g, 65 mmol). An exothermic reaction occurred with evolution of a gas, presumably N_2. Distillation afforded **8** as a colorless liquid that solidified on standing (mp 49–50 °C).

[Bis(trimethylsilyl)methylene]mesitylthioxophosphorane (9). Tri-*n*-butylphosphine (2.1 mL, 8.4 mmol) was added via syringe to a stirred solution of **10** (3.12 g, 8.4 mmol, prepared as described below) in benzene (10 mL) at 0 °C. After the mixture was warmed to room temperature, ^{31}P NMR showed the formation of **9** and $n\text{-}Bu_3P{=}S$ (δ 46.50). The solvent was removed and distillation through a short-path column gave a yellow liquid that solidified in the receiving flask and the condenser. The solids were combined and recrystallized from hexane to give **9** as white crystals (mp 95–100 °C).

Thiaphosphirane (10). Sulfur (0.9 g, 28 mmol) was added to a stirred solution of **2** (4.4 g, 14 mmol) in benzene (80 mL) at room temperature. After the mixture was stirred overnight, the solvent was removed and the solid product was recrystallized from hexane (25 mL) to give **10** as white crystals (mp 139–141 °C). Preliminary experiments showed that the reaction of **2** with 1 equiv of sulfur gave an inseparable mixture of **9**, **10**, and unreacted **2**.

Acknowledgment. We thank the U.S. Office of Naval Research and The Robert A. Welch Foundation for generous financial support of this research.

Registry No. **1**, 92270-32-1; **2**, 89982-70-7; **3**, 92270-33-2; **4**, 89982-71-8; **5**, 92284-16-7; **6**, 89982-77-4; **7**, 89982-76-3; **8**, 89982-72-9; **9**, 89982-73-0; **10**, 89982-74-1; $(Me_3Si)_2CHMgCl$, 86509-05-9; $MesPCl_2$, 6781-96-0.

Synthesis of the First Carbodiarsorane and Related Arsenic Ylides

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Bis(diphenylarsino)methane (1) gives only a monoquaternization product, **2**, with methyl iodide but is converted into the bis(arsonium) salt **4** when methyl fluorosulfate is employed. **2** is the precursor for the monoylide $MePh_2As{=}CHAsPh_2$ (**3**) while **4** yields the first bis(ylide) ("carbodiarsorane") $MePh_2As{=}C{=}AsPh_2Me$ (**5**) on treatment with sodium amide in liquid ammonia at −40 °C. **5** is thermally unstable at room temperature but can be reprotonated with acid to give the corresponding dication of salts **4**.

Introduction

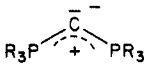
Carbodiphosphoranes,[1-3] $R_3P{=}C{=}PR_3$, have attracted considerable interest as versatile reagents in organic synthesis,[4] as ligands for both main-group and transition metals,[5] and as materials with intriguing physical properties.[6]

A large variety of open-chain and cyclic compounds containing the P=C=P moiety has been prepared as summarized in a recent publication from this laboratory.[7] Results of structural studies of several prototypes have indicated that the PCP bond angle is quite flexible and can vary between 180° and at least 116°.[8,9] The thermal stability of the compounds is quite satisfactory even for strained cyclic species.[10]

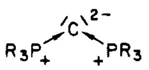
Formulas Ia–c are used for a general description of structure and bonding in carbodiphosphoranes, with the main emphasis on the semiylidic formula Ib. It has been pointed out, however, that according to Ic, pertinent compounds may also be considered as phosphine complexes of elemental carbon,[3] in line with a description of simple phosphorus monoylides as phosphine complexes of methylene, CH_2 (IIb).

$R_3P{=}C{=}PR_3$

Ia



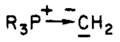
Ib



Ic

$R_3P{=}CH_2$

IIa



$R_3\overset{+}{P}{\rightarrow}\overset{-}{\underline{C}}H_2$

IIb

Analogous carbodiarsoranes, $R_3As{=}C{=}AsR_3$, have not yet been reported,[11] and even monoylides of arsenic of the type $R_3As{=}CH_2$[12-15] are thermally quite unstable materials. The mode of decomposition of the latter is best understood if a dissociation into tertiary arsines and carbenes is assumed. Therefore, carbodiarsoranes could be expected to be carriers or transfer reagents for carbon atoms, and a study was initiated to follow this idea, if suitable precursors could be generated. We report here the synthesis of the title compounds, whose reactivity is presently under investigation.

Experimental Section

General Data. All experiments were carried out under an atmosphere of pure and dry nitrogen. Glassware was dried at 140 °C and filled with nitrogen. Solvents were dried over sodium/benzophenone (diethyl ether, tetrahydrofuran), calcium hydride (benzene, toluene, pentane), or phosphorus pentoxide (dichloromethane, chloroform) and kept under nitrogen after distillation.

Bis(diphenylarsino)methane, **1**, was prepared from triphenylarsine following a literature procedure.[16]

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[(Diphenylarsino)methyl]methyldiphenylarsonium Iodide (2). Compound 1 (7.15 g, 15.1 mmol) was dissolved in 40 mL of dry, carefully distilled methyl iodide (large excess), and the mixture heated with reflux to 40 °C for several hours. The unreacted CH_3I was removed in vacuo and replaced by diethyl ether. The colorless solid was filtered, washed twice with ether, and crystallized from methanol. The product was dried in vacuo: yield 7.38 g (79.4%), mp 173 °C; ^1H NMR ($CDCl_3$) δ 2.77 (s, 3 H, CH_3), 4.12 (s, 2 H, CH_2), 7.37–7.97 (m, 20 H, C_6H_5); ^{13}C NMR (CD_3OD) δ 6.17 (q, $^1J(CH)$ = 140.6 Hz, CH_3), 18.32 (t, $^1J(CH)$ = 142.6 Hz, CH_2) [C_6H_5 resonances at 128.26, 128.71, 129.43, 130.92, 132.22, and 132.74 ppm (in the ^1H decoupled spectrum) have not been assigned, but C_1 at As^V and C_1 at As^{III} could be identified at 123.25 and 137.03 ppm, respectively]. Anal. Calcd for $C_{26}H_{25}As_2I$ (614.22): C, 50.84; H, 4.10; As, 24.4. Found: C, 50.10; H, 4.00; As, 23.3.

Methyldiphenylarsonium (Diphenylarsino)methylide (3, [(Diphenylarsino)methylene]methyldiphenylarsorane). A suspension of 5.05 g (8.20 mmol) of 2 in 50 mL of tetrahydrofuran was treated with 0.69 g of sodium amide (17.7 mmol, excess) at 25 °C with stirring. A yellow color developed, and ammonia was evolved. After 4 days the reaction mixture was filtered and the solvent removed from the filtrate in vacuo. The residue was taken up with 30 mL of toluene; the solution filtered from undissolved material and reduced to a volume of 15 mL in vacuo. After addition of 10 mL of pentane and cooling to −25 °C, a yellow oil separated, which crystallized on standing to yield 3.25 g (81.3%) of a yellow solid, sensitive to air and moisture, mp 87–89 °C, which is soluble in benzene, toluene, and diethyl ether, sparingly soluble in pentane: ^1H NMR (C_6D_6) δ 0.95 (s, 3 H, CH_3), 1.25 (s, 1 H, CH), 6.33–7.03 and 7.28–7.52 (m, 20 H, C_6H_5); ^{13}C NMR (C_6D_6) δ 12.28 (dq, $^1J(CH)$ = 135.7, $^3J(CH)$ = 3.9 Hz, CH_3), 16.11 (dq, $^1J(CH)$ = 152.4 Hz, CH) [C_6H_5 resonances at 127.09, 128.26, 129.04, 130.73, 131.18, and 132.61 ppm (^1H decoupled) were not assigned: δ 136.38 (s, C_1 at As^V), 149.18 (s, C_1 at As^{III}) (no significant splitting in the ^1H coupling experiment)]; IR (Nujol) $\nu(As{=}C)$ 810–870 cm^{-1} (br). Anal. Calcd for $C_{26}H_{24}As_2$ (486.31): C, 64.21; H, 4.97; As, 30.8. Found: C, 62.34; H, 4.92; As, 30.0.

Methylenebis(methyldiphenylarsonium) Bis(fluorosulfate) (4b). A 12.04-g sample of compound 1 (25.5 mmol) was dissolved in 50 mL of dichloromethane. Methyl fluorosulfate (10 mL, 124.5 mmol, large excess) was added and the mixture heated under reflux to 40 °C for 8 h and then stirred for another 16 h at 25 °C. A precipitate was formed, which was filtered and washed twice with 10 mL of chloroform followed by 10 mL of pentane. The white solid was dried in vacuo at 100 °C for 8 h to yield 13.7 g (77%) of an air-stable solid, mp 233 °C dec, which is soluble in trifluoroacetic acid and its mixture with $CDCl_3$ but is sparingly soluble in water and alcohols: ^1H NMR (CF_3COOH) δ 2.25 (s, 6 H, CH_3), 4.38 (s, 2 H, CH_2), 7.30–7.70 (m, 20 H, C_6H_5); ^{13}C NMR ($CF_3COOH/CDCl_3$) δ 8.51 (s, CH_3), 16.96 (s, CH_2), 120.00 (s, C_1), 131.05 (s, $C_{2/6}$), 131.31 (s, $C_{3/5}$), 135.47 (s, C_4) (^1H decoupled). Anal. Calcd for $C_{27}H_{28}As_2F_2O_6S_2$ (700.48): C, 46.30; H, 4.03; As, 21.4. Found: C, 45.26; H, 3.98; As, 21.5.

Bis(methyldiphenylarsoranylidene)methane (5). A 40-mL sample of dry liquid ammonia was condensed onto 2.52 g (3.60 mmol) of **4b** at −60 °C. The heterogeneous mixture was stirred and 0.52 g of sodium amide (13.3 mmol, excess) added in small portions. A deep yellow color developed on warming to −40 °C with continuous agitation for 3 h. The ammonia was then evaporated at temperatures between −25 and −20 °C and replaced by 20 mL of dry, cooled (−20 °C) toluene. Undissolved material, mainly $NaSO_3F$, was filtered at −20 °C, and an upper layer of pentane was carefully generated on the surface of the filtrate at −20 °C. Cooling to −78 °C initiated the formation of yellow microcrystals, which were filtered at −20 °C and dried in vacuo for 2 days while being kept at this temperature: yield 0.73 g (40.6%); mp 76–77 °C dec. The compound is thermally unstable and slowly decomposes when warmed to room temperature. It is air- and moisture-sensitive and soluble in toluene and tetrahydrofuran. Solutions are particularly thermolabile and decompose at 20 °C within a few minutes: ^1H NMR (toluene-d_8, −20 °C) δ 1.07 (s, 6 H, CH_3), 6.48–6.73 and 7.20–7.47 (m, 20 H, C_6H_5); ^{13}C NMR (THF-d_8, −20 °C) δ 18.32 (s, CH_3), 129.30 (s, $C_{2/6}$), 130.40 (s, C_4), 131.77 (s, $C_{3/5}$), 143.01 (s, C_1, br, line width = 8.5 Hz) (^1H decoupled). Anal. Calcd for $C_{27}H_{26}As_2$ (500.34): C, 64.82; H, 5.24; As, 29.9. Found: C, 63.46; H, 5.27; As, 28.7.

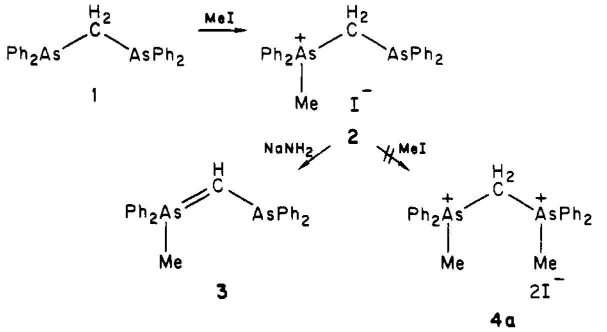
Methylenebis(methyldiphenylarsonium) Dichloride (4c). A small sample of 5 was dissolved in a toluene/pentane mixture (2:1, v/v) at −20 °C and treated with an excess of a solution of dry hydrogen chloride in diethyl ether (1.53 M). The yellow color of the solution disappeared, and a white precipitate was formed, which was filtered and dried in vacuo. Its ^1H and ^{13}C NMR spectra (in CF_3COOH) were identical with those of the fluorosulfate **4b** (above).

Results and Discussion

The synthesis procedures employed successfully for the preparation of carbodiphosphoranes are not applicable to the corresponding arsenic system. Double quaternization of dihalomethanes using tertiary arsines is an extremely slow process that is accompanied by a variety of side reactions,[17] and the reaction of free arsenic ylides, $R_3As{=}CH_2$, with haloarsines or haloarsoranes is unattractive owing to the inherent lability of the monoylides.[12-14]

Therefore, the preparation was based on the ditertiary arsine $Ph_2AsCH_2AsPh_2$, 1, which is easily available.[16] Contrary to a literature report,[18] it was found, however, that treatment of 1 with iodomethane yields only a monoquaternization product 2 even after prolonged reaction times under reflux conditions. The product is isolated in 80% yield and easily identified by elemental analysis and spectral data. As the melting point for 2 (173 °C) is close to the value reported for the alleged double arsonium iodide (172 °C), it appears likely that the earlier conclusions are erroneous.[18]

The monoarsonium salt 2 can be converted into the corresponding ylide 3 by deprotonation of the cation at the bridge position using sodium amide in tetrahydrofuran at ambient temperature. 3 is isolated as a yellow, air-sensitive solid, stable under nitrogen at room temperature. Its composition and structure are confirmed by analytical and NMR data. The ^1H-coupled ^{13}C spectrum consists of a quartet of doublets for the CH_3 carbons and a doublet of quartets for the bridging $=CH$ carbon, thus ruling out an isomeric form with a bridging $>CH_2$ group and a terminal ylidic function, $As{=}CH_2$. This result is in excellent agreement with the observation for the phosphorus analogues.[19] The coupling constant $^1J(CH)$ for the ylidic carbon atom in 3 (152.4 Hz) compares very well with J values for related phosphorus ylides and suggests a trigonal-planar array of ligands for this atom ($CHAs_2$). The parameter for the free monoylides $R_3As{=}CH_2$ are much smaller (130.9–136.7 Hz) and possibly indicative of a sig-



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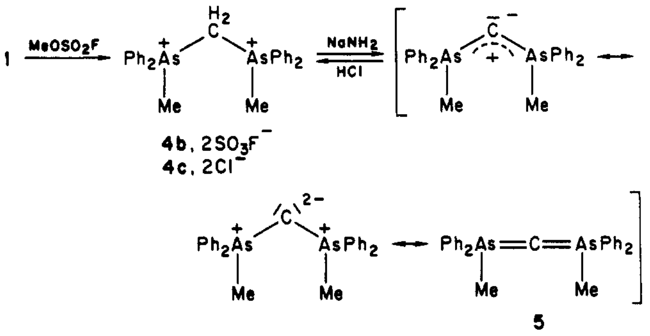
nificant deviation from planarity.[14,15,20,21]

Double quaternization of **1** can be achieved with the more powerful methylating agent CH_3OSO_2F in dichloromethane as a solvent. Yields of the bisquaternary salt **4b** are again close to 80%. The product is soluble in trifluoroacetic acid without decomposition, and ^1H and ^{13}C NMR spectra are thus available (Experimental Section).

After a series of unsuccessful attempts for the conversion of **4b** into a carbodiarsorane, **5**, favorable conditions for its synthesis were found with the system $NaNH_2$/liquid ammonia at −40 °C, followed by a workup at temperatures below −20 °C. A yellow microcrystalline material thus obtained was characterized as **5** by its elemental analyses, NMR spectra, and a reprotonation reaction with anhydrous HCl, yielding the precursor cation (**4c**, Cl for SO_3F in 4).

3 is thermally unstable both in the solid state and even more so in solution (tetrahydrofuran, toluene).

The ^1H and ^{13}C NMR spectra of cooled solutions give signals attributable to four equivalent phenyl and two equivalent methyl groups. The resonance of the central carbon atom could not be observed, even after prolonged signal accumulation under different pulse conditions, due to unfavorable relaxation conditions and/or line broadening caused by the presence of two As quadrupolar nuclei. Carbodiphosphoranes are also known to give no or very weak P=C=P signals.[7]



The chemical properties of **3** and **5** are presently under investigation with special attention directed toward carbon-transfer reactions to other substrates.

Acknowledgment. We are indebted to Deutsche Forschungsgemeinschaft, Bonn-Bad Godesberg, and Fonds der Chemischen Industrie, Frankfurt/Main, for continuous generous support.

Registry No. 1, 21892-63-7; 2, 92219-85-7; 3, 92219-86-8; 4b, 92219-88-0; 4c, 92240-98-7; 5, 92219-89-1; MeI, 74-88-4; $MeOSO_2F$, 421-20-5.

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Structures of Three Hydrogenation Catalysts $[(P\text{-}P)Rh(NBD)]ClO_4$ and Some Comparative Rate Studies Where (P-P) = $(\eta^5\text{-}R^1R^2PC_5H_4)(\eta^5\text{-}R^3R^4PC_5H_4)Fe$ ($R^1 = R^2 = R^3 = R^4 = Ph$; $R^1 = R^2 = Ph$, $R^3 = R^4 = CMe_3$; $R^1 = R^3 = Ph$, $R^2 = R^4 = CMe_3$)

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The compounds $[(P\text{-}P)RhNBD]ClO_4$ [(P-P) = $(\eta^5\text{-}R^1R^2PC_5H_4)Fe(\eta^5\text{-}R^3R^4PC_5H_4)$; $R^1 = R^2 = R^3 = R^4 = CMe_3$, **1**, or Ph, **4**; $R^1 = R^2 = CMe_3$, $R^3 = R^4 = Ph$, **2**; $R^1 = R^3 = CMe_3$, $R^2 = R^4 = Ph$, **3**] are catalyst precursors for the hydrogenation of a range of olefins (1 atm of H_2, 30 °C). The presence of bulky *t*-Bu groups enhances reaction rates except when bulky olefins are the substrates. The most promising combination of steric and electronic effects is seen with *rac*-**3**. **2** crystallizes in the monoclinic space group $P2_1/c$ with $a = 12.894$ (3) Å, $b = 13.913$ (2) Å, $c = 20.775$ (4) Å, $\beta = 113.51$ (2)°, $Z = 4$, and $V = 3417.55$ Å^3. The structure was refined to a conventional R value of 0.031. **3** crystallizes in the monoclinic space group Cc with $a = 18.335$ (2) Å, $b = 10.123$ (2) Å, $c = 19.683$ (4) Å, $\beta = 102.35$ (1)°, $Z = 4$, and $V = 3568.73$ Å^3. The structure was refined to a conventional R factor of 0.019. **4** crystallizes in the orthorhombic space group $Pna2_1$ with $a = 20.070$ (4) Å, $b = 10.665$ Å, $c = 16.747$ (5) Å, $Z = 4$, and $V = 3584.64$ Å^3. The structure was refined to a conventional R factor of 0.026. The bulky *t*-Bu groups cause a lengthening of P–Rh distances, wider P–Rh–P angles, and a rotation of the NBD out of the P–Rh–P plane. Generally the effects range from a maximum in **1** (previously determined) to a minimum in **4**.

Recently we reported[1] the structure of the hydrogenation catlayst precursor $\{[(\eta^5\text{-}((CH_3)_3C)_2PC_5H_4)_2Fe]Rh(NBD)\}ClO_4$, **1**, containing a bulky ferrocene-bridged bis(tertiary phosphine) ligand. The cation shows a very distorted