Contributions to the Little Known Chemistry of Trivinylphosphine and Trivinylarsine

Uwe Monkowius, Stefan Nogai, and Hubert Schmidbaur*

Anorganisch-chemisches Institut der Technischen Universität München, Lichtenbergstrasse 4, D-85747 Garching, Germany

Received August 13, 2002

Trivinylphosphine has been prepared via an improved synthetic method (from triphenyl phosphite). Vi_3P undergoes standard quaternization only with methyl iodide to give high yields of $[MeVi_3P]I$. The reactions with ethyl iodide, ethyl trifluoromethanesulfonate, benzyl bromide, and vinyl bromide failed to give the analogous phosphonium salts, and insoluble polymeric products were obtained instead. Polymerization also occurs upon attempted halogenation using hexachloroethane or elemental iodine. By contrast, trivinylarsine gives the corresponding arsonium salts with MeI, EtI, and BzBr without complications. A mechanism is proposed for the observed differences in reaction behavior taking into account complementary observations from previous investigations. The activation of the vinyl functions upon quaternization of Vi_3P is also evident from the propensity of $[MeVi_3P]I$ to the spontaneous (or base-catalyzed) addition of up to 3 equiv of methanol to give the three salts $[MeVi_nP(CH_2CH_2OMe)_{3-n}]I$ ($n = 1-3$). The three chalkogenides Vi_3PE ($E = O, S, Se$) can be prepared by addition of E to Vi_3P without polymerization, and coordination to AuCl also leads to a stable complex $(Vi_3P)AuCl$. No reaction was observed between Vi_3P and elemental tellurium. The crystal and molecular structures of $[MeVi_3P]I(CHCl_3)$, $[MeVi_2PCH_2CH_2OMe]I$, $[MeVi_3As]I$, $[BzVi_3As]Br$, Vi_3PO, Vi_3PSe, and $(Vi_3P)AuCl$ have been determined, and their conformational characteristics are discussed.

Introduction

The publications on tri*alkyl*- and tri*aryl*phosphines and -arsines and on their organic derivatives and their complexes are legion.[1−4] By contrast, the literature on tri*alkenyl*phosphines and -arsines is very limited,[5,6] and this is particularly true for the standard compounds trivinylphosphine and trivinylarsine. Both species were first prepared by Maier, Seyferth, Stone, Kaesz, and Rochow as late as 1957[7] (over 100 years after the first tri*alkyl*- and tri*aryl*phosphines[8]), and these authors also determined the most important physical properties and carried out a few simple reactions, including oxidation by elemental halogen, quaternization with alkyl halides, ligand scrambling with trihalides, and complex formation with main group and transition metal salts.[7,9,10] The Raman and IR spectra and the NMR patterns were analyzed a few years later.[11−16] Chemical reactions remained largely unexplored, and there are only a few scattered reports on hydrophosphorylations of the isolated compound[17−20] or its complexes (as templates)[21,22] and hydrosulfurizations.[23] These processes were complemented by addition reactions to selected diorgano(vinyl)-phosphines[23] and polymerization of the products.[24,25] The metal complexes hitherto prepared feature only platinum,[9] iron,[21,22] and cobalt,[26,27] and none of the

---

[1] McAuliffe, C. A., Ed. *Transition Metal Complexes of Phosphorus, Arsenic and Antimony Ligands*; Macmillan Press: London, 1973.

[2] Booth, G. *Adv. Inorg. Chem. Radiochem.* **1964**, *12*, 1.

[3] Booth, G. In *Organic Phosphorus Compounds*, Vol. 1; Kosolapoff, G. M., Maier, L., Eds.; Wiley-Intersciences: New York, 1972; p 433.

[4] Mason, R.; Meek, D. W. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 183.

[5] Maier, L. In *Organic Phosphorus Compounds*, Vol. 1; Kosolapoff, G. M., Maier, L., Eds.; Wiley-Intersciences: New York, 1972; p 1.

[6] Cristau, H. J.; Plénat, F. In *The Chemistry of Organophosphorus Compounds*, Vol. 3; Hartley, F. R., Ed.; John Wiley & Sons: Chichester, 1994; p 73.

[7] Maier, L.; Seyferth, D.; Stone, F. G. A.; Rochow, E. G. *J. Am. Chem. Soc.* **1957**, *79*, 5884.

[8] Thénard, P. *C. R. Acad. Sci.* **1845**, *21*, 144.

[9] Maier, L.; Seyferth, D.; Stone, F. G. A.; Rochow, E. G. *Z. Naturforsch.* **1957**, *12b*, 263.

[10] Kaesz, H. D.; Stone, F. G. A. *J. Org. Chem.* **1959**, *24*, 635.

[11] Durig, J. R.; Zhao, W.; Little, T. S. *J. Raman Spectrosc.* **1989**, *20*, 111.

[12] Davidson, G.; Phillips, S. *Spectrochim. Acta* **1978**, *34A*, 949.

[13] Kaesz, H. D.; Stone, F. G. A. *Spectrochim. Acta* **1959**, *15*, 360.

[14] Nyulászi, L.; Bergsträsser, U.; Regitz, M.; Schleyer, P. v. R. *New J. Chem.* **1998**, 651.

[15] Manatt, S. L.; Juvinall, G. L.; Elleman, D. D. *J. Am. Chem. Soc.* **1963**, *85*, 2664.

[16] Anderson, W. A.; Freeman, R.; Reilly, C. A. *J. Chem. Phys.* **1963**, *39*, 1518.

[17] Bampos, N.; Field, L. D.; Messerle, B. A.; Smernik, R. J. *Inorg. Chem.* **1993**, *32*, 4084.

[18] Jia, G.; Drouin S. D.; Jessop, P. G.; Lough, A. J.; Morris, R. H. *Organometallics* **1993**, *12*, 906.

[19] Miedaner, A.; Curtis, C. J.; Wander; S. A.; Goodson, P. A.; DuBois, D. L. *Organometallics* **1996**, *15*, 5185.

[20] Schubert, D. M.; Hackney, M. L. J.; Brandt, P. F.; Norman, A. D. *Phosphorus, Sulfur Silicon* **1997**, *123*, 141.

[21] Edwards, P. G.; Newman, P. D.; Malik, K. M. A. *Angew. Chem., Int. Ed.* **2000**, *39*, 2922.

[22] Edwards, P. G.; Whatton, M. L.; Haigh, R. *Organometallics* **2000**, *19*, 2652.

[23] Paetzold, E.; Michalik, M.; Oehme, G. *J. Prakt. Chem.* **1997**, *339*, 38.

[24] Rabinowitz, R.; Henry, A. C.; Marcus, R. *J. Polym. Sci. A* **1965**, *3*, 2055.

[25] Rabinowitz, R.; Marcus, R. *J. Polym. Sci. A* **1965**, *3*, 2063.

[26] Rehder, D.; Schmidt, J. *Z. Naturforsch.* **1972**, *27 b*, 625.

[27] Cotton, F. A.; Daniels, L. M.; Powell, G. L.; Kahaian, A. J.; Smith, T. J.; Vogel, E. F. *Inorg. Chim. Acta* **1988**, *144*, 109.

10.1021/om020653j CCC: $25.00

structures have been determined. The molecular structure of free trivinylphosphine (in the gas phase) has been analyzed and its inversion barrier calculated by ab initio methods.[11−14]

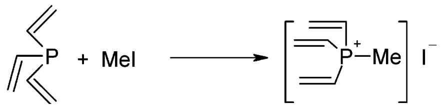
The preparation of trivinylphosphine was originally achieved via the Grignard method using vinylmagnesium bromide[7,9,18] or chloride and PCl_3.[10,23] The synthesis via vinylsodium(potassium) is described in the patent literature,[28] and a direct route from elemental phosphorus via potassium phosphide and acetylene has been reported by Russian workers.[29] All these methods have in common that they require carefully controlled conditions and yet produce only low to moderate yields.[9,10]

In the course of our own hitherto unsuccessful attempts to prepare tetravinylphosphonium salts $[Vi_4P]X$ and finally pentavinylphosphorane Vi_5P we became engaged in synthetic and structural work with trivinylphosphine Vi_3P and its derivatives and complexes. The results are presented in two parts, the first of which is given in the present account dedicated to oxidation, quaternization, addition, and complexation reactions. This work is an extension of recent studies on penta*alkyl*phosphoranes.[30]

Preparation and Quaternization of Trivinylphosphine. In the present study trivinylphosphine was prepared from triphenyl phosphite and vinylmagnesium chloride in tetrahydrofuran. The procedure is similar to that employed successfully for trimethylphosphine.[31] The isolated yield after distillative workup is a reliable 30%. The low to moderate yields arise from P−P coupling reactions of the intermediates. Similar observations have been reported for preparation of most tertiary phosphines with Grignard reagents.[31] The use of phosphites leads to less P−P coupling. The method is more convenient than the Grignard reactions of PCl_3 or PBr_3.[7,9] Trivinylphosphine can be stored for several months at −32° C without polymerization.

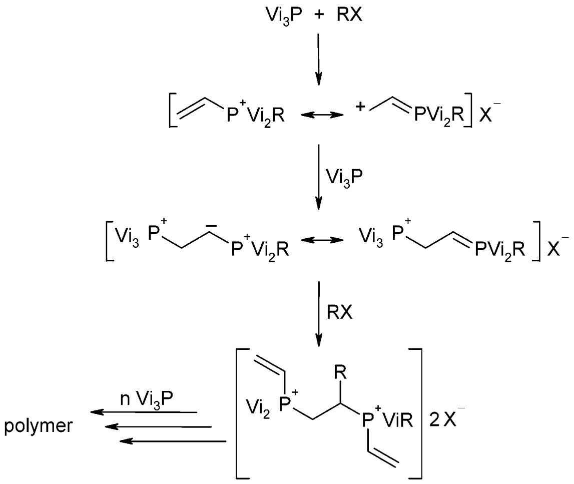
Quaternization of Vi_3P (and Vi_3As) by alkyl halides has already be described by L. Maier et al.[7,9] Surprisingly, the reactions with methyl and ethyl iodide and vinyl bromide gave very different results. While the products $[MeVi_3P]I$ and $[Vi_4P]Br$ (and their arsenic analogues) are reported to be solids with melting points in the expected temperature range, $[EtVi_3P]I$ was found to melt above 327 °C.

In our own experiments, quaternization of Vi_3P with MeI was confirmed[7] to proceed smoothly at room temperature in 92% isolated yield. The product $[MeVi_3P]I$ was obtained as single crystals (as the chloroform solvate), the structure of which was determined, and complementary spectroscopic data were collected (eq 1).



(1)

Scheme 1



By contrast, the corresponding reactions with ethyl iodide, ethyl trifluoromethanesulfonate (EtTf), benzyl bromide, and vinyl bromide failed to give the corresponding simple quaternary phosphonium salts. With ViBr there was no reaction at all, and EtI or BzBr gave only insoluble and intractable materials, which is at variance with the observations in previous studies.[7,9] However, a later communication has a brief comment that the ViBr employed in these earlier studies may have contained EtBr, which was responsible for the product observed,[10] and the high melting point of $[EtVi_3P]I$ is also indicative of polymerization. Even with EtTf, known as a very strong alkylating reagent, only a small amount of $[EtVi_3P]O_3SCF_3$, just sufficient for NMR measurement and mass spectrometry, could by extracted from the polymeric main product. Although the microanalytical data are in general agreement with the expected formulas, $[EtVi_3P]I$, $[EtVi_3P]O_3SCF_3$, and $[Vi_3BzP]Br$, the physical properties suggest long-chain or branched-chain structures.

We can offer the following mechanistic explanation: The reaction of Vi_3P with MeI is rapid owing to the absence of steric effects, and quaternization can go to completion before any side reactions can compete successfully. With EtI, however, the quaternization reaction is slower and the reaction of the produced $[EtVi_3P]^+$ cation with Vi_3P can compete with the reaction of Vi_3P with EtI. Nucleophilic attack of Vi_3P at one of the activated β-carbon atoms of the $[EtVi_3P]^+$ cation leads to diphosphonium dications with intermediate ylide-type stabilization and finally to polyphosphonium polyiodides (Scheme 1). Note that the structures may be linear or branched owing to the trifunctionality of Vi_3P.

The above mechanistic rationalization is supported by the observations made with the corresponding *arsenic* compounds. As already reported in one of the earliest papers,[7] trivinylarsine is readily quaternized by methyl iodide to give high yields of methyltrivinylarsonium iodide, showing an analogous behavior as compared to the trivinylphosphine/methyl iodide reaction. By contrast, both ethyl iodide and benzyl bromide also give only the simple quaternization products $[EtVi_3As]^+I^-$ and $[BzVi_3As]^+Br^-$ with Vi_3As, whereas Vi_3P gave insoluble polymeric products. This difference must be due to the lower nucleophilic character of Vi_3As as compared to Vi_3P. The quaternization reaction therefore is and remains the faster step during the whole reaction process for the arsenic compounds, while with the

---

(28) Forster, D. J. (Union Carbide Corp., New York) U.S. Patent 3,048,638, 1961.

(29) Potapov, V. A.; Amosova, S. V.; Khangurov, A. V. *Bull. Acad. Sci. USSR* **1989**, *38*, 195.

(30) Monkowius, U.; Mitzel, N. W.; Schier, A.; Schmidbaur, H. *J. Am. Chem. Soc.* **2002**, *124*, 6126.

(31) Wolfsberger, W.; Schmidbaur, H. *Synth. React. Inorg. Metal-Org. Chem.* **1974**, *4*, 149.

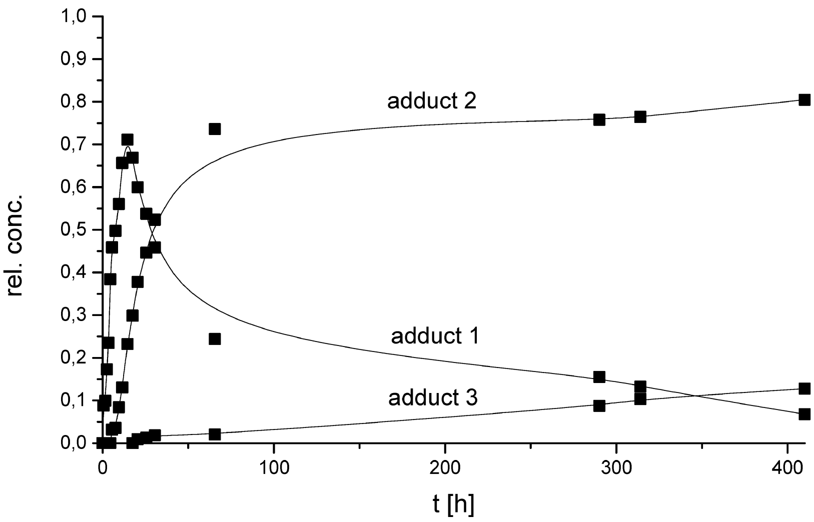
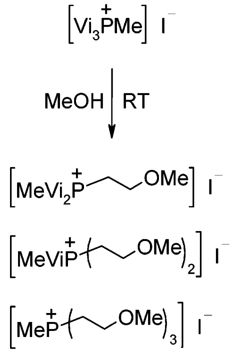


Figure 1. Time-dependent product distribution in the reaction of [MeVi$_3$P]I with methanol at 20 °C in the absence of a catalyst measured by ^{1}H NMR spectroscopy.

phosphorus compounds the nucleophilic attack of the phosphine at the activated vinyl group in the phosphonium salt is able to compete successfully with the quaternization reaction.

Methanol Addition to Methyltrivinylphosphonium Iodide. The proposed propensity of the vinyl groups in [MeVi$_3$P]$^+$ cations for nucleophilic attack is illustrated by the stepwise addition of methanol (eq 2). This reaction was observed during attempts to crystallize the phosphonium salts from alcohols. It proceeds already at room temperature and goes to completion within a period of several days (Figure 1). Catalytic amounts of sodium methanolate accelerate this reaction. A similar behavior is known for the Michael-type addition of alcohols to the vinyl group of tributylvinylphosphonium bromide[32] and of quaternized 1,1-bis(diphenylphosphino)ethylene.[33−35] The products were identified by their analytical and spectroscopic data, and the crystal structure of the primary adduct [MeVi$_2$PCH$_2$CH$_2$OMe]I has been determined.



(2)

This reaction sequence shows that quaternization of Vi$_3$P leads to a significant activation of the vinyl groups, making them susceptible to nucleophilic attack. This activation is clearly the reason for the failure of the above quaternization reaction to give simple 1:1 electrolytes. No reaction is observed between Vi$_3$P and MeOH at ambient temperature.

Oxidation of Trivinylphosphine with Halogens and Chalkogens. The formation of polynuclear phosphonium salts was also observed in attempts to add chlorine or iodine to Vi$_3$P. Treatment of Vi$_3$P in toluene/diethyl ether with elemental iodine leads to an immediate discoloration and formation of an insoluble precipitate. The elemental analysis data of this product approach the values of the proposed formula [Vi$_3$PI]I, but a polymeric structure is suggested for the cation(s) of this material. A similar product is obtained from Vi$_3$P and C$_2$Cl$_6$, but the analytical data are less satisfactory (low in chlorine) and indicate an influence of the chlorocarbon precursor as a polymerization promotor for Vi$_3$P.

Trivinylphosphine is slowly oxidized in air upon prolonged exposure to the atmosphere. A more rapid reaction occurs with hydrogen peroxide or organic peroxides.[36−41] The resulting *trivinylphosphine oxide*, a colorless solid, is also obtained upon oxidation of the corresponding sulfide in air. Single crystals could be grown from diethyl ether at −78 °C.

Trivinylphosphine sulfide[37−41] and *selenide* are obtained from the reaction of Vi$_3$P and sulfur/selenium in tetrahydrofuran at room temperature. The products are obtained in good yields as distillable colorless liquids. Only the selenide could be crystallized by cooling and annealing at −32 °C.

Trivinylphosphine and *tellurium* give no discernible reaction.

(Trivinylphosphine)gold(I) Chloride. Because gold(I) has the most simple coordination chemistry of all metals (with the lowest possible coordination number and a straightforward linear coordination geometry) and

---

(32) Keough P. T.; Grayson, M. *J. Org. Chem.* **1964**, *29*, 631.

(33) Schmidbaur, H.; Herr, R.; Pollok, T.; Schier, A.; Müller, G.; Riede, J. *Chem. Ber.* **1985**, *118*, 3105.

(34) Schmidbaur, H.; Herr, R.; Müller, G.; Riede, J. *Organometallics* **1985**, *4*, 1208.

(35) Schmidbaur, H.; Herr, R.; Riede, J. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 247.

(36) Vullo, W. J. (Hooker Chemical Corp., Niagara Falls, NY) U.S. Patent 3,495,257, 1970.

(37) Maier, L. *Helv. Chim. Acta* **1970**, *53*, 2069.

(38) Collins, D. J.; Rowley, L. E.; Swan, J. M. *Aust. J. Chem.* **1974**, *27*, 841.

(39) King, R. B.; Cloyd, J. C. Jr.; Hendrick, P. K. *J. Am. Chem. Soc.* **1973**, *95*, 5083.

(40) King, R. B.; Cloyd, J. C., Jr. *J. Am. Chem. Soc.* **1975**, *97*, 53.

(41) Weiner, M. A.; Pasternack, G. *J. Org. Chem.* **1967**, *32*, 3707.

because we could rely on our general expertise in gold coordination chemistry,[42] we have chosen gold(I) chloride as the model substrate for trivinylphosphine complexation. (Tetrahydrothiophene)gold(I) chloride reacts readily with Vi_3P in tetrahydrofuran even at −78 °C to give high yields of the 1:1 complex (eq 3). The product

$$Vi_3P + (C_4H_8S)AuCl \longrightarrow C_4H_8S + Vi_3PAuCl \quad \mathbf{(3)}$$

can be crystallized from dichloromethane/pentane at low temperature. The colorless crystals decompose at 65 °C and are light-sensitive. The NMR spectra of the product are as expected (Experimental Section). In the mass spectrum (chemical ionization) the dinuclear chloronium ion $[Cl(AuPVi_3)_2]^+$ is observed with high abundance (89%), followed by $[Vi_3PAu]^+$ (100%). This set of ions is typical for mass spectral patterns of many R_3PAuCl complexes and confirms the high stability of the di(gold)-chloronium cations.[43−45]

Complementary NMR Data. Trivinylphosphine has a ^{31}P NMR signal of −19.01 ppm (in tetrahydrofuran at 20°C), which is shifted upon quaternization by methyl iodide to +12.21 ppm (in chloroform at 20 °C). Similar shifts are observed upon the oxidation with oxygen (17.91 ppm), sulfur (29.02 ppm), and selenium (21.61 ppm, J(PSe) 756.4 Hz). The $^{13}C\{^1H\}$ resonances of Vi_3P appear as doublets at 127.2 [J(PC) 22.8 Hz] and 136.9 [J(PC) 13.0 Hz] and are shifted to 118.3 [J(PC) 82.1 Hz] and 143.0 ppm (s) upon quaternization with MeI. The CH_3 resonance of $[MeVi_3P]I$ is recorded at 8.6 ppm [J(PC) 59.17 Hz]. The $^{13}C\{^1H\}$ signals of the oxide, sulfide, and selenide show the same trend with small variations. These data are presented in the Experimental Section together with the ^1H NMR details, which bring previous results to completion.[11−16]

Crystal and Molecular Structures. Crystals of *methyltrivinylphosphonium iodide*, $[MeVi_3P]I\ (CHCl_3)$, are monoclinic, space group $P2_1/c$, with $Z = 8$ formula units in the unit cell. The lattice contains methyltrivinylphosphonium cations, iodide anions, and chloroform molecules which have no close, sub-van der Waals contacts. The vinyl groups of the cation are disordered over two positions, resembling inverted propellers (Figure 2). All C−P−C angles are near the tetrahedral standard, and all P−C distances are almost equal within the range of standard deviations. The conformation approaches very closely the symmetry of point group C_3, but with a *trans*,*trans*,*trans*-orientation of the vinyl groups and an average torsional angle C(Me)−P−C=C of about 138.1°. It should be noted that the free Vi_3P molecule was calculated to have the C_{3v}-*cis*,*cis*,*cis*-conformation as the ground state with only a small difference in energy for the C_3-symmetrical molecule (*gauche*/*gauche*/*gauche*) with a torsional angle of 133°.[11−14] For Vi_3P the P−C bond length and C−P−C angle were calculated to be 1.823 Å and 99.4°, respectively, as compared to our experimental values for P−C(vinyl) and (vinyl)C−P−C(vinyl) in the $[MeVi_3P]^+$ cation of 1.777 Å and 109.0° (average). A shortening of the P−C bonds and widening of the C−P−C angle of a tertiary phosphine upon quaternization are common phenomena and may be related to the rehybridization of the central atom (→ sp^3).

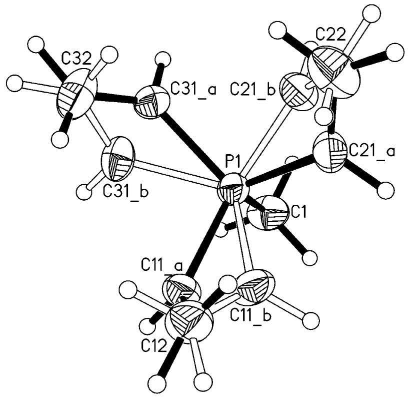


Figure 2. Structure of the cation in crystals of $[MeVi_3P]I(CHCl_3)$. ORTEP, 50% probability ellipsoids. As indicated the three vinyl groups are disordered. Selected bond lengths [Å] and angles [deg]: P1−C1 1.786(2), P1−C11 1.769(6), P1−C21 1.781(6), P1−C31 1.769(6); C11−C12 1.289(4), C21−C22 1.279(5), C31−C32 1.271(4); C11−P1−C21 109.7(3), C11−P1−C31 110.7(3), C21−P1−C31 108.4(3).

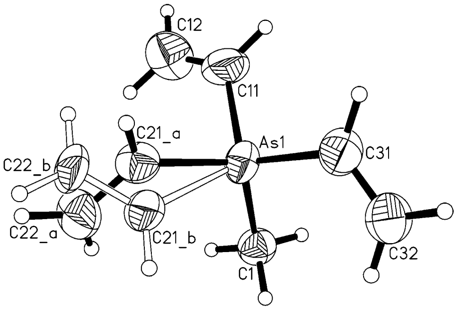


Figure 3. Structure of the cation in crystals of $[MeVi_3As]I$. ORTEP, 50% probability ellipsoids. As indicated, one vinyl group is disordered. Selected bond lengths [Å] and angles [deg]: As1−C1 1.894(4), As1−C11 1.909(5), As1−C21 1.889(8), As1−C31 1.898(4); C11−C12 1.220(6), C21−C22 1.295(14), C31−C32 1.275(6). C11−As1−C21 98.1(4)/118.8(5), C11−As1−C31 110.5(2), C21−As1−C31 107.7(4)/111.5(2).

Methyltrivinylarsonium iodide crystallizes without solvent in the monoclinic space group $P2_1/n$ with $Z = 4$ formula units in the unit cell. One vinyl group has been found to be disordered over two positions for each carbon atom *quasi* reflected at a virtual mirror plane including the atoms C1 and As1 (Figure 3). The conformation is therefore different from that of the phosphonium analogue (above) and is not approaching propeller symmetry. The bond lengths and angles show no anomalies.

Benzyltrivinylarsonium iodide crystallizes without solvent in the monoclinic space group $C2$ with $Z = 8$ formula units in the unit cell. The asymmetric unit contains two crystallographically independent cations and anions that differ significantly in their conformation (Figure 4). The cation containing As2 approaches mirror symmetry, comparable to the situation in $[MeVi_3As]I$ (above, without disorder), while the cation containing As1 has no standard orientation of the three vinyl groups.

---

(42) Schmidbaur, H., Ed. *Gold, Progress in Chemistry, Biochemistry and Technology*; Wiley: Chichester, 1999.

(43) Bayler, A.; Bauer, A.; Schmidbaur, H. *Chem. Ber./Recl.* **1997**, *130*, 115.

(44) Usón, R.; Laguna, A.; Castrillo, M. V. *Synth. React. Inorg. Metal-Org.* **1979**, *9*, 317.

(45) Schmidbaur, H.; Hamel, A.; Mitzel, N. W.; Schier, A.; Nogai, S. *Proc. Natl. Acad. Sci. USA* **2002**, *99*, 4916.

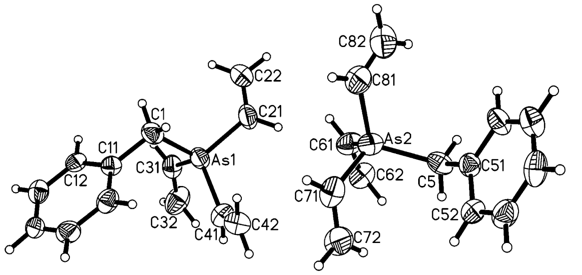


Figure 4. Structures of the two independent cations in crystals of [$BzVi_3As$]Br. ORTEP, 50% probability ellipsoids. Selected bond lengths [Å]: As1−C1 1.937(6), As1−C21 1.900(5), As1−C31 1.905(5), As1−C41 1.910(6); As2−C5 1.925(6), As2−C61 1.909(5), As2−C71 1.904(6), As2−C81 1.948(7).

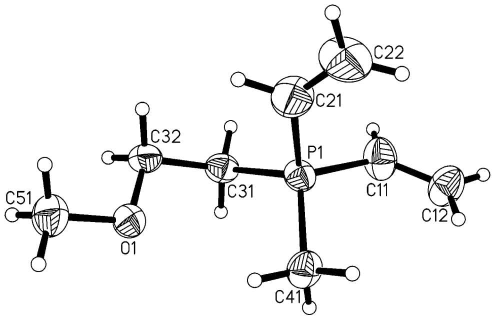


Figure 5. Structure of the cation in crystals of [$MeVi_2PCH_2CH_2OMe$]I. ORTEP, 30% probability ellipsoids. Selected bond lengths [Å]: P1−C11 1.782(5), P1−C21 1.797(5), P1−C31 1.784(5), P1−C41 1.767(5).

Methyl(divinyl)(2-methoxyethyl)phosphonium iodide forms orthorhombic crystals of space group $P2_12_12_1$ with $Z = 4$ formula units in the unit cell composed of iodide anions and [$MeVi_2PCH_2CH_2OMe$]$^+$ cations with no sub-van der Waals contacts (Figure 5). The cations have a pseudo-tetrahedral configuration at the phosphorus atom with P−C bond distances and C−P−C bond angles in the narrow ranges 1.767(5)−1.797(5) Å and 107.6(2)−112.2(2)°. The MeO−CH_2−CH_2−P group is in a *gauche* conformation.

Trivinylphosphine oxide crystallizes in the orthorhombic space group *Pnma* with $Z = 4$ formula units in the unit cell. The monomers are not discernibly associated in the crystal. The molecules have crystallographically imposed mirror symmetry (Figure 6). The P═O bond is found very short at 1.500(1)°, while the three P−C bonds are approximately equal and similar to those in the above reference compounds [1.793(1) (2×) and 1.796(2)°]. The O−P−C angles are larger, the C−P−C bonds smaller than the tetrahedral standard. These results are in good agreement with the plethora of data available for tertiary phosphine oxides.

Regarding the conformation of the Vi_3PO molecule, it should be noted that the deviations from ideal C_{3v} symmetry with *cis*,*cis*,*cis*-orientation of the vinyl groups are very small indeed. In fact, it is only because of the two small torsional angles O−P−C═C of 2.9(2)° for the two symmetry-related vinyl groups that the structure does not conform to the 3-fold symmetry with three vertical mirror planes predicted in calculations for Vi_3P.[11]

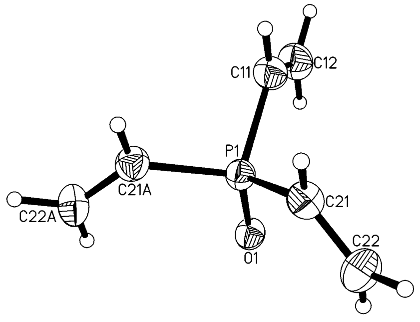


Figure 6. Structure of Vi_3PO. ORTEP, 50% probability ellipsoids. Selected bond lengths [Å] and angles [deg]: P1−O1 1.5004(13), P1−C11 1.796(2), P1−C21 1.7929(14); C11−C21 1.316(3), C21−C22 1.321(2); O1−P1−C11 113.93(9), O1−P1−C21 113.84(6), C11−P1−C21 104.55(6), C21−P1−C21′ 105.12(10).

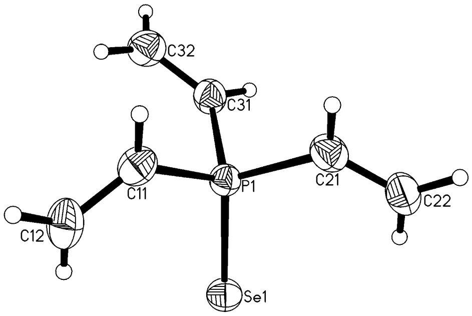


Figure 7. Structure of Vi_3PSe. ORTEP, 50% probability ellipsoids. Selected bond lengths [Å] and angles [deg]: P1−Se1 2.1100(4), P1−C11 1.801(3), P1−C21 1.797(3), P1−C31 1.805(2); C11−C12 1.322(4), C21−C22 1.312(4), C31−C32 1.310(3); Se1−P1−C11 115.12(10), Se1−P1−C21 114.76(10), Se1−P1−C31 105.36(11); C11−P1−C21 104.65(10), C11−P1−C31 105.36(11), C21−P1−C31 104.10(11).

Trivinylphosphine selenide forms orthorhombic crystals of space group $Pna2_1$ with $Z = 4$ formula units in the unit cell. The structure was solved for a racemic twin. The molecules have a *cis*,*cis*,*skew*-conformation with two vinyl groups close to the *cis* orientation [small dihedral angles Se−P−C11═C12 = −12.8(3)° and Se−P−C21═C22 = 17.1(3)°] and one rotated away from this orientation by Se−P−C31═C32 = 114.5(2)° (Figure 7). This conformer was also considered in calculations of the Vi_3P molecule, but was found to be of higher energy. Clearly the more bulky selenium atom requires a conformation offering more space for the incoming chalcogen ligand than provided in the molecule with an all-*cis* orientation of the vinyl groups. The P−Se and P−C distances and the Se−P−C and C−P−C angles show no anomalies.

Crystals of (*Trivinylphosphine)gold(I) chloride*, (Vi_3P)AuCl, are monoclinic, space group $P2_1/c$, with $Z = 8$ formula units in the unit cell. The asymmetric unit contains two crystallographically independent molecules of very similar dimensions which are associated into dimers via a short aurophilic contact [Au1−Au2 3.0934(5) Å] (Figure 8). The two P−Au−Cl axes are slightly bent [P1−Au1−Cl1 172.24(1)°, P2−Au2−Cl2 177.23(9)°], allowing a closer approach of the two metal atoms. The torsional angles P1−Au1−Au2−P2 98.79(9)° and Cl1−Au1−Au2−Cl2 103.08(9)° indicate that the molecular axes are crossed at approximately right angles. The vinyl groups have an almost random orientation, with the Au−P−C═C torsional angles spreading over a wide range. The conformation of the monomers thus shows

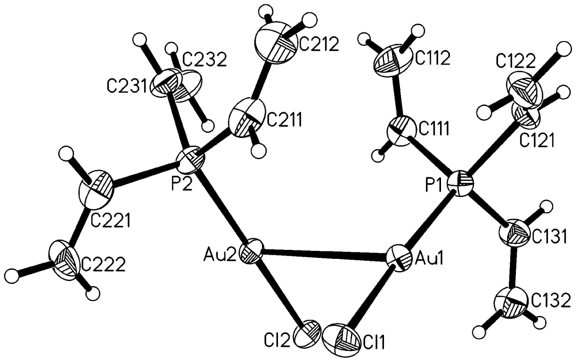


Figure 8. Structure of dimeric ($(Vi_3P)AuCl$). ORTEP, 50% probability ellipsoids. Selected bond lengths [Å]: Au1−P1 2.229(3), Au1−Cl1 2.290(2), Au2−P2 2.226(2), Au2−Cl2 2.290(2), Au1−Au2 3.0934(5).

none of the standard symmetry relations. These distortions probably arise from the close mutual approach of the two monomers, which leads to a restricted rotational movement of the substituents.

Experimental Section

General Procedures. All chemicals used as starting materials were commercially available, except Vi_3As, which was prepared according to literature.[7] Instead of isolation, it was used as a solution in THF, which was obtained by condensing the volatile components from the Grignard reaction.

Reactions were carried out under an atmosphere of purified nitrogen. All solvents were distilled from an appropriate drying agent and stored above molecular sieves (4 Å) and under nitrogen. Mass spectra were recorded on a Hewlett-Packard MS 5971 A spectrometer using EI at 70 eV or on a Finnigan MAT 90 spectrometer using FAB as an ionization method. NMR spectra were obtained at room temperature on JEOL-400 or JEOL-270 spectrometers. Chemical shifts are reported in δ values relative to the residual solvent resonances (^1H,^{13}C). $^{31}P\{^1H\}$ NMR spectra are referenced to external aqueous H_3PO_4 (85%). The single-crystal X-ray diffraction measurements were performed at −130 °C on a Nonius DIP 2020 diffractometer using graphite-monochromated Mo Kα radiation.

Trivinylphosphine. To a solution of ViMgCl (600 mL, 1.7 M in THF, 1.02 mol) cooled to − 78 °C was added in a dropwise manner with rapid stirring triphenyl phosphite (62.6 mL, 74.5 g, 0.24 mol) in THF (200 mL). The reaction mixture was allowed to warm to room temperature, and stirring was continued for 20 h. The volatile components were evaporated at 100 °C and condensed in a flask cooled by liquid nitrogen. The THF was removed by distillation using a Vigreux column at 80 °C. The product was isolated as a colorless liquid by fractional distillation (116 °C, 1013 mbar). Yield: 9.03 g, 30%. NMR (C_6D_6, RT): $^{31}P\{^1H\}$ −19 (s); $^{13}C\{^1H\}$ 136.9 (d, $J = 22.8$ Hz, C1), 127.2 (d, $J = 13.0$ Hz, C2); ^1H 6.2 (ddd, $J = 11.9$ and 18.6 Hz, 3 H, C1−H), 5.7 (ddd, $J = 1.7$, 11.9, and 30.9 Hz, 3 H, C2−H), 5.6 (ddd, $J = 1.7$, 18.6, and 14.1 Hz, 3 H, C2−H).

Trivinylphosphine Oxide. Vi_3PO can be obtained by the treatment of Vi_3P with either hydrogen peroxide or organic peroxides.[36] Vi_3PO is also formed upon the exposure of Vi_3PS to air. Crystals were grown from diethyl ether at −32 °C. NMR ($CDCl_3$, RT): $^{31}P\{^1H\}$ 17.9 (s); $^{13}C\{^1H\}$ 133.7 (s, C2), 130.1 (d, $J = 99.65$ Hz, C1); ^1H 5.9−6.3 (ABCX, 9 H); MS (EI) *m/z* 128 $[M]^+$, 101 $[M - Vi]^+$, 85 $[Vi_2P]^+$, 74 $[ViP]^+$.

Trivinylphosphine Sulfide. A solution of Vi_3P (0.5 g, 4.5 mmol) in THF (20 mL) was stirred with an excess of sulfur (1.0 g, 31 mmol) for 20 h. The solvent was removed under reduced pressure and the residue extracted with pentane (20 mL). Following solvent removal the remaining oil was distilled and the product isolated in quantitative yield as a colorless liquid (58 °C, 0.9 mbar). NMR ($CDCl_3$, RT): $^{31}P\{^1H\}$ 29 (s); (C_6D_6, RT): $^{13}C\{^1H\}$ 132.6 (d, $J = 2.1$ Hz, C2), 131.3 (d, $J = 81.0$ Hz, C1); ^1H 6.2 (ddd, $J = 1.7$, 17.9, and 24.8 Hz, 3 H, C2−H), 6.0 (ddd, $J = 11.4$, 17.9, and 25.0 Hz, 3 H, C1−H), 5.6 (ddd, $J = 1.7$, 11.4, and 45.5 Hz, 3 H, C2−H). MS (EI): *m/z* 128 $[M]^+$, 118 $[M - Vi]^+$, 90 $[M - 2Vi]^+$, 85 $[Vi_2P]^+$. Anal. Calcd for C_6H_9PS (144.18): C, 49.99; H, 6.29; P, 21.48. Found: C, 50.44; H, 6.40; P, 21.60.

Trivinylphosphine Selenide. To a solution of Vi_3P (0.50 g, 4.5 mmol) in THF (20 mL) was added gray selenium (0.28 g, 3.5 mmol) in small portions. The selenium dissolves quickly. After 1 h, the solvent and the excess Vi_3P were removed in vacuo and the product was isolated as a colorless liquid by distillation in quantitative yield (68 °C, 0.9 mbar). Crystallization was achieved by cooling a solution in methylene chloride to −78 °C. NMR (C_6D_6, RT): $^{31}P\{^1H\}$ 21.6 (d, $J = 756.4$ Hz); $^{13}C\{^1H\}$ 133.6 (d, $J = 2.1$ Hz, C2), 130.1 (d, $J = 72.7$ Hz, C1); ^1H 6.1 (ddd, $J = 2.0$, 17.8, and 25.7 Hz, 3 H, C2−H), 6.0 (ddd, $J = 11.0$, 17.8, and 24.1 Hz, 3 H, C1−H), 5.6 (ddd, $J = 2.0$, 11.0, and 47.1 Hz, 3 H, C2−H). MS (EI): *m/z* 192 $[M]^+$, 166 $[M - Vi]^+$, 138 $[M - 2Vi]^+$, 112 $[Vi_3P]^+$, 85 $[Vi_2P]^+$.

(Trivinylphosphine)gold(I) Chloride. (Tetrahydrothiophene)AuCl (0.29 g, 0.90 mmol) in THF (15 mL) was cooled to −78 °C, and a solution of Vi_3P (0.10 g, 0.90 mmol) in THF (15 mL) was slowly added via a syringe. The reaction mixture was stirred for 1 h. The solvent was removed under reduced pressure, yielding a white powder, which was crystallized from a methylene chloride/pentane solution. The compound thermally decomposes above 65 °C and is sensitive to light. Yield: 0.27 g, 87%. NMR ($CDCl_3$, RT): $^{31}P\{^1H\}$ 22.3 (s); $^{13}C\{^1H\}$ 136.3 (d, $J = 6.9$ Hz, C2), 127.1 (d, $J = 59.2$ Hz, C1); ^1H 6.0−6.3 (ABCX, 9 H). MS (FAB): *m/z* 654 (89%) $[2M - Cl]^+$, 309 (100%) $[M - Cl]^+$. Anal. Calcd for C_6H_9PAuCl (345.54): C, 20.86; H, 2.92. Found: C, 20.43; H, 2.64.

Methyl Trivinylphosphonium Iodide. Reference 7. New analytical data: NMR ($CDCl_3$, RT) $^{31}P\{^1H\}$ 12.2 (s); $^{13}C\{^1H\}$ 143.0 (s, C2), 118.3 (d, $J = 82.0$ Hz, C1), 8.6 (d, $J = 59.2$ Hz, Me); ^1H 6.5−7.0 (m, 9 H, Vi), 2.5 (d, $J = 14.25$ Hz, 3 H, Me). MS (FAB): *m/z* 126.9 (100%) $[M]^+$. Anal. Calcd for $C_8H_{13}Cl_3IP$ (as the chloroform solvate) (373.43): C, 25.73; H, 3.51; P, 8.29; Cl, 28.48. Found: C, 25.84; H, 3.56; P, 8.31; Cl, 26.45.

Reaction of Methyl Trivinylphosphonium Iodide with Methanol. $[MeVi_3P]^+I^-$ (20 mg, 0.08 mmol) was dissolved in d_4-methanol (0.4 mL). $^{31}P\{^1H\}$ and ^1H NMR experiments were conducted at regular intervals. The relative concentrations of the addition products were determined from the ^1H NMR signals of the methyl protons.

Analytical data for $[MeVi_2PCH_2CH_2OMe]^+$: NMR (D_3COD, RT) $^{31}P\{^1H\}$ 19.0 (s); ^1H 2.15 (d, $J = 14.64$ Hz, 3 H, Me); MS (FAB) *m/z* 159.0.

Analytical data for $[MeViP(CH_2CH_2OMe)_2]^+$: NMR (D_3COD, RT) $^{31}P\{^1H\}$ 26.0 (s); ^1H 2.04 (d, $J = 14.68$ Hz, 3 H, Me); MS (FAB) *m/z* 191.0.

Analytical data for $[MeP(CH_2CH_2OMe)_3]^+$: NMR (D_3COD, RT) $^{31}P\{^1H\}$ 33.6 (s); ^1H 1.91 (d, $J = 14.64$ Hz, 3 H, Me).

Tris(2-methoxyethyl)methylphosphonium Iodide. $[MeVi_3P]^+I^-$ (0.50 g, 2.0 mmol) and NaOMe (50 mg, 0.9 mmol) were dissolved in methanol (20 mL). After 12 h of stirring the reaction mixture was neutralized with HI (67%, 0.06 mL) and the solvent was removed in a vacuum to leave a yellow oil. The oil was washed with a mixture of acetonitrile and diethyl ether (1:3). Yield: 0.60 g, 85%. NMR ($CDCl_3$, RT): $^{31}P\{^1H\}$ 33.7 (s); $^{13}C\{^1H\}$ 65.3 (d, $J = 7.80$ Hz, C2), 58.8 (s, OMe), 23.5 (d, $J = 50.7$ Hz, C1), 7.4 (d, $J = 51.9$ Hz, Me); ^1H 3.68 (dt, $J = 5.94$ and 20.29 Hz, 6 H, C2−H), 3.24 (s, 9 H, OMe), 2.71 (dt, $J = 5.94$ and 13.11 Hz, 6 H, C1−H), 1.97 (d, $J = 14.35$ Hz, 3 H, Me). MS (FAB): *m/z* 223.1 (100%) $[M]^+$, 191.1 (14.7%) $[M - MeOH]^+$, 159.1 (1.4%) $[M - 2MeOH]^+$. Anal. Calcd for $C_{10}H_{24}IO_3P$ (350.18): C, 34.30; H, 6.91; I, 36.24; P, 8.85. Found: C, 33.92; H, 6.91; I, 35.83; P, 8.37.

Table 1. Crystal Data, Data Collection, and Structure Refinement of $[MeVi_3P]I(CHCl_3)$, $[MeVi_2PCH_2CH_2OMe]I$, and $[MeVi_3As]I$, $[BzVi_3As]Br$

	$[MeVi_3P]I (CHCl_3)$	$[MeVi_2PCH_2CH_2OMe]I$	$[MeVi_3As]I$	$[BzVi_3As]Br$
empirical formula	$C_8H_{13}Cl_3IP$	$C_8H_{16}IOP$	$C_7H_{12}AsI$	$C_{13}H_{16}AsBr$
M	373.40	286.08	297.99	327.09
cryst syst	monoclinic	orthorhombic	monoclinic	monoclinic
space group	$P2_1/c$	$P2_12_12_1$	$P2_1/n$	$C2$
a/Å	7.6539(1)	7.5622(2)	7.1795(1)	26.3940(6)
b/Å	13.7840(2)	11.0516(3)	12.6975(3)	7.4280(2)
c/Å	13.4499(2)	14.2806(5)	11.2310(3)	15.1410(5)
α/deg	90	90	90	90
β/deg	92.6799(5)	90	90.8109(9)	111.9970(11)
γ/deg	90	90	90	90
U/Å^3	1417.43(3)	1193.49(6)	1023.73(4)	2752.37(13)
ρ_{calc}/g cm^{-3}	1.750	1.592	1.933	1.579
Z	4	4	4	8
T/K	143	143	143	143
no. of reflns measd	37 686	48 944	30 487	27 610
no. of reflns unique	3293 [$R_{int} = 0.033$]	2769 [$R_{int} = 0.0485$]	2315 [$R_{int} = 0.041$]	5986 [$R_{int} = 0.053$]
no. of refined params/restraints	146/0	100/0	101/0	272/1
R1 [$I \geq 2\sigma(I)$]	0.0222	0.0279	0.0272	0.0393
wR2	0.0613	0.0705	0.0658	0.0951
weighting scheme	$a = 0.0285$ $b = 0.9336$	$a = 0.0241$ $b = 0.7769$	$a = 0.215$ $b = 1.9153$	$a = 0.0000$ $b = 8.2286$
σ_{fin}(max./min.)/e Å^{-3}	0.856/−0.608	0.572/−0.500	1.087/−0.819	1.130/−0.896

Table 2. Crystal Data, Data Collection, and Structure Refinement of Vi_3PO, Vi_3PSe, and Vi_3PAuCl

	Vi_3PO	Vi_3PSe	Vi_3PAuCl
empirical formula	C_6H_9OP	C_6H_9PSe	C_6H_9AuClP
M	128.10	191.06	344.52
cryst syst	orthorhombic	orthorhombic	monoclinic
space group	$Pnma$	$Pna2_1$	$P2_1/c$
a/Å	9.5130(2)	8.4158(2)	14.0580(2)
b/Å	10.7830(3)	9.0513(2)	8.6270(2)
c/Å	7.0590(3)	10.6198(3)	16.0510(2)
α/deg	90	90	90
β/deg	90	90	107.485(1)
γ/deg	90	90	90
U/Å^3	724.10(4)	808.95(3)	1856.70(6)
ρ_{calc}/g cm^{-3}	1.175	1.569	2.465
Z	4	4	8
T/K	143	143	143
no. of reflns measd	25 094	25 961	65 336
no. of reflns unique	839 [$R_{int} = 0.036$]	1861 [$R_{int} = 0.0372$]	5030 [$R_{int} = 0.075$]
no. of refined params/restraints	65/0	74/1	163/0
R1 [$I \geq 2\sigma(I)$]	0.0353	0.0200	0.0508
wR2	0.1032	0.0484	0.1186
weighting scheme	$a = 0.0677$ $b = 0.2077$	$a = 0.0234$ $b = 0.1362$	$a = 0.0000$ $b = 48.3153$
σ_{fin}(max./min.)/e Å^{-3}	0.258/−0.305	0.481/−0.234	1.936/−2.070

Reaction of Trivinylphosphine with Iodoethane. To a solution of EtI (3 mL) in THF (10 mL) was slowly added a solution of Vi_3P (0.5 g, 4.5 mmol) in THF (10 mL) at −78 °C. A white precipitate formed, which was filtered, washed with THF, and dried in vacuo. The product was insoluble in all organic solvents and in water. Anal. Calcd for $[C_{12}H_{14}PI]_n$: C, 35.84; H, 5.26; P, 11.55; I, 47.34. Found: C, 36.68; H, 5.92; P, 11.53; I, 42.21.

Reaction of Trivinylphosphine with Ethyl Trifluoromethanesulfonate. To a solution of ethyl triflate (0.8 g, 4.5 mmol) in hexane (5 mL) was slowly added a solution of Vi_3P (0.5 g, 4.5 mmol) in THF (5 mL) at −78 °C. After warming to room temperature a yellow precipitate was slowly formed. The reaction mixture was stirred for 20 h. After filtering and washing with THF (10 mL), $[EtVi_3P]O_3SCF_3$ was extracted from the polymeric product with acetonitrile. Yield: 30 mg, 2%. NMR (CD_2Cl_2, RT): $^{31}P\{^1H\}$ 17.6 (s); $^{13}C\{^1H\}$ 144.4 (s, $C2_{Vi}$), 121.2 (q, $J = 320.56$ Hz, CF_3), 116.6 (d, $J = 81.5$ Hz, $C1_{vi}$), 15.7 (d, $J = 55.3$ Hz, $C1_{Et}$), 5.7 (d, $J = 4.6$ Hz, $C2_{Et}$); ^1H 6.8 (ddd, $J = 1.1$, 11.4, and 47.2 Hz, 3 H, $C2_{Vi}$−H), 6.4−6.6 (m, 6 H, $C1_{Vi}$− and $C2_{Vi}$−H), 2.5 (dq, $J = 15.2$ and 7.7 Hz, 2 H, $C1_{Et}$-H), 1.3 (dt, $J = 20.5$ and 7.7 Hz, 3 H, $C2_{Et}$−H). MS (FAB): m/z 141 $[M]^+$. Microanalytical data for the polymeric residue: Anal. Calcd for $[C_9H_{14}F_3O_3PS]_n$: C, 37.24; H, 4.86; P, 10.67; S, 11.05. Found: C, 37.35; H, 5.19; P, 10.26; S, 11.09.

Reaction of Trivinylphosphine with Benzyl Bromide. To a solution of Vi_3P (0.5 g, 4.5 mmol) in THF (10 mL) was added an excess of benzyl bromide (3 mL). The product precipitated out of solution within 1 h. It was filtered, washed with THF, and dried in vacuo. It is insoluble in organic solvents and in water. Anal. Calcd for $[C_{13}H_{16}PBr]_n$: C, 55.15; H, 5.70; P, 10.94; Br, 28.22. Found: C, 53.39; H, 5.91; P, 10.78; Br, 26.69.

Reaction of Trivinylphosphine with Iodide. To Vi_3P (0.5 g, 4.5 mmol) in toluene/diethyl ether (20 mL, 1:1) was slowly added a solution of iodine (1.1 g, 4.5 mmol) in toluene (5 mL) via a dropping funnel. The iodine was immediately decolorized, and a yellow precipitate was formed. The product was filtered, washed with toluene (10 mL), and dried in vacuo. It is insoluble in organic solvents and decomposes in water. Yield: 0.36 g, 25%. Calcd for $[C_6H_9PI_2]_n$: C, 19.69; H, 2.48; P, 8.46; I, 69.36. Found: C, 20.97; H, 2.91; P, 8.07; I, 65.16.

Reaction of Trivinylphosphine with Hexachloroethane. To a solution of hexachloroethane (1.1 g, 4.5 mmol), dissolved in acetonitrile (10 mL), was slowly added a solution of Vi_3P (0.5, 4.5 mmol) in acetonitrile (10 mL). A white solid precipitated, which was filtered, washed with acetonitrile (10 mL), and dried in vacuo. Anal. Calcd for $[C_6H_9PCl_2]_n$: C, 39.4; H, 5.0; P, 16.9; Cl, 38.7. Found: C, 44.40; H, 6.04; P, 17.69; Cl, 28.95.

Methyl Trivinylarsonium Iodide. Reference 7. New analytical data: Subl.p. 154 °C; NMR ($CDCl_3$, RT) $^{13}C\{^1H\}$ 143.0 (s, C2), 118.3 (s, C1), 8.6 (s, Me); ^1H 6.72 (dd, $J = 11.4$ and 18.0 Hz, 3 H, C1−H), 6.65 (d, $J = 10.8$ Hz, 3 H, C2−H), 6.29 (d, 18.0 Hz, 3 H, C2−H), 2.20 (s, 3 H, Me); MS (FAB) *m*/*z* 170.8 (100%) $[M]^+$.

Ethyl Trivinylarsonium Iodide. Reference 7. New analytical data: NMR ($CDCl_3$, RT) $^{13}C\{^1H\}$ 139.70 (s, $C2_{Vi}$), 120.32 (s, $C1_{Vi}$), 21.39 (s, $C1_{Et}$), 7.90 (s, $C2_{Et}$); ^1H 6.97 (dd, $J = 11.38$ and 18.56 Hz, 3 H, $C1_{Vi}$−H), 6.64 (d, $J = 11.62$ Hz, 3 H, $C2_{Vi}$−H), 6.29 (d, 18.56 Hz, 3 H, $C2_{Vi}$−H), 3.20 (q, $J = 7.67$ Hz, 3 H, Me), 1.40 (t, $J = 7.67$ Hz, 3 H, $C2_{Et}$−H); MS (FAB) *m*/*z* 184.9 (100%) $[M]^+$, 170.9 (18%) $[M - CH_2]^+$.

Benzyl Trivinylarsonium Bromide. A solution of Vi_3As in THF (50 mL) was treated with an excess of benzyl bromide (5 mL). After two weeks at room temperature white needles separated. The product was completely precipitated by addition of pentane, filtered, and washed with pentane. Crystallization was achieved from chloroform/diethyl ether. Mp: 121.5 °C. NMR ($CDCl_3$, RT): $^{13}C\{^1H\}$ 139.4 (s, $C2_{Vi}$), 130.3, 129.1, 128.8, 128.5 (all s, phenyl), 120.6 (s, $C1_{Vi}$), 34.6 (s, benzyl−CH_2); ^1H 7.45−7.47 (m, 2 H, ortho-H), 7.24−7.27 (m, 3 H, meta-/para-H), 6.95 (dd, $J = 11.72$ and 18.67 Hz, 3 H, $C1_{Vi}$−H), 6.49 (d, $J = 11.71$ Hz, 3 H, $C2_{Vi}$−H), 6.10 (d, $J = 18.67$ Hz, 3 H, $C2_{Vi}$−H), 4.83 (s, 2 H, benzyl−CH_2). MS (FAB): *m*/*z* 247.1 (100%) $[M]^+$, 128.9 (3.3%) $[Vi_2As]^+$, 117.0 (6.0%) $[MeViAs]^+$. Anal. Calcd for $C_{13}H_{16}AsBr$ (327.09): C, 46.74; H, 4.93; Br, 24.43. Found: C, 46.66; H, 5.01; Br, 24.69.

Crystal Structure Determination. Specimens of suitable quality and size of $[MeVi_3P]I\ (CHCl_3)$, $[MeVi_2PCH_2CH_2OMe]I$, $[MeVi_3P]I$, $[BzVi_3As]Br$, Vi_3PO, Vi_3PSe, and Vi_3PAuCl were mounted on the ends of quartz fibers in inert perfluoropolyalkyl ether and used for intensity data collection on a Nonius DIP2020 diffractometer, employing graphite-monochromated Mo Kα radiation. The structures were solved by a combination of direct methods (SHELXS-97) and difference Fourier syntheses and refined by full matrix least-squares calculations on F^2 (SHELXL-97).[46] The thermal motion was treated anisotropically for all non-hydrogen atoms. The hydrogen atoms of $[MeVi_3P]I\ (CHCl_3)$, $[MeVi_2PCH_2CH_2OMe]I$, $[MeVi_3P]I$, $[BzVi_3As]Br$, Vi_3PSe, and Vi_3PAuCl were calculated in ideal positions and allowed to ride on their parent atoms with fixed isotropic contributions. For Vi_3PO the hydrogen atoms were located and refined isotropically. Absorption corrections for $[MeVi_3P]I\ (CHCl_3)$, $[MeVi_2PCH_2CH_2OMe]I$, $[MeVi_3P]I$, $[BzVi_3As]Br$, Vi_3PSe, and Vi_3PAuCl were carried out using DELABS, as part of the PLATON suite of programs.[47] Further information on crystal data, data collection, and structure refinement are summarized in Table 1.

Acknowledgment. This work was supported by Fonds der Chemischen Industrie.

Supporting Information Available: A listing of the atomic coordinates, bond lengths, bond angles, anisotropic displacement parameters, and torsion angles for the crystal and molecular structures of $[MeVi_3P]I(CHCl_3)$, $[MeVi_2PCH_2CH_2OMe]I$, $[MeVi_3As]I$, $[BzVi_3As]Br$, Vi_3PO, Vi_3PSe, and $(Vi_3P)AuCl$ is available. This material can be obtained, free of charge, via the Internet at http://pubs.acs.org.

OM020653J

---

(46) Sheldrick, G. M. *SHELX-97*, Programs for crystal structure analysis; University of Göttingen: Germany, 1997.

(47) Spek, A. L. *Acta Crystallogr., Sect. A* **1990**, *46*, 194.