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Phosphine-Stabilized Arsenium Salts: Water-Stable, Labile, Coordination Complexes

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A series of air- and water-stable tertiary phosphine-stabilized arsenium salts of the type $R_3P{\rightarrow}AsR_2^+PF_6^-$ has been isolated. In the crystal structures of two chiral triarylphosphine complexes of prochiral methylphenylarsenium hexafluorophosphate, the stereochemistry around arsenic is trigonal pyramidal with the phosphorus atom occupying the apical position, the As–P bond being orthogonal to the plane of the trigonal (lone-pair included) arsenium ion: $Ph_3P{\rightarrow}AsMePh^+\ PF_6^-$, $P2_1/c$, $a = 10.7775(2)$ Å, $b = 17.7987(3)$ Å, $c = 13.3797(2)$ Å, $\beta = 109.066(1)°$, $V = 2425.78(7)$ Å^3, $T = 200$ K, $Z = 4$; $Ph_2(2\text{-}MeOC_6H_4)P{\rightarrow}AsMePh^+\ PF_6^-$, $P\bar{1}$, $a = 10.8077(2)$ Å, $b = 10.9741(2)$ Å, $c = 13.5648(2)$ Å, $\alpha = 99.0162(9)°$, $\beta = 105.2121(9)°$, $\gamma = 116.4717(9)°$, $V = 1318.11(5)$ Å^3, $T = 200$ K, $Z = 2$. The arsenium ion in each case appears to be further stabilized by conjugation of the lone pair with the phenyl group, with which the arsenic and methyl-carbon atoms are almost coplanar. In the crystal structure of the 2-(methoxymethylphenyl)diphenylphosphine adduct of methylphenylarsenium hexafluorophosphate, there operates a counteractive chelate effect in which anchimeric oxygen coordination to arsenic destabilizes the arsenic–phosphorus bond in the six-membered chelate ring. Although they are stable, phosphine-stabilized arsenium salts undergo rapid phosphine exchange and attack at arsenic by anionic carbon and oxygen nucleophiles to give tertiary arsines and arsinous acid esters, respectively, with liberation of the phosphine.

Introduction

Phosphenium (R_2P^+), arsenium (R_2As^+), and stibenium (R_2Sb^+) ions are six-electron, unsaturated species containing lone pairs of electrons and vacant p orbitals, and accordingly display amphoteric properties as bases and Lewis acids.[1] Because of the similar electronegativities of carbon and phosphorus (C, 2.50; P, 2.06) versus silicon (1.74), however, phosphenium ions more closely resemble carbenes (R_2C) in their properties than the isoelectronic silylenes (R_2Si).[2,3] Arsenic has electronegativity 2.20.[2] Phosphenium ions insert into carbon−carbon single bonds, add to double and triple bonds [including 1,3-dienes by 1,4-cycloaddition to give phospholenium salts], and coordinate to transition metals.[4,5] Because of the formally vacant 3p orbital on phosphorus, phosphenium ions also form adducts with phosphines[1b,6] and a comparison has been made of the Lewis acidities of phosphenium and arsenium ions toward pyridine.[7] In general, as had been indicated by mass spectroscopic studies on certain heterocyclic trivalent phosphorus[8] and arsenic compounds,[9] simple phosphenium and arsenium salts isolated contain one or, more frequently, two electron-rich amido or sulfido substituents at phosphorus or arsenic.[4,5] Salts of the type $(R_2N)_2P^+X^-$, **1** (X = BF_4, PF_6,[10] $GaCl_4$ [11]) and **2** (R =

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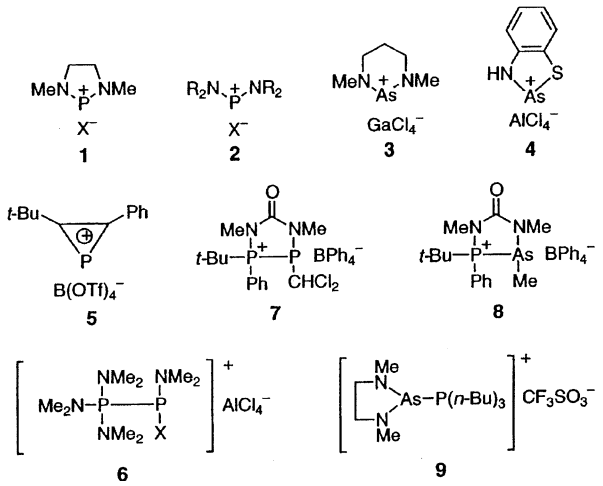
Me, X = $AlCl_4$,[12] PF_6, $GaCl_4$;[13] R = *i*-Pr, X = $AlCl_4$,[14] $GaCl_4$, BPh_4 [13]), and the related compounds **3** [15] and **4** [16] are examples of phosphenium and arsenium salts stabilized in this way, although the aromatic organophosphirenylium salt **5** has been isolated.[17] A significant feature of the structure



of **2** (R = *i*-Pr, X = $AlCl_4$) is the approximate coplanarity of the seven non-hydrogen atoms in the cation, which maximizes dative π-bonding between the lone pairs on nitrogen and the vacant phosphorus 3p orbital.[14] The Lewis acidity of the phosphenium center in **2** (R = Me, X = $AlCl_4$) was demonstrated by the isolation of the phosphine adducts (±)-**6** (X = Cl, NMe_2).[12] The adduct $Ph_3P{\rightarrow}PPh_2^+CF_3SO_3^-$ has been isolated.[18] In the structures of the heterocyclic adducts (±)-**7** and (±)-**8**, it is noteworthy that the tertiary phosphine-*P* atom in each case is located in a position almost orthogonal to the plane containing the remaining two substituents on phosphorus or arsenic.[19] The orthogonal relationship between the phosphine donor and the phosphenium center is also evident in the crystal structure of a related phosphine-stabilized chlorophosphenium salt derived from 1,8-bis[bis(dimethylamino)phosphino]naphthalene.[20] There is NMR evidence for the formation of **9** in a solution containing the simple arsenium salt and tri(*n*-butyl)phosphine.[7]

There are in the literature reports[21−23] of the isolation of adducts between tertiary phosphines, arsines, and stibines and organohalogenophosphines, -arsines, and -stibines that can be formulated as *phosphine-, arsine-, or stibine-stabilized phosphenium, arsenium, and stibenium salts*. For example, in an exothermic reaction, the "dimethylarsinophosphonium salts" $[Me_2As{\cdot}PR_3]X$ (X = Cl, Br, I) separate from diethyl ether upon the addition of the tertiary phosphine to iododimethylarsine. The salts can generally be crystallized from acetone, ethanol, or propanol, although only $[Me_2As{\cdot}PEt_3]I$ was reported to be stable to air and water.[22,23] Triphenylphosphine did not react with the iodoarsine. We find that salts of this type (X = PF_6) are completely stable to air and water and indeed are most conveniently prepared from the arsinous iodide and the tertiary phosphine in dichloromethane in the presence of aqueous ammonium hexafluorophosphate. Despite their stabilities, however, the adducts are highly labile (rapid phosphine exchange) and reactive (ready attack at arsenic by oxygen and carbon nucleophiles). In the solid state, the complexes have structures in which the phosphine is axially coordinated to a two-coordinate arsenium ion, which has a bent structure due to the presence of a stereochemically active lone pair of electrons in the trigonal plane containing the arsenic and the two substituents; the arsenium ion appears to be further stabilized by resonance with aromatic substituents, if these are present. These data are consistent with the formulation of the adducts as *phosphine-stabilized arsenium salts*, for example, $Ph_3P{\rightarrow}AsMe_2^+PF_6^-$. They further resemble in their properties simple, three-membered phosphiranium and phosphirenium salts that have been shown to undergo π-olefin and π-alkyne exchange in solution, respectively, by redistribution or substitution with free π-ligands.[24] Kinetic data for π-alkyne exchange in the phosphirenium salts in chloroform are consistent with the dissociation of the heterocycles into phosphenium salts and alkynes,[25] although high-level ab initio calculations support an associative S_N2-type mechanism for π-ligand exchange in both phosphiranium and phosphirenium salts.[26]

Results and Discussion

Syntheses. The phosphine-stabilized arsenium iodides **10**−**12** crystallize as colorless solids from diethyl ether, following the reaction between the phosphine and iododimethylarsine (Table 1).[22,23] Triphenylphosphine does not react under these conditions. The corresponding hexafluorophosphates **13**−(±)-**16** can be prepared from the iodides by metathesis with ammonium hexafluorophosphate in dichloromethane−water or by direct means from the iodoarsine and the phosphine in dichloromethane in the presence of aqueous ammonium hexafluorophosphate. Unlike the iodides, the hexafluorophosphates melt without sublimation and have good solubilities in moderately polar organic solvents, especially dichloro-

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Table 1. Phosphine-Stabilized Arsenium Salts

compound	mp (°C)	NMR[b] δ(As*Me*)*c*	NMR[b] δ(P)
$Me_3P{\rightarrow}AsMe_2^+I^-$ [a] (**10**)	140 (subl.)	1.34	7.62
$Me_2PhP{\rightarrow}AsMe_2^+I^-$ [a] (**11**)	90 (subl.)	1.32	8.66
$Me_2Ph_2P{\rightarrow}AsMe_2^+I^-$ [a] (**12**)	109 (subl.)	1.30	11.22
$Me_2PhP{\rightarrow}AsMe_2^+PF_6^-$ [d] (**13**)	104106	1.35 (16.9)	7.10
$Me_2PhP{\rightarrow}AsMePh^+PF_6^-$ ((±)-**14**)	127128	1.62 (16.5)	7.73
$MePh_2P{\rightarrow}AsMe_2^+PF_6^-$ (**15**)	162163	1.36 (16.1)	13.07
$MePh_2P{\rightarrow}AsMePh^+PF_6^-$ ((±)-**16**)	124125	1.66 (16.4)	12.87
$Ph_3P{\rightarrow}AsMe_2^+PF_6^-$ (**17**)	173	1.36	19.91
$Ph_3P{\rightarrow}AsMePh^+PF_6^-$ ((±)-**18**)	175	1.69	19.02
$Ph_2(2\text{-}MeOCH_2C_6H_4)P{\rightarrow}AsMePh^+PF_6^-$ ((±)-**19**)	146147	1.61	20.92

[a] These compounds were prepared according to the method given in ref 22. [b] Recorded at 298 K in methanol-d_4 (iodides) or dichloromethane-d_2 (hexafluorophosphates). [c] In parentheses: $^3J_{HP}$ (Hz). [d] Contains $0.5CH_2Cl_2$.

methane. The triphenylphosphine complexes **17** and (±)-**18** were prepared by the two-phase method described above. Conductometric titrations (solvent not specified) had established the following order of nucleophilicity of bases toward iododimethylarsine: Et_3P > Me_2PhP > $MePh_2P$ > py > $Ph_3P{=}O$.[22,23] The ligand (2-methoxymethyl)diphenylphosphine was isolated in 75% yield following its preparation from the Grignard reagent derived from 1-bromo-2-(methoxymethyl)benzene and chlorodiphenylphosphine in tetrahydrofuran. The complex (±)-**19** was prepared from the phosphine and iodomethylphenylarsine by the two-phase method.

NMR Spectra. In the ^{1}H NMR spectra of the iodides **10**−**12** in methanol-d_4 at 298 K, the As*Me* resonances occur at ca. 1.32 ppm compared to 1.98 ppm for iododimethylarsine in the same solvent. In the ^{31}P NMR spectra of the three compounds under similar conditions, the phosphorus resonances lie 39−69 ppm downfield of those for the free phosphines. Phosphorus coupling to the arsenic-methyl protons is absent in the spectra of the iodides in methanol-d_4 at 298 K. These data, taken together with the volatility of the compounds upon heating, are consistent with the following equilibrium:

$$R_3P + IAsMe_2 \rightleftharpoons R_3P \rightarrow AsMe_2^+I^-$$

As for the phosphine-stabilized dimethylarsenium iodides, the chemical shifts for the protons of the As*Me* groups in the hexafluorophosphates **13**, **15**, and **17** are little affected by the nature of the phosphine and indeed at 1.36 ppm in dichloromethane-d_2 are very close in value to those observed for the iodides in methanol-d_4. The As*Me* group chemical shifts in the methylphenylarsenium hexafluorophosphates (±)-**14**, (±)-**16**, and (±)-**18** at ca. 1.66 ppm are also insensitive to the nature of the phosphine. The major difference between the iodides and the hexafluorophosphates in the ^{1}H NMR spectra is the presence of phosphorus coupling to the As*Me* protons in the latter, which is consistent with a slower rate of phosphine exchange. The coupling is absent in the spectra of the triarylphosphine adducts **17**−(±)-**19** at 298 K, however. The ^{1}H NMR spectra for the triphenylphosphine complex (±)-**18** in dichloromethane-d_2 at 298 to 248 K in the As*Me* region are reproduced in Figure 1 (left).

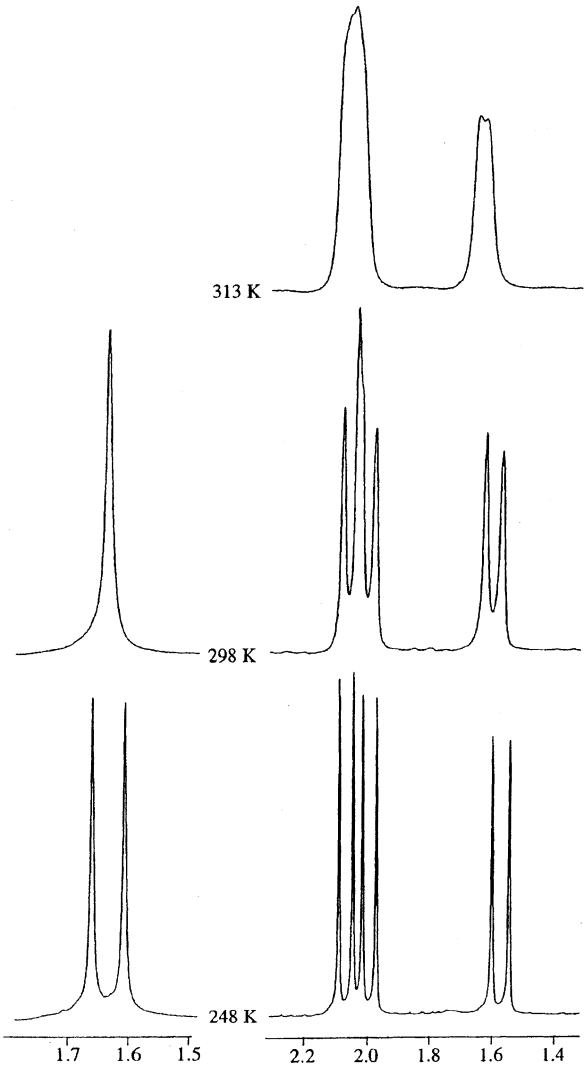

Figure 1. Variable temperature ^{1}H NMR spectra of (±)-**18** (left) and (±)-**14** (right) in dichloromethane-d_2.

On cooling the solution, the singlet for the As*Me* group in the cation of (±)-**18** broadens (T_C = 281 K) and emerges as a doublet at 248 K ($^3J_{HP}$ = 15.9 Hz). From these data, the approximate rate constant (k_C) for P−As bond dissociation in the complex can be calculated from the expression $k_C = 0.5\pi\Delta\nu/\sqrt{2}$, where $\Delta\nu$ is the limiting frequency difference between the coalescing peaks.[27−29] Knowing k_C, the activation barrier for P−As bond dissociation ($\Delta G^{\ddagger}$) can then be obtained from the relationship $\Delta G^{\ddagger} = -RT_C \ln(k_C h/k_B T_C)$, where R, h, and k_B are the gas, Planck, and Boltzmann constants, respectively. For (±)-**18**, $\Delta G^{\ddagger}$ = 62 kJ mol^{-1} at 281 K in dichloromethane-d_2. The ^{1}H NMR spectra for the dimethylphenylphosphine complex (±)-**14** in dichloromethane-d_2 at 313, 298, and 248 K in the As*Me* and in the P*Me* regions are shown in Figure 1 (right). The spectra at 298 K

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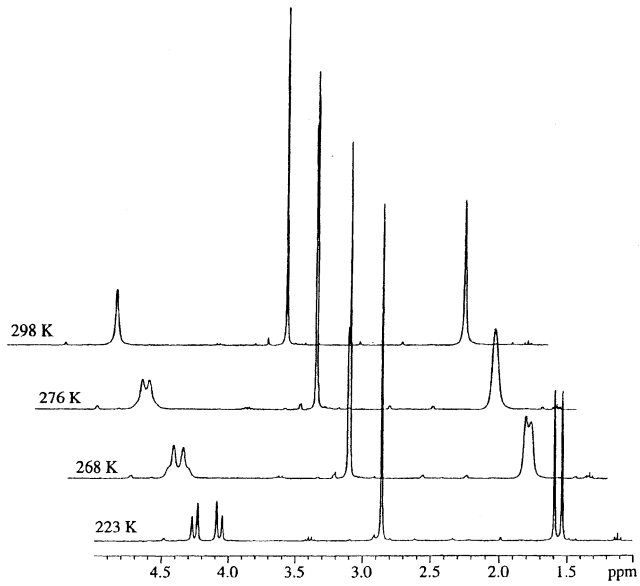

Figure 2. Variable temperature ^{1}H NMR spectra of (±)-**19** in dichloromethane-d_2.

and below are consistent with the presence of a relatively stable phosphine adduct of the prochiral methylphenylarsenium ion. Thus, an apparent triplet (overlapping doublets) is observed for the diastereotopic P*Me* groups in the cation at 298 K, in addition to phosphorus coupling to the As*Me* protons. At 248 K, the resonances for the three methyl groups in the complex are resolved, with $^2J_{HP}$ = 13.2 Hz (P*Me*) and $^3J_{HP}$ = 16.5 Hz (As*Me*). Above 298 K, phosphorus coupling to the As*Me* protons and the diastereotopicity of the P*Me* groups are lost (T_C ca. 313 K), giving $\Delta G^{\ddagger}$ = 69 kJ mol^{-1} for P−As bond dissociation in the dimethylphenylphosphine adduct. The lability of the triphenylphosphine adduct (±)-**18** in solution at 298 K is reminiscent of the behavior of (±)-ClMePhP→PMePh$^+$ OTf$^-$ under similar conditions.[24] The ^{31}P NMR spectrum of the chlorophosphine−phosphenium triflate at 298 K consists of two singlets of equal intensity at +82 and −17 ppm. The low-field resonance is coincident with that of the free chlorophosphine. At 231 K, however, the spectrum of the complex contains the expected four sets of doublets for the two possible diastereomers of the cation (chiral at both chlorophosphine-*P* and phosphenium-*P* stereocenters) in equilibrium. The P−P coupling constant of 351 Hz observed at the slow exchange limit is similar in value to those observed for other similar chlorophosphine−phosphenium adducts,[18,30,31] and the heterocycle (±)-**7**.[18]

The potential anchimeric stabilizing effect at arsenic of a coordinating (2-methoxymethyl)phenyl group on phosphorus was investigated by preparing and characterizing the complex (±)-**19**. The variable temperature ^{1}H NMR spectra for (±)-**19** are reproduced in Figure 2. On cooling the solution, the As*Me* singlet at 1.61 ppm in the spectrum at 298 K broadens (T_C = 273 K) and emerges as a sharp doublet ($^3J_{HP}$ = 16.5 Hz) at the slow exchange limit (248 K), giving $\Delta G^{\ddagger}$ = 60 kJ mol^{-1}. Cooling of the solution led to broadening of the resonance for the CH_2OMe protons in the spectrum, which emerges as an AB quartet (diastereotopic protons) as the cation becomes chiral on the NMR time scale due to coordination of the phosphine to arsenic through phosphorus *and* oxygen. The net strength of the interaction of the (2-methoxymethyl)phenyl-substituted phosphine in (±)-**19** with the arsenium ion is similar to that of triphenylphosphine. An important consequence of the chelate interaction of the phosphine with the arsenic in (±)-**19**, however, is the restriction of rotation of the phosphine about the P−As bond, which will facilitate prochiral face discrimination of the methylphenylarsenium ion in adducts of chiral phosphines. At temperatures below 268 K, the splitting of the O*Me* resonance in the spectrum of (±)-**19** is lost. This may be due to a shift in the position of the equilibrium between the two possible diastereomers, chiral at arsenic and oxygen, in dichloromethane-d_2 at low temperatures. Further support for the *counteractive chelate effect* in the cation of (±)-**19** is found in the crystal structure (see below). One diastereomer of (±)-**19** crystallizes from dichloromethane−diethyl ether by asymmetric transformation of the second kind.[32]

Table 2. Crystallographic Data and Experimental Parameters for (±)-**18** and (±)-**19**

	(±)-**18**	(±)-**19**
empirical formula	$C_{25}H_{23}AsF_6P_2$	$C_{27}H_{27}AsF_6OP_2$
fw, g mol^{-1}	574.32	618.37
cryst syst	monoclinic	triclinic
space group	*P*21/c	*P*$\bar{1}$
a, Å	10.7775(2)	10.8077(2)
b, Å	17.7987(3)	10.9741(2)
c, Å	13.3797(2)	13.5648(2)
α, deg	90	99.0162(9)
β, deg	109.066(1)	105.2121(9)
γ, deg	90	116.4717(9)
V, Å^3	2425.78(7)	1318.11(5)
Z	4	2
D_{calcd}, g cm^{-3}	1.572	1.558
cryst size, mm	0.24 × 0.20 × 0.12	0.25 × 0.24 × 0.23
μ, cm^{-1}	15.92	14.73
instrument	Nonius Kappa CCD	Nonius Kappa CCD
radiation	Mo Kα	Mo Kα
no. unique reflns	5543	7699
no. reflns obsd ($I > 2.00\sigma(I)$)	4898	6161
2*θ* range, deg	755	860
temp, K	200	200
structural refinement	teXsan48	teXsan48
R1,[a] wR2[b]	0.0403, 0.0447	0.0332, 0.0396

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

Crystal Structures. (±)-(Triphenylphosphine)methylphenylarsenium hexafluorophosphate, (±)-**18**, crystallizes in the monoclinic space group $P2_1/c$ with two molecules of each enantiomer of the chiral cation and associated anions arranged about an inversion center in the unit cell (racemic compound; Table 2). The structure of the *R* enantiomer of the cation is depicted in Figure 3.[33] Principal bond distances and angles in the cation are given in the caption. Prominent features of the structure are the following: (a) the P−As

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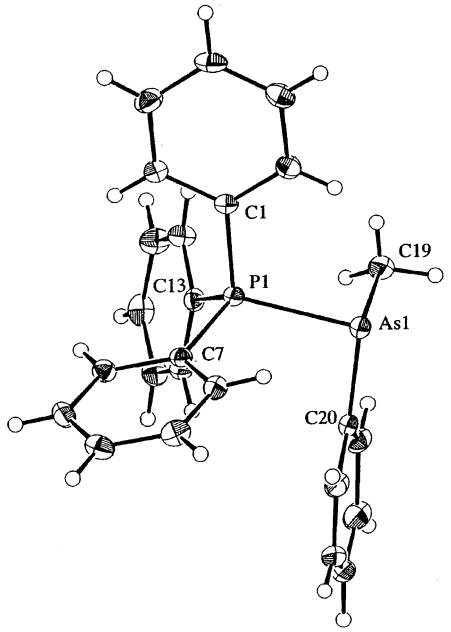

Figure 3. Molecular structure of *R* enantiomer of cation of (±)-**18**. Principal bond lengths (Å) and interbond angles (deg): As1−P1, 2.3480(5); As1−C19, 1.959(2); As1−C20, 1.955(2); P1−C1, 1.804(2); P1−C7, 1.801(2); P1−C13, 1.796(2); P1−As1−C19, 92.31(8); P1−As1−C20, 97.04(6); C19−As1−C20, 101.73(7); As1−P1−C1, 107.73(7); As1−P1−C7, 110.67(7); As1−P1−C13, 112.27(7); C1−P1−C7, 107.82(9); C1−P1−C13, 109.9(1); C7−P1−C13, 108.4(1).

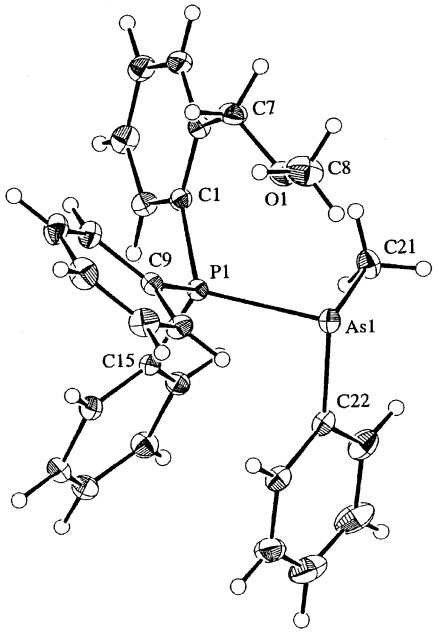

Figure 4. Molecular structure of *R* enantiomer of the cation of (±)-**19**. Principal bond lengths (Å) and interbond angles (deg): As1−P1, 2.3703(5); As1−C21, 1.956(2); As1−C22, 1.957(2); P1−C1, 1.827(2); P1−C9, 1.808(2); P1−C15, 1.809(2); As1···O1, 2.878(1); P1−As1−C21, 95.59(6); P1−As1−C22, 96.99(5); C21−As1−C22, 100.35(8); As1−P1−C1, 115.54(6); As1−P1−C9, 107.86(6); As1−P1−C15, 109.02(6); C1−P1−C9, 108.50(8); C1−P1−C15, 108.06(8); C9−P1−C15, 107.59(8); C7−O1−C8, 111.5(2).

distance of 2.3480(5) Å is longer than the sum of the covalent radii of the two elements, viz., 2.22 Å,[34] and compares closely with the value of 2.346(2) Å for the corresponding bond in the heterocyclic cation of **8**; (b) within small limitations, C19 and As1 are coplanar with the phenyl group (the deviation of C19 from the aromatic plane is 0.192 Å; As1 is 0.165 Å below the plane, the torsion angle C19−As1−C20−C21 being 3.6(2)°); and (c), the angles P1−As1−C19 and P1−As1−C20 are 92.31(8) and 97.04(6)°, respectively. The long P−As bond in the structure is consistent with the highly labile nature of phosphine-stabilized arsenium salts in solution and compares with the P−As distances of 2.3054(19) Å in $P\{As[C(O)Bu\text{-}t]_2\}_3$.[35] The angle C19−As1−C20 of 101.73(7)° within the arsenium plane indicates considerable stereochemical influence of the lone pair on the arsenic. The stereochemistry around arsenic in the adduct is pyramidal with the arsenic being situated in the trigonal plane containing the methyl- and the phenyl-*ipso*-carbon atoms and the stereochemically active lone pair of electrons, and the phosphorus atom occupying the axial coordination site, orthogonal to it. Arsenic in the adduct is exposed at the base of the trigonal pyramid to nucleophilic attack from the enantioface opposite the phosphine.

The (±)-[(2-(methoxymethyl)phenyl)diphenylphosphine]-methylphenylarsenium complex (±)-**19** crystallizes as a racemic compound in the centrosymmetrical space group $P\bar{1}$ with one molecule of each enantiomer of the cation and associated anions in the unit cell (Table 2). The structure of the *R* enantiomer of the cation is depicted in Figure 4; principal distances and angles in the molecule are given in the caption. The planarity of the arsenium ion in the structure is again evident, with As1 and C21 being 0.065 and 0.067 Å, respectively, below (with respect to phosphorus) the plane containing the phenyl group. The As···O distance of 2.878(1) Å in the structure is greater than the sum of the covalent radii of the two atoms (1.92 Å)[34] but less than the sum of the van der Waals radii for the *neutral* atoms (3.5 Å).[36] It is also noteworthy, in light of the ^{1}H NMR data for the compound, which indicated the P−As bond to be similar in strength to the one in the parent triphenylphosphine derivative (±)-**18**, that the P−As distance in (±)-**19** is 2.3703(5) Å, 0.0223 Å longer than that in (±)-**18**. The As−P1 bond, however, remains almost orthogonal to the plane of the arsenium ion, with P1−As1−C21 = 95.59(6)° and P1−As1−C22 = 96.99(5)°. The angle C21−As1−C22 of 100.35(8)° also differs little from the corresponding angle in the triphenylphosphine analogue, despite the interaction between As1 and O1, giving the chelate bite angle P1−As1−O1 of 60.38(8)°.

Chemical Behavior. (a) Phosphine Exchange. Crossover reactions are observed when solutions of similar phosphine-stabilized arsenium complexes are mixed together. Thus, the mixing of equimolar solutions of **15** and (±)-**18** in dichloromethane-d_2 at 20 °C indicated complete redistribution of the phosphines and arsenium ions within the time of mixing and recording the ^{31}P NMR spectrum (ca. 5 min), to give an equilibrium mixture containing the starting materials and (±)-

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16 and **17**. Because of the rapid rate of exchange of the components and the long relaxation times required to obtain accurate integrals of ^{31}P NMR signals (T_1 ca. 20 s), kinetic data for the crossover reaction could not be obtained. Dissociation of the adducts into simple or solvated arsenium ions and free phosphines would provide a low-energy pathway for exchange, but, because of the lone pair of electrons on arsenic in the adducts, a concerted pathway involving pairs of adducts exchanging ligands via four-center head-to-tail transition structures is also feasible. In the gas phase, high level ab initio calculations on ligand exchange in phosphine-stabilized phosphenium cations favor an associative S_N2-type pathway.[37]

(b) Chemical Reactivity. Sodium methoxide and sodium phenoxide react with $Et_3P{\rightarrow}AsMe_2^+I^-$ to give Me_2AsOR (R = Me, Ph) and Et_3P.[22,23] The hexafluorophosphate (±)-**16** behaves similarly, giving (±)-MePhAsOMe and methyldiphenylphosphine in quantitative yields. Treatment of a solution of (±)-**18** in tetrahydrofuran with *n*-butyl lithium−*n*-hexane solution furnished (±)-*n*-BuMePhAs with displacement of triphenylphosphine in similarly high yields. The complete regioselectivity of attack by both types of nucleophiles provides additional compelling support for the formulations of **10**−(±)-**19** as phosphine-stabilized arsenium salts.

Future work will be concerned with the asymmetric syntheses of chiral tertiary arsines and phosphines from prochiral arsenium and phosphenium salts stabilized by enantiomerically pure tertiary phosphines. In principle, it is possible to design and perform a self-replicating synthesis of a particular enantiomerically pure tertiary phosphine from analogous phosphine-stabilized phosphenium salts. Existing enantioselective syntheses of simple noncyclic tertiary arsines of the type (±)-$AsR^1R^2R^3$ [38] and phosphines of the type (±)-$PR^1R^2R^3$ [39] lack generality, although resolutions of both types of compounds can be achieved with almost complete success with the use of enantiomerically pure palladium(II) complexes as resolving agents.[40] There is a need for improved methods of synthesis of enantiomerically pure *unidentate* tertiary phosphines, because there are indications that enantiomers of chiral monotertiary phosphines of this type are superior to related chelate agents for a number of catalytic asymmetric syntheses, for example the asymmetric hydrosilylation of carbon−carbon double bonds.[41]

Conclusion

Phosphine-stabilized arsenium salts of the type $R_3P{\rightarrow}AsR_2^+PF_6^-$ are air-stable, crystalline solids, readily prepared, that undergo facile phosphine exchange and attack at arsenic by anionic carbon and oxygen nucleophiles to give tertiary arsines and arsinous acid esters, respectively, with liberation of the phosphine. Crystal structure determinations on two adducts of methylphenylarsenium hexafluorophosphate gave structural data consistent with the solution properties, including in each case a long bond from phosphorus to arsenic on one enantioface of the prochiral arsenium ion, which leaves the arsenic exposed to nucleophilic attack from the enantioface opposite. The arsenium ions in the two structures are further stabilized by conjugation to the phenyl substituents with which they are coplanar. With the use of enantiomerically pure phosphines as chiral auxiliaries, adducts of prochiral arsenium salts appear to be ideally suited to the asymmetric synthesis of tertiary arsines, chiral at arsenic.

Experimental Section

Solvents were purified by conventional methods and stored under nitrogen. ^{1}H NMR and ^{31}P{^{1}H} NMR spectra were recorded on Varian VXR 300S and Gemini 300 spectrometers operating at 300.1 MHz (^{1}H) and 121.5 MHz (^{31}P), with chemical shifts being referred to internal Me_4Si or residual solvent resonances (^{1}H), and external aqueous H_3PO_4 (^{31}P). Fast atom bombardment (FAB) mass spectra were recorded on a VG Analytical ZAB-2SEQ spectrometer (ionization: 30 keV Cs^+) in a matrix of 3-nitrobenzyl alcohol; electrospray mass spectra (ES MS) were recorded on a VG-QUATTRO II spectrometer. Elemental analyses were performed by staff within the Research School of Chemistry. The phosphines Me_3P,[42] Me_2PhP,[43] and $MePh_2P$ [44] and the arsines Me_2AsI [45] and MePhAsI [46] were prepared by literature methods. The phosphine-stabilized arsenium *iodides* were prepared as previously described.[22]

(Trimethylphosphine-*P*)dimethylarsenium Iodide (10). Transparent needles.[22] ^{1}H NMR (CD_3OD, 298 K): δ 1.34 (s, 6 H, As*Me*), 1.82 (d, $^2J(^1H,^{31}P)$ = 14.0 Hz, 9 H, P*Me*). ^{31}P{^{1}H} NMR (CD_3OD, 298 K): δ 7.62 (s). ES MS: *m*/*z* 181 ([M − I]$^+$), 166 ([M − (MeI)]$^+$).

(Dimethylphenylphosphine-*P*)dimethylarsenium Iodide (11). Transparent needles.[22] ^{1}H NMR (CD_3OD, 298 K): δ 1.32 (s, 6 H, As*Me*), 2.30 (d, $^2J(^1H,^{31}P)$ = 19.7 Hz, 6 H, P*Me*), 7.65−7.89 (m, 5 H, Ar*H*). ^{31}P{^{1}H} NMR (CD_3OD, 298 K): δ 8.66 (s). ES MS: *m*/*z* 244 ([M − I + H]$^+$), 243 ([M − I]$^+$).

(Methyldiphenylphosphine-*P*)dimethylarsenium Iodide (12). Transparent needles.[22] ^{1}H NMR (CD_3OD, 298 K): δ 1.30 (s, 6 H, As*Me*), 2.47 (d, $^2J(^1H,^{31}P)$ = 12.5 Hz, 3 H, P*Me*), 7.57−7.75 (m, 10 H, Ar*H*). ^{31}P{^{1}H} NMR (CD_3OD, 298 K): δ 11.22 (s). ES MS: *m*/*z* 305 ([M − I]$^+$), 200 ([$PMePh_2$]$^+$).

(Dimethylphenylphosphine-*P*)dimethylarsenium Hexafluorophosphate Hemidichloromethane Solvate (13). A solution of ammonium hexafluorophosphate (20 g) in water was added to a solution of the iodide **11** (17.8 g, 48 mmol) in dichloromethane (200 mL). The mixture was vigorously stirred for 30 min., the layers were separated, and the organic fraction was dried ($MgSO_4$) and evaporated to dryness. Crystallization of the residue from dichloromethane−diethyl ether gave the pure product as transparent prisms, mp 104−106 °C. Yield: 16.6 g (80%). ^{1}H NMR (CD_2Cl_2, 298 K): δ 1.35 (d, $^3J(^1H,^{31}P)$ = 16.9 Hz, 6 H, As*Me*), 2.20 (d, J $^1H,^{31}P)$ = 14.2 Hz, 6 H, P*Me*), 7.59−7.82 (m, 5 H, Ar*H*). ^{31}P{^{1}H} NMR (CD_2Cl_2, 298 K): δ 7.10 (s, Me_2Ph*P*), −143.68 (sept., *P*F_6^-). FAB MS: *m*/*z* 243 ([M − PF_6]$^+$), 138 ([Me_2PhP]$^+$). Anal. Calcd for $C_{10}H_{17}AsF_6P_2{\cdot}0.5CH_2Cl_2$: C, 29.3; H, 4.2. Found: C, 29.6; H, 4.2.

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(Methyldiphenylphosphine-*P*)dimethylarsenium Hexafluorophosphate (15). This compound was prepared as described as for **13,** but with the use of **12** (4.77 g, 11.0 mmol) and excess ammonium hexafluorophosphate in water. Transparent needles from dichloromethane−diethyl ether, mp 162−163 °C. Yield: 4.48 g (90%). ^{1}H NMR (CD_2Cl_2, 298 K): δ 1.36 (d, $^3J(^1H,^{31}P)$ = 16.1 Hz, 6 H, As*Me*), 2.43 (d, $^2J(^1H,^{31}P)$ = 12.6 Hz, 3 H, P*Me*), 7.60−7.86 (m, 10 H, Ar*H*). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 298 K): δ 13.07 (s, $MePh_2P$), −143.71 (sept., PF_6^-). FAB MS: *m/z* 305 ([M − PF_6]$^+$), 200 ([$MePh_2P$]$^+$). Anal. Calcd for $C_{15}H_{19}AsF_6P_2$: C, 40.0; H, 4.3. Found C, 39.9; H, 4.1.

(2-Methoxymethylphenyl)diphenylphosphine. Chlorodiphenylphosphine (8.39 g, 38 mmol) in tetrahydrofuran (THF; 20 mL) was slowly added to a stirred solution (0 °C) of the Grignard reagent prepared from 1-bromo-2-methoxymethylbenzene (7.86 g, 39.1 mmol) and magnesium (0.95 g, 39.1 mmol) in THF (70 mL). After the addition was complete, the reaction mixture was heated under reflux for 30 min and then cooled. The THF was removed in vacuo, and diethyl ether (50 mL) was added to the residue, followed by a solution of ammonium chloride (5 g) in water (25 mL). The organic phase was separated, dried ($MgSO_4$), filtered, and evaporated to dryness. The pale yellow solid that remained was recrystallized from hot methanol, affording almost colorless needles of the pure product, mp 93−94 °C. Yield: 8.68 g (75%). ^{1}H NMR (300.1 MHz, CD_2Cl_2, 298 K): δ 3.24 (s, 3 H, O*Me*), 4.61 (s, 2 H, CH_2), 6.88−7.51 (m, 14 H, Ar*H*). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 298 K): δ −15.58 (s). EI MS: *m/z* 306 ([M]$^+$), 291 ([M − Me]$^+$). Anal. Calcd for $C_{20}H_{19}OP$: C, 78.4; H 6.3. Found C, 78.2; H 6.1.

General Procedure for the Two-Phase Synthesis of Phosphine-stabilized Dimethyl- and Methylphenylarsenium Hexafluorophosphates ((±)-14, (±)-16, 17, (±)-18, and (±)-19). The tertiary phosphine (10 mmol) was added to a solution of the iodoarsine (10 mmol) in dichloromethane (50 mL), followed by a solution of ammonium hexafluorophosphate (ca. 40 mmol) in water (50 mL). The mixture was stirred vigorously for ca. 30 min., the phases were separated, and the organic fraction was dried ($MgSO_4$), filtered, and evaporated to dryness. The residues were crystallized from dichloromethane−diethyl ether.

(±)-(Dimethylphenylphosphine-*P*)methylphenylarsenium Hexafluorophosphate ((±)-14). Transparent prisms, mp 127−128 °C. Yield: 86%. ^{1}H NMR (CD_2Cl_2, 298 K): δ 1.62 (d, ^3J $^1H,^{31}P)$ = 16.5 Hz, 3 H, As*Me*), 2.03 (d, $^2J(^1H,^{31}P)$ = 13.2 Hz, 3 H, P*Me*), 2.08 (d, 2$J(^1H,^{31}P)$ = 13.2 Hz, 3 H, P*Me*), 7.27−7.74 (m, 10 H, Ar*H*). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 298 K): δ 7.73 (s, Me_2PhP), −143.74 (sept, PF_6^-). ES MS: *m/z* 306 [(M + H) − PF_6]$^+$, 305 ([M − PF_6]$^+$). Anal. Calcd for $C_{15}H_{19}AsF_6P_2$: C, 40.0; H, 4.3. Found: C, 39.9; H, 4.2.

(±)−(Methyldiphenylphosphine-*P*)methylphenylarsenium Hexafluorophosphate ((±)-16). Transparent needles, mp 124−125 °C. Yield: 96%. ^{1}H NMR (CD_2Cl_2, 298 K): δ 1.66 (d, $^3J(^1H,^{31}P)$ = 16.4 Hz, 3 H, As*Me*), 2.21 (d, $^2J(^1H,^{31}P)$ = 13.1 Hz, 3 H, P*Me*), 7.19−7.82 (m, 15 H, Ar*H*). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 298 K): δ 12.87 (s, $MePh_2P$), −143.72 (sept, PF_6^-). FAB MS: *m/z* 367 ([M − PF_6]$^+$). Anal. Calcd for $C_{20}H_{21}AsF_6P_2$: C, 46.9; H, 4.1. Found: C, 47.0; H, 4.4.

(Triphenylphosphine-*P*)dimethylarsenium Hexafluorophosphate (17). Transparent prisms, mp 173 °C. Yield: 78%. ^{1}H NMR (CD_2Cl_2, 298 K): δ 1.36 (s, 6 H, As*Me*), 7.58−7.87 (m, 15 H, Ar*H*). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 298 K): δ 19.91 (s, Ph_3P), −143.75 (sept, PF_6^-). FAB MS: *m/z* 367 ([M − PF_6]$^+$). Anal. Calcd for $C_{20}H_{21}AsF_6P_2$: C, 46.9; H, 4.1. Found: C, 46.7; H, 4.0.

(±)-(Triphenylphosphine-P)methylphenylarsenium Hexafluorophosphate ((±)-18). Transparent prisms, mp 175 °C. Yield: 84%. ^{1}H NMR (CD_2Cl_2, 298 K): δ 1.69 (s, 3 H, As*Me*), 7.05−7.85 (m, 20 H, Ar*H*). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 298 K): δ 19.02 (s, Ph_3P), −143.76 (sept, PF_6^-). FAB MS: *m/z* 429 ([M - PF_6]$^+$), 262 ([Ph_3P]$^+$). Anal. Calcd for $C_{25}H_{23}AsF_6P_2$: C, 52.3; H, 4.0. Found C, 52.0; H, 4.2.

(±)-[(2-Methoxymethylphenyl)diphenylphosphine-*O,P*]methylphenylarsenium Hexafluorophosphate ((±)-19). Colorless prisms, mp 146−147 °C. Yield: 40%. ^{1}H NMR (CD_2Cl_2, 298 K): δ 1.61 (s, 3 H, As*Me*), 2.92 (s, 3 H, O*Me*), 4.18 (m, 2 H, CH_2), 7.09−7.82 (m, 19 H, Ar*H*). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 298 K): δ 20.92 (s, $Ph_2(2\text{-}MeOCH_2C_6H_4)P$), −143.84 (sept, PF_6^-). FAB MS: *m/z* 473 ([M − PF_6]$^+$) 291 ([$Ph_2PC_6H_4CH_2O$]$^+$) Anal. Calcd for $C_{27}H_{27}AsF_6OP_2$: C, 52.4; H 4.4. Found: C, 52.6; H 4.5.

Crystal Structures. Single-crystal X-ray diffraction data for (±)-**18** and (±)-**19** were collected at 200 K using a Nonius Kappa CCD diffractometer. Details are given in Table 2. Data were processed using Denzo and Scalepack software[47] and corrected for absorption.[48] The structure of (±)-**18** was solved by direct methods[49] and (±)-**19** by heavy-atom techniques.[50] All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included at calculated positions. Full matrix least-squares refinement on *F* was performed in each case using teXsan software.[51]

Supporting Information Available: Additional crystallographic data and figures (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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