Reaction of Lithium Diphenylphosphide, Diphenylarsenide, and Diphenylstibide with 1,2-Dichloroethylenes. The Preparation of Some New Bidentate Ligands and their Monosubstituted Precursors

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Contrary to previous work, lithium diphenylarsenide reacts with *trans*-1,2-dichloroethylene to produce *trans*-1,2-bis(diphenylarsino)ethylene. Lithium diphenylarsenide also reacts with excess of *cis*- or *trans*-1,2-dichloroethylene at 0 °C to yield the corresponding (2-chlorovinyl)diphenylarsine stereospecifically, but only the 1,2-bis(diphenylphosphino)ethylenes have been obtained under analogous conditions using lithium diphenylphosphide. The *cis*- and *trans*-(2-chlorovinyl)diphenylarsine also react stereospecifically with $\mathrm{Li[PPh_2]}$ to yield *cis*- and *trans*-1-diphenylarsino-2-diphenylphosphinoethylene in high yield. *cis*-(2-Chlorovinyl)diphenylarsine and sodium dimethylarsenide yield only *cis*-1-dimethylarsino-2-diphenylarsinoethylene, in contrast to the reaction of the latter with *cis*-1,2-dichloroethylene when both *cis*- and *trans*-1,2-bis(dimethylarsino)ethylene result. The preparation of 1-diphenylarsino-2-diphenylphosphinoethane, and the reactions of sodium diphenylstibide with *cis*- and *trans*-1,2-dichloroethylene, are also described.

VINYLIC substitution reactions have been intensively investigated.[1] The reaction may proceed with retention, racemisation, or inversion of configuration with respect to the starting material. The reactions of *cis*- and *trans*-1,2-dichloroethylene with alkali-metal derivatives of secondary phosphines and arsines are of interest [2,3] not only from the stereochemical and mechanistic viewpoint but also because the products are potentially very useful ligands towards transition-metal ions. Aguair and Daigle [4] showed that *cis*- and *trans*-ClCH:CHCl react with lithium diphenylphosphide to form the corresponding 1,2-bis(diphenylphosphino)ethylene with complete retention of configuration and in high yield. Similarly, lithium diphenylarsenide and *cis*-ClCH:CHCl produce *cis*-1,2-bis(diphenylarsino)ethylene, but these workers claim [5] that *trans*-ClCH:CHCl forms *trans*-$\mathrm{Ph_2AsCH{:}CHAsPh_2}$ in low yield accompanied by much diphenylarsinic acid. Sodium dimethylarsenide, however, reacts [6-8] with *cis*-ClCH:CHCl to produce $\mathrm{Me_2AsCH{:}CHAsMe_2}$ in only 30% yield with a *cis* : *trans* isomer distribution of *ca.* 1 : 10.

Bidentate phosphines [9] and arsines [10] have provided co-ordination chemists with useful ligands, and our own interest in this preparative organogroup 5B chemistry is in the synthesis of new ligands. Here we report an extension of recent organogroup 5B syntheses including a fundamental correction of some previous work, and our own attempts to prepare the monosubstituted halogenoethylenes, *cis*- and *trans*-$\mathrm{ClCH{:}CHEPh_2}$ (E = P, As, or Sb) and asymmetric disubstituted ethylenes $\mathrm{Ph_2ECH{:}CHE'Ph_2}$ ($E \neq E' =$ P or As).

EXPERIMENTAL

All the reactions and manipulations were under an atmosphere of dry nitrogen. Tetrahydrofuran (thf) was dried by distillation from sodium diphenylketyl immediately before use. Infrared spectra were obtained on a Perkin-Elmer 621 spectrometer in Nujol and hexachlorobutadiene (hcb) mulls, ^{1}H n.m.r. spectra in $\mathrm{CDCl_3}$ solution on a Varian A60 spectrometer with $\mathrm{SiMe_4}$ as internal standard.

Lithium Diphenylphosphide.—A solution of triphenylphosphine (52.4 g, 0.2 mol) in dry thf was treated with lithium metal (3.5 g, 0.5 g-atom) which had been cut into small pieces in a stream of nitrogen; the mixture was heated under reflux for 4 h and then allowed to cool. The resulting dark red solution was filtered through a glass-wool plug to remove excess of lithium and then treated dropwise with t-butyl chloride (11.0 g, 0.12 mol) (**CAUTION**: exothermic reaction). Lithium diphenylarsenide was prepared similarly from triphenylarsine (61.2 g, 0.2 mol), lithium (3.5 g, 0.5 g-atom), and $\mathrm{Bu^tCl}$ (11.0 g, 0.12 mol).

trans-*1,2-Bis(diphenylarsino)ethylene.*—Lithium diphenylarsenide solution (0.20 mol) was added dropwise to a vigorously stirred solution of *trans*-ClCH:CHCl (9.7 g, 0.10 mol) in thf (80 cm^3). When the reaction was complete, as evidenced by the disappearance of the bright red colour of $\mathrm{Li[AsPh_2]}$ and the formation of a pale cream solution, the thf was removed under reduced pressure and the residue cautiously hydrolysed with saturated aqueous ammonium chloride solution (100 cm^3); chloroform (100 cm^3) was added, thoroughly shaken, and the organic layer separated and dried over anhydrous sodium sulphate. Removal of the chloroform and recrystallisation of the residue from $\mathrm{EtOH-CH_2Cl_2}$ yielded white crystals (58% yield) (Found: C, 64.3; H, 4.8; Cl, 0.0. $\mathrm{C_{26}H_{22}As_2}$ requires C, 64.5; H, 4.5; Cl, 0.0%), m.p. 102 °C.

cis-*(2-Chlorovinyl)diphenylarsine.*—Lithium diphenylarsenide solution (0.2 mol) was added dropwise very slowly and with vigorous stirring to *cis*-ClCH:CHCl (36.6 g, 0.4 mol)

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in thf (300 cm^3), the temperature being maintained at *ca.* 0 °C by external ice–salt cooling. When the addition was complete the milky solution was rapidly hydrolysed with aqueous $[NH_4]Cl$ solution (100 cm^3), and the thf layer was separated and dried over anhydrous $Na_2[SO_4]$. The thf was subsequently removed by rotatory evaporation and the resulting oil shaken thoroughly with n-hexane (50 cm^3) at which point it solidified to a white powder. Recrystallisation from $EtOH–CH_2Cl_2$ yielded white crystals (72% yield) (Found: C, 57.7; H, 4.1; Cl, 12.2. $C_{14}H_{12}AsCl$ requires C, 57.8; H, 4.1; Cl, 12.2%), m.p. 98 °C.

trans-(2-Chlorovinyl)diphenylarsine was prepared similarly in 58% yield (Found: C, 58.6; H, 4.4; Cl, 12.5%), m.p. 97 °C.

cis-1-*Diphenylarsino*-2-*diphenylphosphinoethylene*.— *cis*-(2-Chlorovinyl)diphenylarsine (29.0 g, 0.1 mol) in thf (50 cm^3) was treated dropwise with $Li[PPh_2]$ solution (0.1 mol) with vigorous stirring. The product was worked up in the usual way, yield 68% (Found: C, 70.6; H, 4.7; Cl, 0.1. $C_{26}H_{22}AsP$ requires C, 70.9; H, 5.0; Cl, 0.0%), m.p. 105 °C.

trans-1-Diphenylarsino-2-diphenylphosphinoethylene was prepared in an analogous manner to the *cis* isomer from *trans*-(2-chlorovinyl)diphenylarsine, yield 60% (Found: C, 70.6; H, 4.9; Cl, 0.0%), m.p. 97 °C.

cis-1-*Dimethylarsino*-2-*diphenylarsinoethylene*.—A solution of $Na[AsMe_2]$ [11] was prepared from sodium (6.9 g, 0.3 g-atom), iododimethylarsine (23.2 g, 0.1 mol), and thf (100 cm^3), filtered, and added dropwise to a vigorously stirred solution of *cis*-(2-chlorovinyl)diphenylarsine (17.5 g, 0.06 mol) in thf (100 cm^3) at 0 °C over 1.5 h. The brown solution formed was stirred for another hour and then hydrolysed with aqueous $[NH_4]Cl$ solution (100 cm^3). The thf layer was separated and dried over anhydrous $Na_2[SO_4]$, after which the thf was removed under reduced pressure and the product heated to 100 °C (1.0 mmHg) to remove any volatile impurities.* The product was a slightly brownish air-sensitive oil, yield 63% (Found: C, 53.6; H, 5.2; Cl, 0.0. $C_{16}H_{18}As_2$ requires C, 53.4; H, 5.0; Cl, 0.0%).

Attempted Preparation of cis-1,2-*Bis*(*diphenylstibino*)*ethylene*.—Sodium diphenylstibide in liquid ammonia [12] was prepared from chlorodiphenylstibine (18.3 g, 0.06 mol) and sodium (2.7 g, 0.12 g-atom) in liquid ammonia at −33 °C. The solution was transferred to a solid carbon dioxide-cooled dropping funnel and added dropwise with stirring to *cis*-$ClCH{:}CHCl$ (3.0 g, 0.03 mol) in thf (50 cm^3) at −33 °C. The solution was stirred until the colour faded to fawn (*ca.* 4 h), when the ammonia was allowed to evaporate and the residue was treated with water (200 cm^3) and dichloromethane (100 cm^3). The organic layer was separated, dried, and rotatory evaporated to leave a dark oil which, on recrystallisation from $EtOH–CH_2Cl_2$, deposited a white solid (Found: C, 50.4; H, 3.7. $C_{24}H_{20}OSb_2$ requires C, 50.7; H, 3.5%), m.p. 79 °C.

(2-*Chloroethyl*)*diphenylarsine*.—Lithium diphenylarsenide (0.5 mol) in thf (as above) was added dropwise over 3 h to a vigorously stirred solution of 1,2-dichloroethane (4.0 mol) in thf (200 cm^3) at 0 °C. The resulting cloudy white solution was evaporated at 25 °C under reduced pressure and the residue treated with saturated aqueous $[NH_4]Cl$ solution (100 cm^3) and chloroform (100 cm^3). The chloroform layer was separated, the water layer was extracted with chloroform (100 cm^3), and the combined organic extracts dried over anhydrous $Na_2[SO_4]$. The chloroform was distilled off and the residue distilled. The product was a colourless oil, b.p. 144—148 °C (2 mmHg), yield 72% (Found: C, 57.6; H, 4.9; Cl, 12.4. $C_{14}H_{14}AsCl$ requires C, 57.6; H, 4.9; Cl, 12.2%). Air oxidation of this compound is quite rapid and yields the white arsine oxide.

(2-Chloroethyl)diphenylphosphine was prepared similarly from $Li[PPh_2]$ and a 20-fold excess of 1,2-dichloroethane at 0 °C. After hydrolysis and removal of the chloroform *in vacuo* a clear oil was obtained which slowly solidified on standing, yield 79% (Found: C, 67.0; H, 5.6; Cl, 14.5. $C_{14}H_{14}ClP$ requires C, 67.4; H, 5.6; Cl, 14.4%), m.p. 40 °C.

1-Diphenylarsino-2-diphenylphosphinoethane was prepared in an analogous manner to the ethylene compound from (2-chloroethyl)diphenylarsine and $Li[PPh_2]$. The product was recrystallised from $EtOH–CH_2Cl_2$ to yield white crystals (62%) (Found: C, 70.8; H, 5.6; Cl, 0.2. $C_{26}H_{24}AsP$ requires C, 70.5; H, 5.4; Cl, 0.0%), m.p. 120 °C.

RESULTS AND DISCUSSION

trans-1,2-*Bis*(*diphenylarsino*)*ethylene*.—The reaction of *trans*-1,2-dichloroethylene with lithium diphenylarsenide gave *trans*-$Ph_2AsCH{:}CHAsPh_2$ in *ca.* 55% yield. This result contrasts with that reported by Aguiar *et al.*[5] who obtained only *ca.* 10% of the diarsine and considerable quantities of diphenylarsinic acid, $Ph_2AsO(OH)$. We repeated this reaction several times and obtained a high yield of the diarsine, but no arsinic acid, on any occasion. Thus, the *trans*-$ClCH{:}CHCl–Li[AsPh_2]$ reaction is analogous to the corresponding reaction of lithium diphenylphosphide [4] yielding the *trans*-disubstituted product in high yield and with retention of configuration.

cis- *and* trans-1,2-*Bis*(*diphenylstibino*)*ethylene*.—The reaction of *cis*- or *trans*-1,2-dichloroethylene with diphenylstibide was investigated to see if the stereospecificity of the reactions was maintained with an antimony nucleophile. The $[SbPh_2]^-$ ion is thermally unstable and, although it can be prepared in thf at low temperatures, the synthesis using liquid ammonia as solvent is faster and more convenient. At the low temperatures used (< -33 °C) the reaction of sodium diphenylstibide with *cis*- or *trans*-dichloroethylene was slow, taking several hours to approach completion. However, after hydrolysis and recrystallisations from benzene and dichloromethane, white powders were obtained. Analytical data and ^1H n.m.r. and mass spectra show the products to be bis(diphenylstibino) ether, $Ph_2SbOSbPh_2$.[13] Varying the mode of addition (*i.e.* adding the $Na[SbPh_2]$ to the $ClCH{:}CHCl$ and *vice versa*) or the solvent (neat NH_3 or NH_3–thf) did not alter the nature of the product, and no evidence for the production of either *cis*- or *trans*-1,2-bis(diphenylstibino)ethylene was obtained. It has been subsequently shown [13] that $Ph_2SbOSbPh_2$ can result from air oxidation of tetra-

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* 1 mmHg ≈ 13.6 × 9.8 Pa.

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phenyldistibane under certain conditions, and hence we now conclude that the reaction of Na[SbPh$_2$] with *cis*- or *trans*-ClCH:CHCl proceeds with elimination to yield Ph$_2$SbSbPh$_2$ and acetylene, the former subsequently oxidising during work-up due to its extreme air sensitivity.[14] Elimination also occurs in preference to substitution in the reaction of Na[SbPh$_2$] with 1,2-dichloroethane [15] or *o*-dichlorobenzene,[13] although other dihalogenoalkanes react normally to yield Ph$_2$Sb(CH$_2$)$_n$SbPh$_2$.[12,16]

Monosubstitution.—The slow addition of lithium diphenyl-phosphide and -arsenide to an excess of *cis*- or *trans*-1,2-dichloroethylene diluted with thf at 0 °C was investigated to see if monosubstituted chloroethylenes can be obtained. Lithium diphenylphosphide and *cis*-ClCH:CHCl, even in a 1 : 30 ratio, yielded only the diphosphine *cis*-Ph$_2$PCH:CHPPh$_2$, as shown by elemental analysis, ^{1}H n.m.r., i.r. (Table), and mass-spectral [17] evidence. The reaction with *trans*-ClCH:CHCl also yielded only disubstituted products. The monosubstitution of PPh$_2$ into dichloroethylene appears to activate the second chlorine to substitution to such an extent that even in dilute solution in the presence of a large excess of ClCH:CHCl the other phosphide ions preferentially attack the Ph$_2$PCH:CHCl intermediates. This may be due to the electronegative phosphorus making the carbon attached to the chlorine more positive and hence more susceptible to nucleophilic attack. By contrast, under similar conditions Li[AsPh$_2$] and excess of *cis*- or *trans*-ClCH:CHCl yielded the corresponding ClCH:CHAsPh$_2$ stereospecifically in high yield; with due care the amount of diarsine produced can be restricted to <5%. Clearly the AsPh$_2$ group initially attached does not activate substitution at the other C–Cl bond to the same extent as does the PPh$_2$ group, in keeping with the reduced electronegativity of the former. Not unexpectedly, attempts to produce monosubstitution with Na[SbPh$_2$] again resulted in elimination.

Physical and spectroscopic data for the compounds

Compound	M.p. (θ_c/°C)	^{1}H N.m.r. [a] Vinyl	^{1}H N.m.r. [a] Phenyl	I.r. data (cm^{-1}) ν(C=C)	I.r. data (cm^{-1}) C–H out-of-plane def.
cis-Ph$_2$PCH:CHPPh$_2$	108	2.75 (s)	2.73 (m)	1 580	
trans-Ph$_2$PCH:CHPPh$_2$	107	3.20 (s)	2.71 (m)		970
cis-Ph$_2$PCH:CHAsPh$_2$	110	2.45, 2.55 (d)	2.70 (m)	1 575	
trans-Ph$_2$PCH:CHAsPh$_2$	97	3.07, 3.10 (d)	2.72 (m)		998
cis-Ph$_2$AsCH:CHAsPh$_2$	110	2.94 (s)	2.68 (m)	1 570	
trans-Ph$_2$AsCH:CHAsPh$_2$	102	3.05 (s)	2.60 (m)		985
cis-Ph$_2$AsCH:CHCl	98	3.4, 3.6 (s)	2.78 (m)	1 540	
trans-Ph$_2$AsCH:CHCl	97	3.2, 3.4 (s)	2.60 (m)		990
cis-Ph$_2$AsCH:CHAsMe$_2$ [b]		3.40, 3.48 (s)	2.80 (m)	1 580	

[a] τ Referenced to internal SiMe$_4$; s = singlet, d = doublet, and m = multiplet. [b] AsMe$_2$ Resonance at τ 9.0.

As previously reported by Tzschach and Lange,[18] (2-chloroethyl)diphenylarsine, As(CH$_2$CH$_2$Cl)Ph$_2$, is readily obtained from Li[AsPh$_2$] and excess of ClCH$_2$CH$_2$Cl. In contrast to *cis*-ClCH:CHCl, 1,2-dichloroethane and Li[PPh$_2$] will form (2-chloroethyl)diphenylphosphine when a large excess of the dichloroethane is employed in the reaction. The compound has been reported previously but, apparently, has not been completely characterised.[19,20] When pure, P(CH$_2$CH$_2$Cl)Ph$_2$ is a white solid which appears to be stable under nitrogen for several weeks at room temperature but attempts to distil it result in self-quaternisation.[19] The mass spectrum confirmed its identity, exhibiting a strong parent ion at *m/e* 248 [77% (^{35}Cl)] and a base peak of [P(C$_{12}$H$_8$)]$^+$ (*m/e* 183).

Arsine–Phosphine Compounds.—The successful isolation of *cis*- and *trans*-(2-chlorovinyl)diphenylarsine means that arsines–phosphine, *cis*- and *trans*-1-diphenylarsino-2-diphenylphosphinoethylene, are readily obtainable by reaction with Li[PPh$_2$], the reaction again being stereospecific. The base-catalysed addition of diphenylarsine, AsPh$_2$H, to ethynyldiphenylphosphine, P(C:CH)Ph$_2$, has recently been shown [21] to yield *trans*-Ph$_2$PCH:CHAsPh$_2$, but the route reported here is the only known method of preparing the *cis* isomer; because of the difficulty of preparing P(C:CH)Ph$_2$, our route also seems to be the most attractive method of obtaining the *trans* isomer. The reaction of (2-chloroethyl)diphenylarsine with Li[PPh$_2$] similarly produces the saturated analogue 1-diphenylarsino-2-diphenylphosphinoethane, Ph$_2$PCH$_2$CH$_2$AsPh$_2$, also obtainable from AsPh$_2$H and diphenylvinylphosphine.[21]

In view of the racemisation observed in the reaction of Na[AsMe$_2$] with *cis*-1,2-dichloroethylene,* we decided to react Na[AsMe$_2$] with *cis*-(2-chlorovinyl)diphenylarsine. Surprisingly, this afforded *cis*-1-dimethylarsino-2-diphenylarsinoethylene in high yield and stereospecifically. The fact that only one product is produced was shown by the ^{1}H n.m.r. spectrum which exhibited only vinyl resonances consistent with the *cis* isomer. G.l.c. examination

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* The products of the reaction of Na[AsMe$_2$] and *trans*-ClCH:CHCl do not seem to have been satisfactorily characterised.[6]

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on a 2-m 3% SE 30 column at 200 °C showed only one component to be present. Conclusive identification of the single product as the *cis* isomer is provided by the observation of ν(C=C) at 1 580 cm^{-1}, and the absence of any band at 920—980 cm^{-1},[6] in the i.r. spectrum of the oil, and by the preparation of a series of nickel(II) complexes [22] which clearly contain a bidentate chelate (*trans*-vinylic ligands cannot chelate).

Properties.—The characteristic i.r. and ^{1}H n.m.r. spectral data are shown in the Table. The vinylic protons in a *cis* compound generally absorb at lower field than those of the *trans* analogue, and in the cases of the phosphorus ligands the vinyl proton resonance is split into a doublet by ^{31}P ($I = \frac{1}{2}$). *cis* and *trans* Isomers were also distinguishable by their i.r. spectra,[23] the former showing a moderately weak ν(C=C) band at *ca.* 1 580 cm^{-1} and the latter a strong band at *ca.* 970—990 cm^{-1}. As previously reported,[17] mass spectra cannot distinguish between the isomers; that both isomers yielded identical mass spectra suggests that free rotation about the double bond occurs in the parent ion $[H_2C_2E_2Ph_2]^+$ (E = P or As). Mass spectra were, however, of considerable use in identification of the products. Further characterisation of many of the compounds reported here has been achieved by preparation of transition-metal complex derivatives (refs. 22, 24, and 25 and refs. therein).

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