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First Isolation and Kinetic Study of Hypervalent 10-As-5 Organoarsenic Compounds with a C-Apical, O-Equatorial Configuration

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Hypervalent organoarsenic compounds violating the apicophilicity concept were isolated for the first time, and the energy of isomerization of these arsoranes to the more stable stereoisomers appeared to be lower than that of the phosphorus analogues based on the kinetic studies.

Hypervalent compounds of the main group elements have been attractive subjects for both experimental and theoretical chemists for a long time.[1] Especially, hypervalent phosphorus (phosphorane) chemistry,[1,2] which is deeply related to the phosphoryl transfer reaction in biological systems,[3] has elucidated the significant fundamental properties of pentacoordinated molecules. Pentacoordinate compounds usually prefer to take the trigonal-bipyramidal (TBP) geometry, and there are two distinct sites in the TBP structure: the apical and equatorial sites. The apical bond is polarized; therefore, more electronegative substituents prefer to occupy the apical site (apicophilicity), and the presence of three equatorial substituents 90° away from the apical positions favors sterically less-demanding substituents in the latter positions.[4] In addition, hypervalent compounds undergo a rapid intramolecular site exchange of substituents, and the mechanism is usually interpreted by Berry pseudorotation (BPR).[5]

By using the Martin ligand (**A**; Figure 1),[6] we have succeeded in freezing the BPR in order to isolate a series of phosphoranes violating the apicophilicity concept[7] with an O-equatorial, C-apical configuration (O-equatorial).[8,9] These phosphoranes are kinetically stabilized products and can still be converted into the corresponding more stable stereoisomers with a C-equatorial, O-apical configuration (O-apical). Furthermore, we have developed a new bidentate ligand bearing two C_2F_5 groups (**B**; Figure 1) that was more effective for freezing the BPR of the phosphoranes than the Martin ligand.[10]

Unlike the situation at phosphorus centers, little is known about hypervalent arsenic species (arsoranes) because arsorane chemistry often suffers from a faster BPR than phosphorus.[11] For example, the activation free energy of Ph_2PF_3 at its coalescence temperature (379 K) was 18.7 kcal mol^{-1},[12] whereas only one fluorine signal of Ph_2AsF_3 observed at room temperature was not decoalesced even at −90 °C.[13] A

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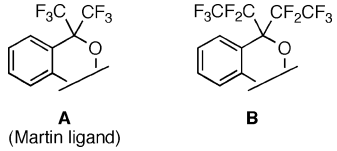


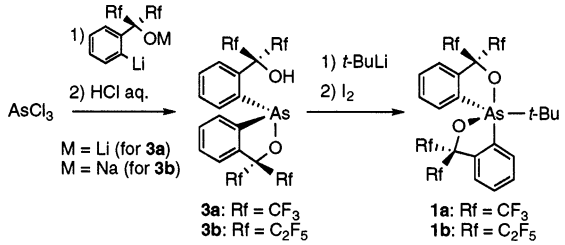
Figure 1. Bidentate ligands for freezing BPR.

theoretical study shows that the energy of the BPR for AsF_5 (3.0 kcal mol^{-1}) is lower than that for PF_5 (4.3 kcal mol^{-1}).[14] As we have done for phosphorane chemistry,[15,16] thorough investigation of each isolated isomer of the arsoranes would lead to determination of the general and fundamental properties of the chemistry of the pentacoordinate molecules. In this context, we next focused on the isolation of two 10-As-5[17] arsorane isomers using bidentate ligands **A** and **B**. We now present the first characterization of the pentacoordinate arsoranes with reversed apicophilicity (**1**: O-equatorial) and a kinetic study of their pseudorotation to the more stable O-apical isomers (**2**).[18]

We chose the *t*-butyl group as a monodentate ligand because it was the most effective ligand for slowing the isomerization of the series of O-equatorial phosphoranes to the O-apical isomer.[8] Compounds **3** were prepared by the treatment of $AsCl_3$ with 2-fold amounts of the corresponding bidentate ligand (Scheme 1).[19] Compound **3a** showed four distinct fluorine signals corresponding to the CF_3 groups in the ^{19}F NMR spectrum (δ = −73.7, −73.9, −76.2, and −77.2 ppm for **3a** at 25 °C), and the two aromatic rings were unequivalently observed in the ^1H NMR spectrum. This shows that compound **3a** is a tricoordinate arsine and is in clear contrast to the phosphorus analogue existing as a hydrophosphorane with an equatorial P−H bond.[20] The arsoranes with the reversed apicophilicity, **1a** and **1b**, could then be synthesized from the corresponding arsines, **3a** and **3b**, respectively, using our method for the synthesis of the O-equatorial spirophosphoranes.[9] Because the O-equatorial arsoranes were quantitatively converted to the corresponding O-apical isomers (**2**) when heated in solution, the O-equatorial arsoranes were proven to be kinetically stabilized and thermodynamically unstable species. These are the first isolated arsoranes with a reversed apicophilicity that still undergo stereomutation to the more stable stereoisomers.

The solid-state structures of the O-equatorial spiroarsoranes (**1a** and **1b**) and the O-apical counterparts (**2a** and **2b**) were confirmed by an X-ray crystallographic analysis. The ORTEP

Scheme 1



diagrams for the O-equatorial arsoranes are shown in Figure 2.[21] For the O-equatorial isomers, the bond distances of As1−O1 [1.962(2) Å for **1a** and 1.978(2) Å for **1b**] and As1−C2 [1.978(4) Å for **1a** and 1.986(3) Å for **1b**] are longer than those of As1−O2 [1.828(3) Å for **1a** and 1.817(2) Å for **1b**] and As1−C1 [1.954(4) Å for **1a** and 1.936(3) Å for **1b**], respectively. This implies that the former two correspond to apical bonds and the latter two are equatorial bonds, indicating that the structures of **1** still keep the TBP, even though they are distorted from the ideal TBP geometry to some extent, as indicated by the apical bond angles O1−As1−C2 [162.07(14)° for **1a** and 164.55(13)° for **1b**]. It is noted that the differences between the apical and equatorial distances for **1a** (As−O, 0.13 Å; As−C, 0.02 Å) are smaller than those for **1b** (As−O, 0.16 Å; As−C, 0.05 Å). That is, the distortion of **1a** toward the rectangular-pyramid (RP) geometry along the Berry coordinate is greater than that of

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(21) CCDC-639282 (**1a**), -639283 (**1b**), -639284 (**2a**), and -639285 (**2b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Crystals suitable for the X-ray structural determination were mounted on a Mac Science DIP2030 imaging plate diffractometer and irradiated with graphite-monochromated Mo Kα radition (λ = 0.710 73 Å) at −100 °C for the data collection. The unit cell parameters were determined by separately autoindexing several images in each data set using the DENZO program (MAC Science).[23] For each data set, the rotation images were collected in 3° increments with a total rotation of 180° about the ϕ axis. The data were processed using *SCALEPACK*. The structure was solved by a direct method with the *SHELX-97* program.[24] Refinement on F^2 was carried out using the full-matrix least squares with the *SHELX-97* program.[24] All non-hydrogen atoms except for the disordered atoms were refined using anisotropic thermal parameters. Crystallographic data for **1a**: monoclinic system, space group $P2_1/c$ (No. 14), a = 8.3040(3) Å, b = 16.0250(7) Å, c = 17.9010(10) Å, β = 99.950(2)°, V = 2346.28(19) Å^3, Z = 4, D_{calc} = 1.745 g cm^{-3}, data/param = 4781/337, R1 [$I > 2\sigma(I)$] = 0.0508, wR2 (all data) = 0.1424, GOF = 1.144. Crystallographic data for **1b**: monoclinic system, space group $P2_1/c$ (No. 14), a = 12.714(2) Å, b = 13.013(2) Å, c = 18.608(2) Å, β = 109.1290(10)°, V = 2908.6(7) Å^3, Z = 4, D_{calc} = 1.864 g cm^{-3}, data/param = 6597/437, R1 [$I > 2\sigma(I)$] = 0.0605, wR2 (all data) = 0.1704, GOF = 1.075. Crystallographic data for **2a**: orthorhombic system, space group $P2_12_12_1$ (No. 19), a = 11.6890(2) Å, b = 12.0290(2) Å, c = 16.6230(3) Å, V = 2337.31(7) Å^3, Z = 4, D_{calc} = 1.751 g cm^{-3}, data/param = 3129/334, R1 [$I > 2\sigma(I)$] = 0.0435, wR2 (all data) = 0.1427, GOF = 1.101. Crystallographic data for **2b**: triclinic system, space group $P\bar{1}$ (No. 2), a = 10.5300(2) Å, b = 11.9040(3) Å, c = 12.7020(4) Å, α = 76.8420(10)°, β = 74.5350(10)°, γ = 78.0960(10)°, V = 1476.16(7) Å^3, Z = 2, D_{calc} = 1.837 g cm^{-3}, data/param = 6527/445, R1 [$I > 2\sigma(I)$] = 0.0509, wR2 (all data) = 0.1817, GOF = 1.194.
(22) Detailed kinetic measurements for the isomerization of **4b** to **5b** were not performed. As reported in ref 9, however, it took 3 weeks for the isomerization of **4b** to **5b** at 468 K. Therefore, $\Delta G^{\ddagger}_{298}$ was estimated using the rate constant (ca. 2 × 10^{-6} s^{-1}) obtained at 468 K assuming that $\Delta S^{\ddagger}$ = ca. −10 eu.
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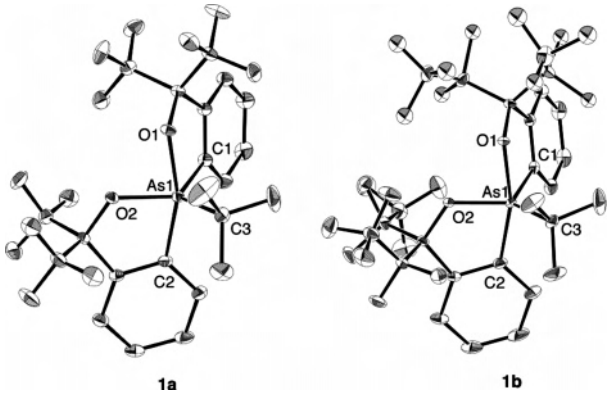
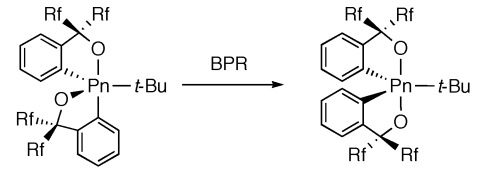


Figure 2. ORTEP diagrams of **1a** and **1b** showing the thermal ellipsoids at the 30% probability level. Selected bond lengths (Å) and angles (deg) for **1a**: As1−O1, 1.962(2); As1−O2, 1.828(3); As1−C1, 1.954(4); As1−C2, 1.978(4); As1−C3, 2.006(4); O1−As1−C2, 162.07(14); O2−As1−C1, 123.86(15); O2−As1−C3, 113.55(16); C1−As1−C3, 119.53(17). Those for **1b**: As1−O1, 1.978(2); As1−O2, 1.817(2); As1−C1, 1.936(3); As1−C2, 1.986(3); As1−C3, 2.014(3); O1−As1−C2, 164.55(13); O2−As1−C1, 116.80(12); O2−As1−C3, 118.59(14); C1−As1−C3, 121.65(15).

Scheme 2



1a: Pn = As, Rf = CF_3
1b: Pn = As, Rf = C_2F_5
4a: Pn = P, Rf = CF_3
4b: Pn = P, Rf = C_2F_5

2a: Pn = As, Rf = CF_3
2b: Pn = As, Rf = C_2F_5
5a: Pn = P, Rf = CF_3
5b: Pn = P, Rf = C_2F_5

1b, and the lower distortion of **1b** could be due to steric repulsion of the two nearest C_2F_5 groups.

Kinetic measurements for the isomerization of **1** to **2** were performed in *p*-*t*-butyltoluene over the temperature range of 60−80 °C for **1a** to **2a** and 85−105 °C for **1b** to **2b** (Scheme 2). The activation parameters for the CF_3 derivatives (**1a** to **2a**) are $\Delta H^{\ddagger} = 26.0 \pm 0.3$ kcal mol^{-1}, $\Delta S^{\ddagger} = -2.1 \pm 0.8$ eu, and $\Delta G^{\ddagger}_{298} = 26.6$ kcal mol^{-1}, and those for the C_2F_5 derivatives (**1b** to **2b**) are $\Delta H^{\ddagger} = 28.2 \pm 0.7$ kcal mol^{-1}, $\Delta S^{\ddagger} = -0.6 \pm 2.0$ eu, and $\Delta G^{\ddagger}_{298} = 28.4$ kcal mol^{-1}. The activation free energies for the arsoranes ($\Delta G^{\ddagger}_{298}$) are much lower than those for the corresponding phosphoranes (31.1 kcal mol^{-1} for **4a** to **5a**[7] and ca. 38 kcal mol^{-1} for **4b** to **5b**).[22] For not only the phosphoranes[10] but also the arsoranes, the C_2F_5 group appeared to be more effective for freezing the pseudorotation than the CF_3 group. Interestingly, when all of the CF_3 groups are replaced by the C_2F_5 groups, the activation free energy for the phosphoranes increases by 7 (38 − 31.1) kcal mol^{-1}, whereas that for the arsoranes increases by only 2 (28.4 − 26.6) kcal mol^{-1}.

In an attempt to synthesize an O-equatorial arsorane with an *n*-butyl group instead of the *t*-butyl group, we observed the O-equatorial isomer only when using the bidentate ligand **B** after treatment with iodine. Although we have not successfully isolated this species because of the relatively fast isomerization to the O-apical isomer at room temperature (ca. 25% isomerized in 30 min), this result implies that the O-equatorial arsoranes could be isolated if a monodentate ligand slightly larger than the *n*-butyl group is employed. This enables us to investigate the reactivity of the α-carbanion derived from the arsorane with a $-CH_2R$-type monodentate ligand, which should be compared to the α-carbanion from benzylphosphorane, which produced the stable hexacoordinate oxaphosphetane ate complex.[15] We are now expanding the present chemistry for the synthesis of a variety of arsoranes and stiboranes.

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Supporting Information Available: Experimental details and crystal structures of the O-apical isomers (**2a** and **2b**). This material is available free of charge via the Internet at http://pubs.acs.org.

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