarsoranes are in pentacoordinated state or not in solution. The ^{19}F NMR spectrum of fluoroarsorane **5** shows a singlet at −94.6 ppm corresponding to the apical fluorine atom attached to the arsenic atom. This chemical shift is comparable to those of the reported fluoroarsoranes having the apical fluorine atoms, e.g., −87.3 ppm for Ph_3AsF_2 and −99.7 ppm for $(PhCH_2)_3AsFCl$.[13] Thus, **5** should also maintain the pentacoordination with the apical fluorine atom in solution as well as in the crystal structure. In the ^{13}C NMR spectrum of fluoroarsorane **5**, signals of the *ipso*-carbon atoms connected to the arsenic atom are observed as doublets coupled with the apical fluorine atom [δ = 147.2 (d, $^2J_{CF}$ = 2 Hz) and 139.4 (d, $^2J_{CF}$ = 2 Hz)], thus providing further evidence for **5** containing a covalent As–F bond also in solution.



7 **8**

^{31}P NMR: δ –17.8 ^{31}P NMR: δ 70.9

^{1}H NMR: δ 8.53-8.33 ^{1}H NMR: δ 8.10-6.75

Figure 3 Comparison of NMR chemical shifts between the Martin's bromophosphorane (left) and phosphonium bromide (right).

The ^{1}H NMR spectra of arsoranes **4**, **5**, and **6** are similar. The singlets for the ortho protons of the Xyl group are observed at $\delta = 7.82$ for **4**, 7.97 for **5**, and 7.69 for **6** ppm. The *ortho* protons of the tridentate ligand resonate at $\delta = 8.21$–8.19 for **4**, 7.91 for **5**, and 8.28–8.26 ppm for **6**. As shown by Granoth and Martin, the aromatic protons *ortho* to the hypervalent central atom are shifted downfield compared to those of the corresponding onium species.[14] For example, the ^{1}H NMR spectrum of phosphorane **7** shows the downfield-shifted *ortho* proton of the bidentate ligand at $\delta = 8.53$–8.33, whereas the *ortho* protons of phosphonium bromide **8** resonate at $\delta = 8.10$–6.75 (Figure 3). Thus, the very similar ^{1}H NMR signals of **4**, **5**, and **6** imply that these monohalides also adopt the trigonal bipyramidal (TBP) structure in solution.

In conclusion, we successfully synthesized a series of monohalogenated arsoranes using a novel tridentate ligand, which occupies one apical and two equatorials sites in a trigonal bipyramidal structure. The solid state structures of the fluoro (**5**) and bromo (**6**) derivatives were unambiguously determined by single crystal X-ray diffraction. NMR measurements indicate that these haloarsoranes exist in the pentacoordinate state also in solution.

EXPERIMENTAL

Melting points were measured using a Yanaco micro melting point apparatus. The ^{1}H (400 MHz), ^{13}C (100 MHz), and ^{19}F (376 MHz) NMR spectra were recorded using a JEOL EX-400 or a JEOL AL-400 spectrometer. The ^{1}H NMR chemical shifts (δ) are given in ppm downfield from Me_4Si, and were determined by referencing to residual chloroform ($\delta = 7.26$ ppm) and dimethyl sulfoxide ($\delta = 2.49$ ppm). The ^{13}C NMR chemical shifts (δ) are given in ppm downfield from Me_4Si, and were determined by referencing to chloroform-*d* ($\delta = 77.00$ ppm). The ^{19}F NMR chemical shifts (δ) are given in ppm downfield from the external $CFCl_3$. The elemental analyses were performed using a Perkin-Elmer 2400 CHN elemental analyzer. Tetrahydrofuran (THF) and diethyl ether (Et_2O) were freshly distilled from Na-benzophenone, and the other solvents were distilled from CaH_2. Preparative thin layer chromatography was carried out on Merck silica gel $60GF_{254}$ plates. Merck silica gel 60 was used for the column chromatography.

1,1-Bis-(2-iodophenyl)-2,2,2-trifluoroethyl Methoxymethyl Ether (1)

To a mixture of 1,1-bis(2-iodophenyl)-2,2,2-trifluoroethanol[10] (6.87 g, 13.6 mmol) and NaH (60% in oil, 1.09 g, 27.3 mmol) under argon, THF (27 mL) was added at 0°C, and the resulting mixture was stirred for 20 min. Methoxymethyl chloride (2.10 mL, 27.6 mmol) was then added at the same temperature. After stirring for 1 h at 0°C, the reaction was quenched with H_2O at 0°C, and the mixture was extracted with Et_2O (3 × 40 mL). The organic layer was washed with brine (100 mL), dried over anhydrous K_2CO_3, and the solvent was evaporated. The crude product was purified by column chromatography on silica gel (*n*-hexane:CH_2Cl_2 = 1:1, $R_f = 0.30$), followed by recrystallization from *n*-hexane to afford a white solid of **1** (7.10 g, 13.0 mmol, 95%). ^{1}H NMR ($CDCl_3$): δ = 8.2–7.9 (br s, 2H), 8.07 (d, J = 8 Hz, 1H), 7.96 (d, J = 8 Hz, 1H), 7.47 (t, J = 8 Hz, 1H), 7.34 (br s, 1H), 7.03 (t, J = 8 Hz, 2H), 4.74 (d, J = 6 Hz, 1H, OCH_2O), 4.66 (d, J = 6 Hz, 1H, OCH_2O), 3.60 (s, 3H, OCH_3). ^{13}C NMR ($CDCl_3$): δ = 143.7 (CH), 143.3 (CH), 137.7 (C), 133.5 (C), 130.0 (CH), 127.2 (CH), 124.6 (q, $^1J_{CF}$ = 291 Hz, CF_3), 93.4 (OCH_2O, CH_2), 85.2 (q, $^2J_{CF}$ = 28 Hz, CCF_3), 57.4 (OCH_3, CH_3). ^{19}F NMR ($CDCl_3$): δ = −69.0 (br s). Mp: 45.0–49.0°C. Elemental analysis: Calcd for $C_{16}H_{13}F_3I_2O_2$: C 35.06, H 2.39. Found: C 35.18, H 2.35%.

Dichloro(3,5-dimethylphenyl)arsine (XylAsCl_2)

XylAsCl_2 was prepared in a manner similar to the synthesis of acenaphthene-5-dichloroarsine.[15] To a suspension of 3,5-dimethylaniline (5.00 mL, 40.1 mmol) in H_2O (225 mL), conc. aq. HCl (25 mL) was added at room temperature. To the mixture cooled to 0°C, $NaNO_2$ (2.50 g, 36.2 mmol) in H_2O (20 mL) was added dropwise. The resulting mixture was then stirred for 1 h at 0°C to generate a diazonium salt. The solution of the diazonium salt kept at 0°C was added dropwise to a mixture of As_2O_3 (6.99 g, 36.2 mmol), $NaHCO_3$ (7.01 g, 83.5 mmol), KOH (24.0 g, 428 mmol), and $CuSO_4 \cdot 5\ H_2O$ (1.50 g, 6.02 mmol) in H_2O (200 mL) at room temperature, and the resulting mixture was stirred overnight at room temperature. The mixture was filtered to remove the solid materials, and the filtrate was condensed to ca. 200 mL by boiling. To the resulting solution, 6M aq. HCl (300 mL) was added, and the mixture was cooled to 0°C to give a white precipitate, which was collected by filtration to afford a white powder of 3,5-dimethylphenylarsonic acid (4.91 g, 21.3 mmol, 59%). ^{1}H NMR (DMSO-d_6): δ = 7.34 (s, 2H), 7.29 (s, 1H), 2.33 (s, 6H).

To a suspension of 3,5-dimethylphenylarsonic acid (1.66 g, 7.19 mmol) in *n*-hexane (16 mL), PCl_3 (2.4 mL, 34 mmol) was added dropwise under argon at room temperature, and the mixture was refluxed for 1 h. The supernatant was then transferred to another flask, and the solvent was evaporated in vacuo to afford a colorless crystalline solid of dichloro(3,5-dimethylphenyl)arsine (502 mg, 2.00 mmol, 28%). ^{1}H NMR ($CDCl_3$): δ = 7.46 (s, 2H), 7.16 (s, 1H), 2.39 (s, 6H).

Synthesis of cis-2

To a solution of **1** (548 mg, 0.999 mmol) in Et_2O (10 mL), *n*-BuLi (1.66 M solution in *n*-hexane, 1.21 mL, 2.01 mmol) was added under argon at 0°C, and the mixture was stirred for 15 min at the same temperature. To the mixture, a solution of XylAsCl_2 (252 mg, 0.995 mmol) in Et_2O (10 mL) at 0°C was added, then the resulting mixture was stirred for 2 h at room temperature. The reaction was then quenched with H_2O at room temperature.

The mixture was next extracted with Et_2O, the organic layer was washed with brine, dried over $MgSO_4$, and the solvent was evaporated. The crude mixture was purified by column chromatography (SiO_2, CH_2Cl_2:*n*-hexane = 1:3, $R_f = 0.30$) to give a white powder of ***cis*-2** (345 mg, 0.790 mmol, 79%). ^{1}H NMR ($CDCl_3$): 8.09 (d, $J = 8$ Hz, 2H), 7.43 (t, $J = 8$ Hz, 2H), 7.31–7.24 (m, 4H), 6.97 (s, 1H), 6.96 (s, 2H), 4.66 (s, 2H), 3.69 (s, 3H), 2.23 (s, 6H). ^{13}C NMR ($CDCl_3$): $\delta = 142.3$ (C), 139.7 (C), 138.2 (C), 133.1 (CH), 132.6 (CH), 132.1 (CH), 131.1 (CH), 130.1 (CH), 128.9 (CH), 127.9 (CH), 124.3 (q, $^1J_{CF} = 283$ Hz, *C*F_3), 93.4 (CH_2), 81.8 (q, $^2J_{CF} = 29$ Hz, *C*CF_3), 57.4 (CH_3), 21.2 (CH_3). ^{19}F NMR ($CDCl_3$): $\delta = -78.8$ (s). Mp: 134.9–138.5°C (dec.). Elemental analysis: Calcd for $C_{24}H_{22}AsF_3O_2$: C 60.77, H 4.67. Found: C 60.45, H 4.54%.

Synthesis of cis-3

To a solution of ***cis*-2** (23 mg, 0.048 mmol) in CH_2Cl_2 (1.0 mL), CF_3CO_2H (0.075 mL, 1.0 mmol) was added at room temperature, and the mixture was stirred for 2.5 h. The mixture was then evaporated to dryness to give a white powder of ***cis*-3** (20 mg, 0.046 mmol, 95%). ^{1}H NMR ($CDCl_3$): $\delta = 8.13$ (d, $J = 8$ Hz, 2H), 7.45 (t, $J = 8$ Hz, 2H), 7.30–7.22 (m, 4H), 6.99 (s, 1H), 6.96 (s, 2H), 3.04 (s, 1H), 2.22 (s, 6H). ^{13}C NMR ($CDCl_3$): $\delta = 142.7$ (q, $^3J_{CF} = 3$ Hz, C), 140.1 (C), 138.1 (C), 135.3 (C), 132.9 (CH), 132.8 (CH), 131.2 (CH), 128.6 (CH), 128.2 (CH), 127.4 (CH), 124.9 (q, $^1J_{CF} = 286$ Hz, *C*F_3), 76.7 (q, $^2J_{CF} = 30$ Hz, *C*CF_3), 21.1 (CH_3). ^{19}F NMR ($CDCl_3$): $\delta = -79.0$ (s). Mp: 188.2–191.1°C. Elemental analysis: Calcd for $C_{22}H_{18}AsF_3O$: C 61.41, H 4.22. Found: C 61.09, H 3.98%.

Chloroarsorane 4

To a solution of ***cis*-3** (84 mg, 0.195 mmol) in CH_2Cl_2 (1.0 mL) under argon, SO_2Cl_2 (0.080 mL, 1.0 mmol) was added at room temperature and the mixture was stirred for 20 min. The solvent was then removed *in vacuo* to give a white powder of **4**. ^{1}H NMR ($CDCl_3$): $\delta = 8.21$–8.19 (m, 2H), 7.82 (s, 2H), 7.70 (br s, 2H), 7.42–7.40 (m, 4H), 7.20 (s, 1H), 2.40 (s, 6H). ^{19}F NMR ($CDCl_3$): $\delta = -72.1$ (br s).

Fluoroarsorane 5

To a solution of ***cis*-3** (84 mg, 0.195 mmol) in CH_2Cl_2 (1.0 mL) under argon, SO_2Cl_2 (0.080 mL, 1.0 mmol) was added at room temperature. After stirring for 1 h at ambient temperature, the mixture was evaporated in vacuo to give a white solid of **4**. To the solid was added CsF (62 mg, 0.49 mmol) and THF (2.0 mL). The resulting mixture was stirred overnight at room temperature and the reaction was then quenched with H_2O. The mixture was then extracted with Et_2O, the organic layer was washed with brine, dried over $MgSO_4$, and evaporated. The residue was recrystallized from CH_3CN to afford colorless plate-like crystals of **5** (39 mg, 0.086 mmol, 44%). ^{1}H NMR ($CDCl_3$): $\delta = 7.97$ (s, 2H), 7.91 (d, $J = 8$ Hz, 2H), 7.72 (d, $J = 8$ Hz, 2H), 7.38 (t, $J = 8$ Hz, 2H), 7.32 (t, $J = 8$ Hz, 2H), 7.26 (s, 1H), 2.41 (s, 6H). ^{13}C NMR ($CDCl_3$): $\delta = 147.2$ (d, $^2J_{CF} = 2$ Hz, C), 139.4 (d, $^2J_{CF} = 2$ Hz, C), 137.9 (C), 137.7 (C), 134.8 (CH), 131.4 (d, $^3J_{CF} = 7$ Hz, CH), 130.5 (CH), 129.7 (CH), 128.0 (CH), 125.5 (q, $^1J_{CF} = 282$ Hz, C), 122.4 (q, $^4J_{CF} = 3$ Hz, CH), 80.7 (q, $^2J_{CF} = 33$ Hz, C), 21.4 (CH_3). ^{19}F NMR ($CDCl_3$): $\delta = -72.0$ (br s, 3F), -94.6 (s, 1F). Mp: 216.0–217.5°C. Elemental analysis calcd for $C_{22}H_{17}AsF_4O$: C 58.94, H 3.82. Found: C 58.72, H 3.78%.

Bromoarsorane 6

To a solution of **5** (13 mg, 0.029 mmol) in CH_2Cl_2 (1.0 mL) under argon, TMSOTf (0.010 mL, 0.055 mmol) was added at room temperature, and the mixture was stirred for 40 min. The volatiles were then removed in vacuo. To the residue, Et_2O (1.0 mL) was added. To the resulting suspension, a suspension of $MgBr_2 \cdot OEt_2$ (10 mg, 0.040 mmol) in Et_2O (4.0 mL) was added at room temperature, and the mixture was stirred overnight. The solvents were removed in vacuo, and the residue was dissolved in CH_2Cl_2. The resulting solution was filtered through Celite, and the solvent was evaporated in vacuo to give a white powder of **6** (15 mg), which contained a small amount of hydrolyzed compounds. ^{1}H NMR ($CDCl_3$): $\delta = 8.28$–8.26 (m, 2H), 7.69 (s, 2H), 7.69–7.67 (m, 2H), 7.45–7.40 (m, 4H), 7.17 (s, 1H), 2.39 (s, 6H). ^{19}F NMR ($CDCl_3$): $\delta = -72.1$ (br s).

Single Crystal X-Ray Analysis of 5 and 6

Single crystals suitable for X-ray diffraction were mounted on a Rigaku SCXmini diffractometer and irradiated with graphite monochromated Mo-$K\alpha$ radiation ($\lambda = 0.71073$ Å) at 173 K for the data collection. The data were processed using the Rigaku SCXmini program. The structure was solved by a direct method using the SHELXS-97 program.[16] Refinement on F^2 was carried out using the full-matrix least-squares method of the SHELXL-97 program.[16] All nonhydrogen atoms were refined using the anisotropic thermal parameters. The hydrogen atoms were included in the refinement along with the isotropic thermal parameters. Crystallographic data for **5**: monoclinic system, space group $P2_1/c$ (no. 14), $a = 9.0281(4)$ Å, $b = 12.8285(6)$ Å, $c = 16.1043(8)$ Å, $\beta = 93.8790(10)^\circ$, $V = 1860.88(15)$ Å^3, $Z = 4$, $D_{calc} = 1.600$ g cm^{-3}, data/param = 4278/255, R_1 ($I > 2\sigma(I)$) = 0.0241, wR_2 (all data) = 0.0648, $GOF = 1.011$. **6**: monoclinic system, space group $P2_1/n$ (no. 14), $a = 8.7858(17)$ Å, $b = 7.7016(15)$ Å, $c = 27.834(5)$ Å, $\beta = 96.097(5)^\circ$, $V = 1872.7(6)$ Å^3, $Z = 4$, $D_{calc} = 1.806$ g cm^{-3}, data/param = 4274/255, R_1 ($I > 2\sigma(I)$) = 0.0435, wR_2 (all data) = 0.1077, $GOF = 1.056$.

CCDC-708805 (**5**) and CCDC-708806 (**6**) contain the supplementary crystallographic data for this article. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

REFERENCES

1. K.-Y. Akiba, *Chemistry of Hypervalent Compounds* (Wiley-VCH, New York, 1999).
2. A. C. Hengge, *Acc. Chem. Res.*, **35,** 105 (2002).
3. (a) W. S. Wadsworth, Jr., *Org. React.*, **25,** 73 (1977); (b) J. I. G. Cadogan, *Organophosphorus Reagents in Organic Synthesis* (Academic Press, New York, 1979); (c) B. E. Maryanoff and A. B. Reitz, *Chem. Rev.*, **89,** 863 (1989); (d) E. Vedejs and M. J. Peterson, *Top. Stereochem.*, **21,** 1 (1994).
4. A. Augustine, G. Ferguson, and F. C. March, *Can. J. Chem.*, **53,** 1647 (1975).
5. (a) M. B. Hursthouse and I. A. J. Steer, *J. Organomet. Chem.*, **27,** C11 (1971); (b) N. Bricklebank, S. M. Godfrey, H. P. Lane, C. A. Mcauliffe, R. G. Pritchard, and J.-M. Moreno, *J. Chem. Soc., Dalton Trans.*, 3873 (1995).
6. (a) R. C. L. Mooney, *J. Am. Chem. Soc.*, **62,** 2955 (1940); (b) P. A. W. Dean, D. C. Craig, M. L. Scudder, and I. G. Dance, *Acta Cryst. C*, **C59,** m484 (2003).
7. E. Collins, D. J. Sutor, and F. G. Mann, *J. Chem. Soc.*, **193,** 4051 (1963).
8. W. Assenmacher and M. Jansen, *Z. Anorg. Allg. Chem.*, **621,** 143 (1995).

9. The crystal structures of the triphenylarsine hydrohalides (Ph_3AsOHX: X = Cl, Br) show the arsonium form, in which a hydrogen bond between the hydroxyl proton and halogen atom is observed; for $PhAs^+–OH\cdots X^-$: see G. Ferguson and E. W. Macaulay, *J. Chem. Soc., Chem. Commun.*, 1288 (1968).
10. Synthesis of parent 1,1-bis(2-iodophenyl)-2,2,2-trifluoroethanol: S. Matsukawa, H. Yamamichi, Y. Yamamoto, and K. Ando, *J. Am. Chem. Soc.*, **131,** 3418 (2009).
11. (a) M. Nakamoto, S. Kojima, S. Matsukawa, Y. Yamamoto, and K.-Y. Akiba, *J. Organomet. Chem.*, **643–644,** 441 (2002); (b) S. Matsukawa, K. Kajiyama, S. Kojima, S.-Y. Furuta, Y. Yamamoto, and K.-Y. Akiba, *Angew. Chem. Int. Ed.*, **41,** 4718 (2002), and references therein.
12. K. Tamao, T. Hayashi, and Y. Ito, *Organometallics*, **11,** 2099 (1992).
13. C. G. Moreland, M. H. O'Brien, C. E. Douthit, and G. G. Long, *Inorg. Chem.*, **7,** 834 (1968).
14. I. Granoth and J. C. Martin, *J. Am. Chem. Soc.*, **103,** 2711 (1981).
15. R. J. Garascia, G. W. Batzix, and J. O. Kroeger, *J. Org. Chem.*, **25,** 1271 (1960).
16. G. M. Sheldrick, *Acta Cryst.*, **A64,** 112 (2008).