an oxo ion to give a five-coordinate intermediate, (b) rupture of one Mo–O bond to give a five-coordinate intermediate possessing one monodentate pentanedionato ligand, (c) complete dissociation of one pentanedionato ligand, and (d) twist mechanisms which exchange methyl groups without metal–ligand bond breaking.

Oxo dissociation is not an attractive mechanism because (a) the interchange occurs even in the nonpolar solvent benzene and (b) the Mo–O oxo bonds are probably stronger than those to the 2,4-pentanedionato ligands (see the molecular structure data). Complete dissociation of a pentanedionato ligand requires rupture of two Mo–O bonds. This mechanism, which seems less likely than the one-bond rupture, may be eliminated since the 100-MHz spectra indicate no exchange with excess 2,4-pentanedionato. The pentanedionato signals remain sharp although the resonances of the complex show broadening and coalescence. However, a definite choice between the twist mechanism and the single-bond rupture mechanism cannot be made on the basis of presently available data.

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The Synthesis of Chelating Ligands Incorporating Secondary and Primary Phosphines and Arsines

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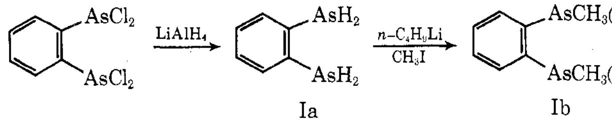
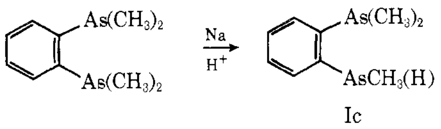
The coordination chemistry of the bis(secondary arsine) ligand (Ib) is potentially interesting because of the similarity of the derived dianion to the intriguing dithiolate systems, the latter ligands behaving as metal-stabilized radicals[1] upon coordination and forming, in some cases, complexes having unusual molecular geometries.[2] The catalytic activity of phosphido complexes[3] and the ability of primary phosphines to form thermally stable polymers[4] are additional topics to be included in a projected study. Accordingly, we have synthesized a number of primary and secondary phosphines and arsines by means of sequences 1–3.



(1)



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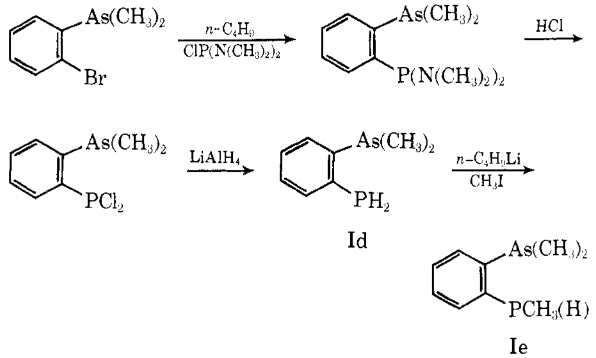

(3)

Results and Discussion

All the derivatives (Ia–e) are air-sensitive and must be prepared and handled in inert atmospheres. The synthetic procedures adopted are fairly standard and call for little comment. The cleavage of a methyl group from *o*-phenylenebis(dimethyl)arsine by sodium in liquid ammonia is somewhat unusual since earlier work[5] would lead one to expect cleavage of the arsenic–phenyl bond by alkali metals; approximately 15–25% of phenyldimethylarsine was detected in the final distillates of this reaction and it is likely that the preferential cleavage is a steric effect.

An attempt to cleave selectively the P–CH_3 bond in 1-(dimethylphosphino)-2-(dimethylarsino)benzene using similar conditions led to a mixture of Ie and the secondary arsine–tertiary phosphine derivative which we were unable to separate.

The use of the –$N(CH_3)_2$ blocking group in scheme 3 developed by Burg and Slota[6] and utilized by Wagner and coworkers[7] in the synthesis of *p*-phenylenediphosphines worked well in the present instance although the overall yield of Id (from *o*-bromophenyldimethylarsine) was low.

Pmr Spectra of the Ligands.[8]—Magnetic resonance data for the various ligands are collected in Table I. As an analytical tool pmr spectroscopy has proved invaluable for confirming the purity of the highly air-sensitive ligands; it has, in addition, demonstrated in certain of the molecules magnetic nonequivalence of chemically equivalent protons providing thereby a conclusive demonstration of the identity of the ligand. For example, examination of the 100-MHz spectrum of *o*-phenylene-*As*,*As*,*As'*-trimethyldiarsine reveals the presence of three nonequivalent methyl groups; the doublet centered at τ 8.8 results from the CH_3 group attached to the hydrogen-bearing arsenic atom, the protons of the two methyl groups on the arsenic atom ortho to the asymmetric center are nonequivalent as a result of this asymmetry. From models it can be seen that the methyl groups on the tertiary arsenic are not interchangeable by any symmetry operation and are thus diastereotopic.[9] It has been demon-

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[1] G. N. Schrauzer, *Accounts Chem. Res.*, **2**, 72 (1969), and references therein.

[2] A. E. Smith, G. N. Schrauzer, V. P. Mayweg, and W. Heinrich, *J. Amer. Chem. Soc.*, **87**, 5798 (1965).

[3] B. C. Benson, R. Jackson, K. K. Joshi, and D. T. Thompson, *Chem. Commun.*, 1506 (1968); D. T. Thompson, British Patent 1,182,932 (March 1970).

[4] A. B. Burg and R. I. Wagner, *J. Amer. Chem. Soc.*, **75**, 3872 (1953).

[5] K. Issleib and H. Völker, *Chem. Ber.*, **94**, 392 (1961).

[6] A. B. Burg and P. J. Slota, *J. Amer. Chem. Soc.*, **80**, 1107 (1958).

[7] E. M. Evleth, L. D. Freeman, and R. I. Wagner, *J. Org. Chem.*, **27**, 2192 (1962).

[8] Unless stated otherwise, pmr spectra were obtained at room temperature on neat liquids (TMS as internal standard) at 60 MHz. Chemical shifts are given as ppm on the τ scale.

[9] K. Mislow and M. Raban, *Top. Stereochem.*, **1**, 1 (1967).

TABLE I

NUCLEAR MAGNETIC RESONANCE DATA FOR MOLECULES Ia–e

Compound	Proton chem shift,[d] ppm				Coupling constants, Hz		
	As–*H*	P–*H*	As–*CH*$_3$	P–*CH*$_3$	J_{CH_3-H}	J_{P-H}	J_{CH_3-P}
o-$C_6H_4(AsH_2)_2$	6.3 (1)	. . .	. . .	. . .	. . .	. . .	. . .
o-$C_6H_4[As(CH_3)H]_2$	6.2 (4)[a]	. . .	8.8 (2)[b]	. . .	6.8	. . .	. . .
o-$C_6H_4[As(CH_3)_2]As(CH_3)H$	6.1 (4)	. . .	8.9 (2)[c]	. . .	. . .	. . .	. . .
			8.8 (2)		7.0		
o-$C_6H_4[As(CH_3)_2]PH_2$	. . .	6.0 (2)	9.0 (1)	. . .	. . .	200.0	. . .
o-$C_6H_4[As(CH_3)_2]P(CH_3)H$	. . .	5.7 (8)	8.9 (2)	8.8 (4)	7.0	200.0	3.7

[a] The 100-MHz spectrum resolves an eight-line pattern resulting from diastereotopic nuclei ($\Delta\nu$ = 1.6 Hz). [b] The 100-MHz spectrum resolves a four-line pattern resulting from diastereotopic nuclei ($\Delta\nu$ = 0.8 Hz). [c] The 100-MHz spectrum resolves a two-line pattern resulting from diastereotopic nuclei ($\Delta\nu$ = 1.1 Hz). [d] Numbers in parentheses show the multiplicities of the lines.

strated that protons (also fluorine) in such diastereotopic groups frequently show chemical shift nonequivalence and such nuclei are termed anisochronous.[9] Similarly the spectrum of *o*-phenylenebis(methylarsine) shows two overlapping quartets resulting from nonequivalent protons attached to arsenic in the meso form and *d* and *l* forms, respectively; it can be seen readily from models that the hydrogen atoms bonded to arsenic in the *d* and *l* isomers are in identical environments since the molecule possesses a C_2 axis. Similar conclusions can be drawn from an examination of the As–CH_3 region of the spectrum.

Interest in the synthesis and complexation of optically active phosphine and arsine ligands is currently very high,[10] and evidently the reported phenomena will have a useful role to play in the characterization of such ligands.

Experimental Section

All reactions were conducted in an atmosphere of dry nitrogen. Proton resonance spectra were obtained on Varian A-56/60 or HA 100 spectrometers.

The preparation of *o*-phenylenebis(dichloroarsine) followed the method given by Eberly and Smith[11] except that CH_2Cl_2 rather than CS_2 was used as the extracting solvent and that the product was distilled (150–160° (0.3 mm)) rather than crystallized. Other starting materials were synthesized by reported methods.

o-**Phenylenediarsine (Ia).**—A solution was prepared of 46.5 g of *o*-phenylenebis(dichloroarsine)[11] in 400 ml of anhydrous ether and 125 ml of hot benzene. The filtered, cooled solution was then added to a cold (0°) solution of 6.9 g of lithium aluminum hydride in 400 ml of anhydrous ether, care being taken to keep the temperature below 5°. After the slow addition, the mixture was warmed to reflux for 15 min and then cooled to −10° and hydrolyzed with 150 ml of 7 *M* HCl. Two layers resulted and the organic layer after separation was dried over Molecular Sieve 4A and the solvent removed. The crude product was fractionally distilled (2 mm) yielding 12 g of product, bp 76–79°. *Anal.* Calcd for $C_6H_8As_2$: C, 31.30; H, 3.48. Found: C, 30.78; H, 3.43.

o-**Phenylenebis(methylarsine) (Ib).**—A solution of 4.65 g of *o*-phenylenediarsine in 50 ml of deoxygenated tetrahydrofuran was cooled to 0° and to it was added 29.5 ml of 1.37 *M* *n*-butyllithium in hexane slowly, with stirring. The solution became orange and upon completion of the addition it was allowed to warm to room temperature. A solution of 3.84 g of bromomethane in 10 ml of ether was then added dropwise. The now colorless solution was then freed from solvent by distillation in a stream of dry nitrogen and the residue, consisting of a white solid (LiBr) in a viscous oil, was extracted with dry degassed benzene. The benzene was removed by distillation and the resulting oil was fractionally distilled (1.5 mm). A colorless oil, 76°, was obtained as the major product and its identity confirmed by pmr spectroscopy. The yield of pure *o*-phenylenebis(methylarsine) was 1.3 g. *Anal.* Calcd for C_8H_6As: C, 38.1; H, 2.4. Found: C, 37.6; H, 2.3.

o-**Phenylene-*As,As,As′*-trimethylarsine (Ic).**—A solution of 30.5 g of *o*-phenylenebis(dimethylarsine)[12] in 20 ml of ether was added to 300 ml of liquid ammonia. Small pieces of sodium (4.9 g) were then added slowly to the solution which became deep red. Ammonium chloride (12 g) was added and the now colorless solution was left to evaporate in a stream of dry nitrogen. The resulting residue was slowly hydrolyzed at −15° with 7 *M* HCl until the ether-insoluble material became gummy and adhered to the flask. More deoxygenated ether was then added and the ether layer was decanted and dried over Molecular Sieve 4A. After removal of the solvent the resultant viscous light yellow oil was fractionally distilled (0.5 mm) yielding 18.8 g of a colorless liquid, (bp 76–78°). *Anal.* Calcd for $C_9H_{14}As_2$: C, 39.7; H, 5.1. Found: C, 39.4; H, 4.9.

o-**(Dimethylarsino)phenylbis(dimethylamino)phosphine.**—A solution of 92 g (0.35 mol) of *o*-bromophenyl(dimethylarsine)[13] in 500 ml of ether was treated dropwise with 270 ml of *n*-C_4H_9Li solution (1.31 *M*). After the addition, the solution was refluxed for 10 min and stirred at room temperature for 1 hr. It was then transferred to a dropping funnel with a pressure equalizer and added to a solution of 54.3 g (51.2 ml) of $ClP(N(CH_3)_2)_2$[14] in 250 ml of ether cooled to −78°. The addition was over a 2-hr period and after completion the solution was allowed to warm slowly to room temperature. The solution containing precipitated LiCl was filtered and the ether removed. Distillation at 0.6 mm yielded the following fractions: 40–100°, 5 g; 127–140°, 48 g. The major fraction was used in the next step of the synthesis without further purification.

o-**(Dimethylarsino)phenyldichlorophosphine.**—A solution of *o*-(dimethylarsino)phenylbis(dimethylamino)phosphine (45 g) in ether (500 ml) was cooled to −78° and treated with a slight excess of gaseous HCl (0.75 mol) generated by reaction of excess concentrated H_2SO_4 and HCl. Removal of dimethylammonium chloride by filtration, followed by evaporation of the ether, yielded a pale yellow oil. Distillation at 0.2 mm gave 25 g of a colorless oil, bp 118–122°. *Anal.* Calcd for $C_8H_{10}AsCl_2P$: Cl, 25.1. Found: Cl, 24.4.

o-**(Dimethylarsino)phenylphosphine (Id).**—A solution of 22 g of the above dichloride (0.078 mol) in 50 ml of ether was added dropwise to $LiAlH_4$ (7.6 g, 0.2 mol) in 150 ml of ether kept at −20°. After the addition the solution was stirred at room temperature for 1 hr and then cooled to −78° and hydrolyzed with 1:1 HCl. Separation and drying of the organic layer followed by fractional distillation (0.2 mm) gave 10 g of a colorless liquid, bp 82–84°. *Anal.* Calcd for $C_8H_{12}AsP$: C, 44.9; H, 5.6. Found: C, 44.0; H, 4.9.

o-**(Dimethylarsino)phenylmethylphosphine (Ie).**—A solution of 5.7 g of *o*-(dimethylarsino)phenylphosphine (0.27 mol) in 50 ml of ether was treated with a solution of *n*-C_4H_9Li (1.31 *M*; 20.6 ml) in hexane. After the addition the solution was stirred for 1 hr and then treated with CH_3I (3.8 g) in 20 ml of anhydrous ether. After being stirred for 1 hr further deoxygenated water was added in sufficient quantity just to dissolve the LiI and the ether was decanted from the resulting semisolid mass. Drying and fractional distillation (97–98° (0.5 mm)) yielded 5.1 g of the product. *Anal.* Calcd for $C_9H_{14}AsP$: C, 48.0; H, 4.9. Found: C, 47.8; H, 4.7.

1-(Dimethylarsino)-2-(dimethylphosphino)benzene.—A stirred solution of *o*-bromophenyl(dimethylarsine)[13] (24.2 g, 0.093 mol) in 50 ml of anhydrous ether was treated dropwise with a solution of *n*-C_4H_9Li (1.30 *M*; 71.2 ml) in hexane. During the addition

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[11] K. C. Eberly and G. E. P. Smith, *J. Org. Chem.*, **22**, 1710 (1957).

[12] R. D. Feltham, A. Kasenally, and R. S. Nyholm, *J. Organometal. Chem.*, **7**, 285 (1967).

[13] E. R. H. Jones and F. G. Mann, *J. Chem. Soc.*, 4472 (1955).

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the mixture refluxed gently and it was subsequently allowed to attain room temperature over a 1-hr period. Dimethylchlorophosphine[15] (7.5 g, 0.09 mol) in 50 ml of anhydrous ether was then slowly added to the solution, the temperature being maintained at 0–5°. After the addition of water the organic layer was separated, dried, and fractionally distilled (0.2 mm). A forerun of 3.4 g of material boiling at 45–50° (phenyldimethylarsine) was rejected; the product (15.0 g; bp 80–81°) was analytically and spectroscopically (pmr) pure. *Anal.* Calcd for $C_{10}H_{16}AsP$: C, 49.6; H, 6.6. Found: C, 49.2; H, 6.5. Pmr spectrum: singlet τ 8.97, doublet (center τ 8.95; $J_{CH_3-P} = 4$ Hz).

Reaction of the product with sodium in liquid ammonia following the method given for Ic above gave a product which after fractional distillation was shown (nmr) to contain both P–H and As–H bonds. Other separation techniques (*e.g.*, spinning-band column) were not attempted.

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[15] We thank Dr. G. W. Parshall for kindly providing us with the preparative details for this compound.

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The Reaction of Tertiary Phosphines with Dichloramines

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The reactions of trisubstituted phosphines with chloramine,[1,2] methylchloramine,[2] and dimethylchloramine[3–5] had been previously reported from this laboratory, but the reactions of *N,N*-dichloroalkylamines with trisubstituted phosphines have not yet been reported. We decided to look into these reactions, in order not only to synthesize new compounds but also to compare the action of dichloramines on tertiary phosphines with the corresponding action of compounds containing P–Cl bonds.[6,7]

It was found, in the cases studied here, that the principal products of reactions of dichloramines with tertiary phosphines are the respective *N*-chloro-*N*-alkylaminotriphenylphosphonium chlorides, and no compounds containing nitrogen–nitrogen bonds were formed.

Experimental Section

Materials.—Triphenylphosphine was obtained from Aldrich Chemical Co. and checked for purity by its melting point and comparison of its infrared spectrum with that of a known sample.[8] Tributylphosphine was obtained from Peninsular ChemResearch and distilled before use, the fraction boiling at 125–130° (21 mm) being retained; lit.[9] bp 149.5° (50 mm). Coleman's method[10] was used to prepare dry diethyl ether solutions of *N,N*-dichloromethylamine and *N,N*-dichloroethylamine; these solutions were stored in a refrigerator over Linde Molecular Sieve 4A prior to use. The molarities of the solutions were determined by adding aliquot portions of the solutions to acidified potassium iodide solution and titration of the iodine released with standard sodium thiosulfate solution. Solutions of both dichloramines showed the strong absorption at 3100 Å (ϵ 370–375) known[11] to be characteristic of dichloramines.

All solvents were dried over calcium hydride or distilled and stored over Linde Molecular Sieve 4A until used.

Apparatus.—Manipulations of reactants and products were performed in an inert-atmosphere box (Vacuum Atmospheres Corp. Dri-Train HE-93B), and reactions were run under a dry nitrogen flush; such precautions were necessitated by the hygroscopic nature of the products of reaction. Ultraviolet spectra were recorded on a Cary Model 14 spectrophotometer; nmr spectra were taken with a Varian A-60A spectrometer; infrared spectra were measured on Beckman IR-10 spectrometer.

Analyses.—With the exception of chloride analyses, analytical data were obtained by the Galbraith Microanalytical Laboratory. Chloride analyses were performed in this laboratory using the Volhard method, after the compounds had been hydrolyzed in sodium hydroxide solution and any resulting oxidizing species had been reduced with SO_2.

Formation of *N*-Chloro-*N*-methylaminotriphenylphosphonium Chloride.—In a 250-ml round-bottom flask was placed 8.87 g (33.8 mmol) of triphenylphosphine, along with 50 ml of dry diethyl ether and a magnetic stirbar. The flask was capped witn a pressure-equalizing funnel, and a flow of dry nitrogen was maintained while 154 ml of 0.22 *M* diethyl ether solution of *N,N*-dichloromethylamine (33.9 mmol) was added over a 0.5-hr period. Stirring was maintained throughout the addition, as was external cooling by means of an ice bath. The reaction mixture containing a white solid, which immediately began to form in the reactant vessel, was stirred an additional 15 min; the solid was then removed by filtration in the drybox and was pumped dry (yield 8.03 g, 74.9% of the theoretical weight of $[(C_6H_5)_3PNClCH_3]Cl$ based on the triphenylphosphine used). The reaction solution was titrated for residual oxidizing capacity and a titer corresponding to 4.17 mmol of unreacted *N,N*-dichloromethylamine was found. The solid was dissolved in the minimum amount of chloroform and reprecipitated by the addition of dry diethyl ether;[12] mp 145–149° dec. *Anal.* Calcd for $[(C_6H_5)_3PNClCH_3]Cl$: N, 3.87; Cl, 19.58; P, 8.55; C, 63.00; H, 5.01. Found: N, 3.62; Cl, 19.4; P, 9.11; C, 63.22, H, 5.74. The infrared and nmr spectra of the solid are given in Tables I and II. In spite of the somewhat less than satisfactory hydrogen analysis, the evidence overwhelmingly supports the formula assigned. The reaction was repeated three times with substantially the same results.

Formation of *N*-Chloro-*N*-ethylaminophosphonium Chloride.—This synthesis was carried out in a manner analogous to the previous example using 7.55 g of triphenylphosphine (28.8 mmol) in 50 ml of diethyl ether and 102 ml of a 0.283 *M* diethyl ether solution of *N,N*-dichloroethylamine (28.8 mmol). The solid product, which weighed 9.85 g (90.9% of the theoretical weight of $[(C_6H_5)_3PNClC_2H_5]Cl$ based on triphenylphosphine) was filtered off and recrystallized as above; mp 184–185° dec. *Anal.* Calcd for $[(C_6H_5)_3PNClC_2H_5]Cl$: N, 3.72; Cl, 18.85; P, 8.23. Found: N, 4.01; Cl, 19.1; P, 9.11. There was 2.0 mmol of unreacted *N,N*-dichloroethylamine found in the reaction liquor. The infrared and nmr spectra of the solid are given in Tables I and II.

Reaction of Tributylphosphine with *N,N*-Dichloromethylamine.—A solution of 7.63 g (37.8 mmol) of tributylphosphine in 50 ml of dry ether and 49 ml of 0.76 *M* *N,N*-dichloromethylamine (37.2 mmol) were mixed according to the procedure described above. The solution clouded immediately and a colorless oil separated. We were unable to bring about the crystallization

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[11] V. L. Heasley, P. Kovacic, and R. M. Lange, *J. Org. Chem.*, **31**, 3050 (1966).

[12] It should be noted that if recrystallization is attempted by this method, the solid exhibits an extreme tendency to form oils. Repeated washings with ether will usually result in crystallization, however.