Synthesis and Properties of Group 5B Ligand Analogues of *o*-Phenylenebis(dimethylarsine), *o*-$C_6H_4(EMe_2)(E'Me_2)$ where E, E' = P, N, As, or Sb

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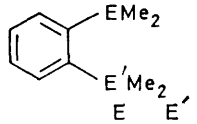
Lithium dimethylphosphide prepared from lithium and PMe_2Ph in tetrahydrofuran reacts with *o*-dichlorobenzene to produce *o*-phenylenebis(dimethylphosphine). Similar reactions using the appropriate *o*-bromophenyl derivatives *o*-$C_6H_4Br(Y)$ (Y = NMe_2, $AsMe_2$, or $SbMe_2$) yield *o*-$C_6H_4(PMe_2)Y$. *o*-Phenylenebis(dimethylstibine) is best prepared from (*o*-bromophenyl)dimethylstibine and $Na[SbMe_2]$. Preparations for the other members of the series, *o*-$C_6H_4(AsMe_2)(SbMe_2)$, *o*-$C_6H_4(AsMe_2)(NMe_2)$, and *o*-$C_6H_4(SbMe_2)(NMe_2)$, and for (*o*-methoxyphenyl)- and (*o*-methylthiophenyl)-dimethylphosphine *o*-$C_6H_4(PMe_2)Z$ (Z = OMe or SMe) are reported. The ^1H and ^{31}P n.m.r. and mass spectra of the ligands, intermediates, and quaternary derivatives are reported and discussed.

o-PHENYLENEBIS(DIMETHYLARSINE), *o*-$C_6H_4(AsMe_2)_2$ (1), was first prepared by Chatt and Mann [1] in 1939, and largely through the work of Nyholm and co-workers its co-ordination chemistry is known in considerable detail. These studies revealed that this diarsine was unique among known Group 5B ligands in its ability to promote unusual co-ordination numbers and oxidation states.[2] In view of this, the analogues (Scheme 1) are potentially very useful ligands, but in fact very little of their co-ordination chemistry has been examined. Although several of these ligands have been prepared [3-9] the syntheses are difficult and often tedious. Here we report syntheses for these ligands, using whenever possible readily available starting materials. During the course of our work the diphosphine (2) was shown [3] to be at least as versatile as the diarsine, and a rich co-ordination chemistry can be anticipated for all these ligands.



	E	E′		E	E′
(1)	As	As	(6)	Sb	N
(2)	P	P	(7)	P	As
(3)	Sb	Sb	(8)	P	Sb
(4)	P	N	(9)	As	Sb
(5)	As	N			

SCHEME 1

EXPERIMENTAL

Proton n.m.r. spectra of the ligands were obtained for ≃50% solutions in $CDCl_3$ on Perkin-Elmer R12 and R32 spectrometers, and for the methiodides in $CDCl_3$ or $S(CD_3)_2O$, referenced to internal $SiMe_4$. Phosphorus-31 n.m.r. spectra were obtained for ≃50% solutions in C_6H_6 on a JEOL FX60 and referenced to 85% H_3PO_4. Mass spectra were recorded as described previously.[10]

All reactions were conducted under a dry dinitrogen atmosphere. **CAUTION:** The ligands and intermediates are malodorous and are presumed to be highly toxic. Reactions involving the manipulation of dimethylphosphine, tetramethyldiphosphane, and trimethylstibine involve a considerable fire hazard since all three are pyrophoric. In general, bromine-water scrubbers were attached to the apparatus to remove malodorous and inflammable materials from the gas stream before discharge into the fume hood.

Tetrahydrofuran (B.D.H. Ltd.) was dried by refluxing for several days over sodium and freshly distilled from sodium diphenylketyl before use. *NNN'N'*-Tetramethyl-*o*-phenylenediamine (Eastman Kodak) was fractionated (b.p. 95–97 °C, 14 Torr).† (*o*-Bromophenyl)dimethylarsine [11] and *o*-phenylenebis(dimethylarsine) [12] were obtained by literature routes.

(o-Bromophenyl)dimethylamine.[13]—*o*-Bromoaniline (100 g, 0.6 mol) was melted and poured into vigorously stirred water (200 cm^3). Dimethyl sulphate (76 g, 0.6 mol) was added, and the mixture stirred until it became homogeneous (*ca.* 1 h). It was cooled to 0 °C and neutralised with 10% aqueous potassium hydroxide. The methylation and neutralisation was repeated twice more, and the mixture extracted with diethyl ether (4 × 250 cm^3). The combined ether extracts were dried over anhydrous sodium sulphate, the ether evaporated, and the residue distilled *in vacuo* (b.p. 100—102 °C, 12 Torr), yield 83 g (70%).

A monomethiodide was obtained by refluxing the product (1 cm^3) with iodomethane (4 cm^3) in acetonitrile (25 cm^3), and recrystallising the product from acetonitrile (Found: C, 32.0; H, 4.3; N, 4.2. $C_9H_{13}BrIN$ requires C, 31.6; H, 3.9; N, 4.1%), m.p. 157 °C.

(o-Bromophenyl)dimethylstibine.—This was prepared by the method of Cook *et al.*,[9] except that the stibonic acid was dissolved in cold concentrated hydrochloric acid and the sulphur dioxide reduction carried out at 0 °C (60%). The monomethiodide was prepared by reaction with excess of iodomethane in diethyl ether, and the white precipitate was recrystallised from ethanol (Found: C, 24.3; H, 3.4. $C_9H_{13}BrISb$ requires C, 24.0; H, 3.2%), m.p. 145—147 °C.

Attempted Preparation of (o-Bromophenyl)dimethylphosphine.—(*o*-Bromophenyl)dichlorophosphine [14] (26 g, 0.1 mol) in diethyl ether (200 cm^3) was treated with the Grignard reagent prepared from magnesium (4.8 g, 0.2 mol) and iodomethane (28.5 g, 0.2 mol) in diethyl ether (150 cm^3). After hydrolysis the ether layer was dried over anhydrous sodium sulphate. Distillation yielded appreciable amounts of benzene, and the residue (1.5 g) boiled over the range 30—48 °C (0.2 Torr) (see text).

† Throughout this paper: 1 Torr = (101 325/760) Pa.

(o-*Dimethylaminophenyl*)*dimethylphosphine*, (4).—Dimethylphenylphosphine (27.6 g, 0.2 mol) was added to a vigorously stirred suspension of lithium (4.5 g, 0.65 mol) (lithium hammered into thin sheets and cut into small strips under argon is satisfactory) in tetrahydrofuran (thf) (400 cm^3). After *ca.* 10 min the mixture developed a dark green colour and became hot. It was cooled in ice and stirred for *ca.* 12 h. The dark red solution produced was filtered through glass wool to remove excess of lithium, cooled to 0 °C, and treated dropwise with t-butyl chloride (11.0 g, 0.12 mol). The product is $Li[PMe_2]$, *ca.* 0.12 mol. After 30 min, (o-bromophenyl)dimethylamine (24.0 g, 0.12 mol) was added slowly with stirring, and the mixture refluxed for 1 h. The brown (or brown-purple) solution was cautiously hydrolysed with dexygenated water (200 cm^3) (**CARE:** some dimethylphosphine evolved), the organic layer separated, and dried over anhydrous sodium sulphate. The solvent was removed at atmospheric pressure, and the residual oil fractionated *in vacuo*. The fraction boiling at <70 °C (3 Torr) was rejected (largely *NN*-dimethylaniline), and the ligand obtained at 82 °C (3.5 Torr), yield 13 g (60%).

A monomethiodide was prepared by quaternisation with excess of iodomethane and recrystallised from ethanol (Found: C, 41.2; H, 6.2; N, 4.1. $C_{11}H_{19}INP$ requires C, 40.9; H, 5.9; N, 4.2%), m.p. 195—197 °C (decomp.).

(o-*Dimethylaminophenyl*)*dimethylarsine*, (5).—*Method* 1. (o-Bromophenyl)dimethylamine (20 g, 0.1 mol) diluted with thf (100 cm^3) was added to a solution of sodium dimethylarsenide prepared [12] from sodium (10.4 g, 0.45 mol), iododimethylarsine (50 g, 0.22 mol), and thf (400 cm^3). The mixture was refluxed for 1 h, cooled, hydrolysed with deoxygenated water (200 cm^3), and the organic layer separated and dried. After removal of the solvent, the product was distilled *in vacuo* yielding *NN*-dimethylaniline, (o-bromophenyl)dimethylaniline, b.p. <60 °C (1 Torr), and the ligand, b.p. 67 °C (1.5 Torr), yield 13.5 g (60%) based on o-$C_6H_4Br(NMe_2)$.

Method 2. The Grignard reagent prepared from (o-bromophenyl)dimethylamine was treated with iododimethylarsine as described by Mann and Stewart,[7] yield 70%. The monomethiodide was prepared in the usual way (Found: C, 36.0; H, 5.3; N, 3.7. $C_{11}H_{19}AsIN$ requires C, 36.0; H, 5.1; N, 3.8%), m.p. 220—222 °C (decomp.) [lit.,[7] 221—222 °C].

(o-*Dimethylaminophenyl*)*dimethylstibine*, (6).—*Method* 1. Bromodimethylstibine [15] (24 g, 0.1 mol) was added to a solution of sodium (4.6 g, 0.2 mol) in liquid ammonia (400 cm^3) at −78 °C. The mixture was stirred for 3 h, and then transferred *via* neoprene tubing to a dropping funnel cooled by solid CO_2, and added slowly to (o-bromophenyl)-dimethylamine (20 g 0.1 mol) in thf (200 cm^3) precooled to −40 °C. When addition was complete the mixture was allowed to warm to room temperature, stirred for 1 h, and then hydrolysed with deoxygenated water (200 cm^3). The organic layer was separated, dried, and distilled yielding *NN*-dimethylaniline and an unidentified compound, b.p. <60 °C (1 Torr) (2 g), and the ligand, b.p. 82—84 °C (1 Torr), yield 14.5 g (53%).

Method 2. The Grignard reagent was prepared from (o-bromophenyl)dimethylamine (20 g, 0.1 mol) and magnesium (3 g, 0.125 mol) in diethyl ether (200 cm^3), and refluxed for 1 h to ensure complete reaction. Bromodimethylstibine (24 g, 0.1 mol) in thf (100 cm^2) was added dropwise with stirring, and the white suspension refluxed for 1 h. Work-up as above yielded the ligand (12 g, 45%).

The monomethiodide was recrystallised from ethanol–diethyl ether (Found: C, 32.3; H, 5.3; N, 3.6. $C_{11}H_{19}INSb$ requires C, 31.9; H, 4.8; N, 3.4%), m.p. 227—228 °C (decomp.).

o-*Phenylenebis*(*dimethylphosphine*), (2).—A solution of lithium dimethylphosphide (0.12 mol) prepared as above was treated dropwise with *o*-dichlorobenzene (8.8 g, 0.06 mol), and the mixture refluxed for 2 h. It was cooled, hydrolysed with deoxygenated water (100 cm^3), the organic layer separated, dried ($Na_2[SO_4]$), and distilled. The first fraction b.p. <60 °C (1 Torr) is largely PMe_2Ph (*ca.* 2.5 g) and is followed by the ligand, b.p. 80—83 °C (0.5 Torr), yield 4.7 g (40%).

A monomethiodide was prepared as above, and recrystallised from ethanol (Found: C, 38.9; H, 5.1; I, 37.5. $C_{11}H_{19}IP_2$ requires C, 38.8; H, 5.6; I, 37.4%), m.p. 275 °C (decomp.).

The above reaction was also carried out by adding $Li[PMe_2]$ dropwise to *o*-dichlorobenzene at 0 °C. The mixture was stirred for 1 h at 0 °C and then hydrolysed. Distillation yielded a considerable amount of PMe_2H with the organic solvents, followed by some *o*-dichlorobenzene, b.p. <50 °C (1 Torr), a fraction of b.p. 60—65 °C (1 Torr) (*ca.* 9 g), and a second fraction of b.p. 80—85 °C (0.5 Torr) (*ca.* 3 g). The latter was identified as the diphosphine. The first fraction formed a methiodide (Found: C, 34.8; H, 4.5; Cl, 10.7. $C_9H_{13}ClIP$ requires C, 34.4; H, 4.2; Cl, 11.2%), m.p. 298 °C (decomp.) (lit.,[6] 303—305 °C).

(o-*Dimethylphosphinophenyl*)*dimethylarsine*, (7).—A thf solution (200 cm^3) of (*o*-bromophenyl)dimethylarsine (31.0 g, 0.12 mol) was cooled to 0 °C and treated dropwise with a solution of lithium dimethylphosphide (0.12 mol) prepared as above. When addition was complete the dark solution was stirred for 1 h at room temperature, and finally refluxed for 2 h. Hydrolysis and work-up in the usual way yielded a low-boiling fraction, b.p. <70 °C (*ca.* 4 g), largely $AsMe_2Ph$, followed by the ligand, b.p. 92 °C (0.5 Torr), yield 12.5 g (43%).

Quaternisation with iodomethane and recrystallisation of the product from ethanol–diethyl ether yielded a monomethiodide (Found: C, 34.6; H, 5.2; I, 33.1. $C_{11}H_{19}AsIP$ requires C, 34.4; H, 4.95; I, 33.0%), m.p. 210—212 °C (decomp.).

(o-*Dimethylphosphinophenyl*)*dimethylstibine*, (8).—(o-Bromophenyl)dimethylstibine (27.4 g, 0.12 mol) was dissolved in thf (200 cm^3) cooled to 0 °C and vigorously stirred. A solution of lithium dimethylphosphide (0.12 mol) was added very slowly, dropwise. The mixture was stirred at room temperature for 3 h, gently refluxed for another hour, and then hydrolysed and worked-up as usual. Distillation gave $SbMe_2Ph$ (3.5 g), b.p. <60 °C (1 Torr), and the ligand, b.p. 96—98 °C (1 Torr), yield 10 g (29%).

A monomethiodide was prepared as above and recrystallised from ethanol–diethyl ether (Found: C, 30.9%; H, 4.6. $C_{11}H_{19}IPSb$ requires C, 30.6; H, 4.4%), m.p. 192—194 °C (decomp.).

o-*Phenylenebis*(*dimethylstibine*), (3).—A solution of sodium dimethylantimonide in liquid ammonia was prepared as described above from sodium (4.6 g, 0.2 g. atom), $SbBrMe_2$ (23.0 g, 0.1 mol), and liquid ammonia (200 cm^3), and transferred to a cooled (−78 °C) dropping funnel. (o-Bromophenyl)dimethylstibine (30.0 g, 0.1 mol) was dissolved in thf (100 cm^3) and cooled to −78 °C, and the antimonide solution added dropwise over *ca.* 3 h. After the first 30 min the red colour was no longer discharged instantly, the

cooling bath was removed, and the mixture allowed to warm up slowly. At the end of 3 h, the ammonia was boiled off and the greyish suspension refluxed for 15 min, cooled, hydrolysed, and worked-up as usual. Distillation yielded Sb_2Me_4 (*ca.* 1.5 g), b.p. 46 °C (0.5 Torr), a mixture (*ca.* 3 g) of $SbMe_2Ph$ and *o*-$C_6H_4Br(SbMe_2)$, b.p. <80 °C (0.5 Torr), and finally the ligand, b.p. 112 °C (0.2 Torr), yield 5.5 g (22%).

The monomethiodide was prepared using iodomethane in acetone solution, and recrystallised from acetone (Found: C, 25.5; H, 3.2; I, 24.1. $C_{11}H_{19}ISb_2$ requires C, 25.3; H, 3.6; I, 24.3%), m.p. 135—137 °C (decomp.).

(*o-Dimethylarsinophenyl*)*dimethylstibine*, (9).—This was prepared by the method of Cook *et al.*[9] in 60% yield and in 35% yield from sodium dimethylantimonide and (*o*-bromophenyl)dimethylarsine in thf–liquid ammonia, analogous to the preparation of (3). The monomethiodide was also prepared (C, 28.1; H, 4.1. $C_{11}H_{19}AsISb$ requires C, 27.8; H, 4.0%), m.p. 178—180 °C (decomp.).

(*o-Methoxyphenyl*)*dimethylphosphine*.— *o*-Bromoanisole (18.7 g, 0.1 mol) in thf (200 cm^3) was treated dropwise at 0 °C with lithium dimethylphosphide (0.10 mol), at such a rate that the red phosphide colour was discharged rapidly. As the reaction progressed this discharge became slower, the mixture was heated to reflux, and the remaining phosphide added. The product was hydrolysed, separated, and the organic layer dried ($Na_2[SO_4]$). Distillation yielded an unidentified low-boiling fraction (*ca.* 1 g), 30—35 °C, followed by the ligand, b.p. 70—72 °C (2 Torr), yield 9 g (53%).

The monomethiodide was also prepared (Found: C, 38.9; H, 5.5; I, 41.1. $C_{10}H_{13}IO$ requires C, 38.7; H, 5.2; I, 40.95%), m.p. 265 °C (decomp.).

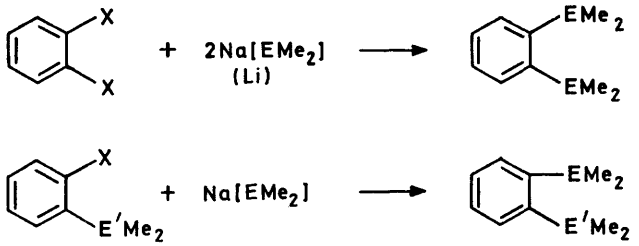
(*o-Methylthiophenyl*)*dimethylphosphine*.—*o*-Bromophenyl methyl sulphide [16] (20.3 g, 0.1 mol) and lithium dimethylphosphide (0.1 mol) were allowed to react as described for the *o*-methoxy-analogue. Fractionation of the products yielded the ligand, b.p. 68—70 °C (1 Torr), yield 10 g (58%), and higher-boiling fractions, b.p. >85 °C (1 Torr), which were largely phosphorus free.

A methiodide derivative was prepared in the usual way, but was not obtained analytically pure even after several recrystallisations. The ^1H n.m.r. spectrum showed the expected absorptions for the monomethiodide, and another P–Me resonance with $^2J(PH)$ *ca.* 16 Hz suggesting a phosphorus (V) impurity. A pure palladium(II) complex, $[PdLCl_2]$, was isolated on reaction of the ligand with $Na_2[PdCl_4]$ in ethanol.

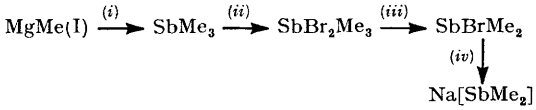
RESULTS AND DISCUSSION

The most widely used syntheses for bidentate Group 5B donor ligands involve the reaction of the alkali-metal derivatives of secondary phosphines, arsines, or stibines with an appropriate organohalide.[17] The best route to *o*-phenylenebis(dimethylarsine) (1), developed by Feltham and co-workers [12] is from *o*-dichlorobenzene and sodium dimethylarsenide in tetrahydrofuran. The possibility of developing this into a general route for the ligands in Scheme 1 was investigated (Scheme 2). The first step was to determine the best syntheses for the required intermediates $Na[EMe_2]$ and *o*-$C_6H_4X(E'Me_2)$.

$Na[EMe_2]$ *or* $Li[EMe_2]$.—Sodium dimethylarsenide is conveniently prepared from iododimethylarsine and sodium in thf in yields of *ca.* 45%.[12] Sodium dimethylstibide is thermally unstable and must be prepared and used at low temperatures. The route in Scheme 3 gives overall yields of *ca.* 40%.[15,18]

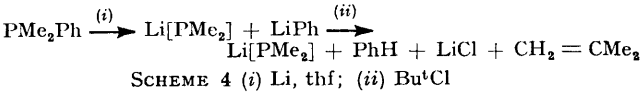


SCHEME 2 X = Cl or Br; E = P, As, or Sb; E ≠ E'



SCHEME 3 (*i*) $SbCl_3$; (*ii*) Br_2; (*iii*) Heat, *ca.* 30 Torr; Na liquid NH_3

Direct reaction of $SbBr_2Me_3$ with sodium also yields $Na[SbMe_2]$,[19] but on a large scale the yields are variable and the extra step is preferable. Sodium dimethylphosphide has previously been made by two routes: from sodium and tetramethyldiphosphine disulphide * $Me_2(S)PP(S)Me_2$ in 1,4-dioxan [3] and from sodium and tetramethyldiphosphane in liquid ammonia.[20,21] The first route has been used by Warren and Bennett [3] to prepare the diphosphine (2), but although the second is suitable for the preparation of diphosphinoalkanes [20,21] it fails for aromatic analogues (see below). An alternative synthesis in thf was sought. Neither $P_2Me_4S_2$ nor P_2Me_4 is cleaved by sodium in thf at ambient temperatures, whilst under reflux any $Na[PMe_2]$ produced would rapidly attack the solvent.[22] The use of chlorodimethylphosphine is unattractive since it is pyrophoric, moisture sensitive, and its preparation is lengthy.[23] However, recalling that lithium diphenylphosphide is readily prepared from lithium and triphenylphosphine in thf,[24,25] the corresponding reaction with dimethylphenylphosphine was investigated. In fact, providing the thf is rigorously dry, this reaction yields $Li[PMe_2]$ in *ca.* 70% yield, and the phenyl-lithium produced can be destroyed by t-butyl chloride in the usual way [24] (Scheme 4).



SCHEME 4 (*i*) Li, thf; (*ii*) Bu^tCl

Unchanged PMe_2Ph was not recovered, so the cleavage of the phenyl group is probably complete, and the *ca.* 70% 'yield' of $Li[PMe_2]$ reflects some attack on the thf. However, if the reaction is conducted at room temperature, the losses are not unacceptable, and since PMe_2Ph can be easily prepared in quantity and is much easier to store and manipulate than PMe_2Cl or P_2Me_4

* Tetramethyl-1,2-dithioxodi-λ^5-phosphane.

this is a very convenient route to $Li[PMe_2]$. Rather surprisingly, PMe_2Ph did not appear to be cleaved by lithium or sodium in 1,4-dioxan even under reflux.

o-$C_6H_4Br(EMe_2)$ *Compounds.*—(*o*-Bromophenyl)-dimethylamine (*o*-bromo-*NN*-dimethylaniline) was obtained by Gilman's method [13] from dimethyl sulphate and *o*-bromoaniline. An attempt to use trimethyl phosphate as the alkylating agent produced an uncontrollably violent reaction and a very poor yield. The literature preparations were also used for *o*-$C_6H_4Br(AsMe_2)$ [7,11] and *o*-$C_6H_4Br(SbMe_2)$ [9] with minor modifications. Hart [6] first prepared *o*-$C_6H_4Cl(PMe_2)$ from *o*-bromochlorobenzene, lithium, and PMe_2Cl; as an alternative we treated (*o*-bromophenyl)dichlorophosphine *o*-$C_6H_4Br(PCl_2)$ [14] with MgMe(I), but obtained only traces (<2%) of the expected *o*-$C_6H_4Br(PMe_2)$, along with small amounts of *o*-$C_6H_4Br_2$, *o*-C_6H_4BrCl, phenylphosphine $PPhH_2$, and (*o*-bromophenyl)phosphine *o*-$C_6H_4Br(PH_2)$, identified by a combination of ^1H n.m.r. and mass spectrometry. The (*o*-bromophenyl)dimethylphosphine was not separated by fractionation, but treatment with iodomethane and fractional crystallisation of the product yielded a pure sample of the monomethiodide [*o*-$C_6H_4Br(PMe_3)$]I. This reaction was repeated several times with the same result. The failure to produce useful amounts of *o*-$C_6H_4Br(PMe_2)$ is surprising, since the *o*-$C_6H_4Br(PPh_2)$ is obtained in *ca.* 50% yield using MgBr(Ph).[14]

On one occasion the reaction of $Li[PMe_2]$ with *o*-$C_6H_4Cl_2$ at 0 °C (Experimental section) yielded a mixture of *o*-$C_6H_4Cl(PMe_2)$ and *o*-$C_6H_4(PMe_2)_2$ in ratio 3 : 1, which could be separated by fractionation. The reaction was not further investigated but may be a viable route to the former.

Ligands.—*o*-$C_6H_4(PMe_2)_2$ (2). Although sodium dimethylphosphide in liquid ammonia and α,ω-dichloroalkanes produced good yields of $Me_2P[CH_2]_nPMe_2$,[20,21] the reaction with *o*-dichlorobenzene did not produce significant amounts of the diphosphine (2). At low temperatures the reaction was very slow, whilst on warming or during replacement of the ammonia by thf the reaction often became uncontrollably violent. However, the reaction of *o*-$C_6H_4Cl_2$ with $Li[PMe_2]$ in thf (Experimental section) produced *ca.* 40% yield of (2). In general all the ligands prepared from $Li[PMe_2]$–thf contained small amounts of impurities as shown by the presence of a number of absorptions in the range τ 7—9 in the ^1H n.m.r. spectra, only some of which were coupled to phosphorus. These impurities were difficult to remove by fractionation, but caused no problems when metal complexes were being prepared, and can be ignored in routine syntheses. Warren and Bennett [3] reported similar problems in 1,4-dioxan, and no doubt the impurities in the present case arise from some attack on the solvent by the $Li[PMe_2]$.

o-$C_6H_4(SbMe_2)_2$ (3). The reaction of $Na[SbMe_2]$ with *o*-$C_6H_4Cl_2$ in liquid ammonia produced large amounts of black insoluble solid, and distillation of the ether-soluble products gave tetramethyldistibane Sb_2Me_4, as the main antimony-containing product. The distibine, (3), was not isolated from this reaction, although by treatment of the ether extract with nickel(II) bromide in n-butanol a very small amount of purple complex, identical with a genuine sample of $[Ni\{o\text{-}C_6H_4(SbMe_2)_2\}Br_2]$ was produced. Shewchuk and Wild [5] used *o*-bromoiodobenzene in this reaction and reported *ca.* 9% yield of (3). The addition of (*o*-bromophenyl)dimethylstibine [9] to $Na[SbMe_2]$ in liquid ammonia also produced large amounts of a black solid, consistent with the report of Cook *et al.*[9] that aryl-C–$SbMe_2$ bonds are readily cleaved by excess of nucleophile. Inverse addition which ensured that the nucleophile ($SbMe_2^-$) was never present in large excess much reduced the quantity of black decomposition products, and work-up of the ether-soluble products yielded the distibine (3), dimethyl(phenyl)stibine, tetramethyldistibane, and sometimes unchanged *o*-$C_6H_4Br(SbMe_2)$, from which the distibine was separated by fractionation. The yields vary widely: on one occasion 35% was achieved, but usually *ca.* 20%. *o*-Phenylenebis(dimethylstibine) is the most difficult ligand to obtain of the whole series, but the syntheses reported here does produce it in reasonable yield, although the preparation is still lengthy.

o-$C_6H_4(NMe_2)(EMe_2)$ (E = P, As, *or* Sb) (4)—(6). These ligands are readily made from *o*-$C_6H_4Br(NMe_2)$ and the appropriate $Li(Na)[EMe_2]$ in thf in yields of 45—60%; the only major by-product is *NN*-dimethylaniline which is easily separated by fractionation. It is also possible to form the Grignard reagent from *o*-$C_6H_4Br(NMe_2)$, and treat this with EMe_2X (X = halide), and the arsine [7] and stibine [8] have been previously obtained by this route. Yields are comparable and either route is satisfactory.

o-$C_6H_4(EMe_2)(E'Me_2)$(7)—(9). The arsine–stibine (9) was prepared by Cook *et al.*[9] from *o*-$C_6H_4Br(SbMe_2)$ and $Na[AsMe_2]$ in thf in *ca.* 60%, providing care was taken to avoid excess of nucleophile which caused much decomposition. The alternative route from $Na[SbMe_2]$ and *o*-$C_6H_4Br(AsMe_2)$ in liquid ammonia, although it uses the more readily available (*o*-bromophenyl)dimethylarsine, gives a poorer yield (*ca.* 35%) and a less pure product. The preparation of the phosphine–arsine (7) from $Li[PMe_2]$ and *o*-$C_6H_4Br(AsMe_2)$ was straightforward (*ca.* 43%), but the phosphine–stibine (8) was considerably more elusive. Decomposition of *o*-$C_6H_4Br(SbMe_2)$ by the nucleophile (PMe_2^-) was even more troublesome than in the case of (9), indeed the addition of the stibine to $Li[PMe_2]$ in thf produced a very complicated mixture and much black product, and although *o*-$C_6H_4(PMe_2)(SbMe_2)$ was among the products it was not isolated in useful yield. Inverse addition was more successful yielding *ca.* 30% (8).

o-$C_6H_4(PMe_2)(YMe)$ (Y = O *or* S). (*o*-Methoxyphenyl)dimethylphosphine has previously been prepared [26] from dichloro(*o*-methoxyphenyl)phosphine and methyl-lithium. It can be obtained directly from $Li[PMe_2]$ and *o*-bromoanisole in thf, which was unexpected since Mallion and Mann [27] found that anisole

Physical data

Compound	B.p. (θ_c/°C), P/Torr	Ligands: ^{1}H n.m.r.[b]	Ligands: ^{31}P n.m.r.[c]	Mass spectra[a]: Parent	Mass spectra[a]: Base		Methiodides: ^{1}H n.m.r.[d]
o-$C_6H_4Br(NMe_2)$	108—110, 15	7.5 (s), 6 H, NMe_2		199 (87)	198 (100)	C_8H_9BrN	7.4 (s), 9 H, NMe_3
o-$C_6H_4Br(PMe_2)$	[e]	9.0 (d) (4), 6 H, PMe_2					7.6 (d) (15), 9 H, PMe_3
o-$C_6H_4Cl(PMe_2)$	60—62, 1	8.95 (d) (4), 6 H, PMe_2	+49.4 (6)	172 (80)	124 (100)	C_7H_9P	7.65 (d) (14.4), 9 H, PMe_3
o-$C_6H_4Br(AsMe_2)$	88—90, 1	8.9 (s), 6 H, $AsMe_2$		260 (11)	91 (100)	C_7H_7	7.6 (s), 9 H, $AsMe_3$
o-$C_6H_4Br(SbMe_2)$	75—76, 0.5	9.1 (s), 6 H, $SbMe_2$		306 (6)	91 (100)	C_7H_7	8.05 (s), 9 H, $SbMe_3$
o-$C_6H_4(NMe_2)_2$	95—97, 14	7.35 (s), 12 H, NMe_2		164 (100)		$C_{10}H_{16}N_2$	6.25 (s), 9 H, NMe_3; 7.3 (s), 6 H, NMe_2
(2) *o*-$C_6H_4(PMe_2)_2$	80—83, 0.5	8.8 (t) (4), 12 H, PMe_2	+54.65 (4)	198 (87)	183 (100)	$C_9H_{13}P_2$	7.4 (d) (14), 9 H, PMe_3, 8.75 (d) (3.5), 6 H, PMe_2
(1) *o*-$C_6H_4(AsMe_2)_2$	100, 1	8.85 (s), 12 H, $AsMe_2$		286 (16)	271 (100)	$C_9H_{13}As_2$	7.65 (s), 9 H, $AsMe_3$; 8.75 (s), 6 H, $AsMe_2$
(3) *o*-$C_6H_4(SbMe_2)_2$	112—115, 0.2	9.1 (s), 12 H, $SbMe_2$		378 (9)	91 (C_7H_7) [f]		7.95 (s), 9 H, $SbMe_3$; 8.9 (s), 6 H, $SbMe_2$
(4) *o*-$C_6H_4(NMe_2)(PMe_2)$	82, 3.5	7.35 (s), 6 H, NMe_2; 8.8 (d) (4), 6 H, PMe_2	+52.16 (4)	181 (42)	166 (100)	$C_9H_{13}NP$	7.35 (s), 6 H, NMe_2; 7.8 (d) (15), 9 H, PMe_3
(5) *o*-$C_6H_4(NMe_2)(AsMe_2)$	67, 1.5	7.3 (s), 6 H, NMe_2; 8.85 (s), 6 H, $AsMe_2$		225 (35)	210 (100)	$C_9H_{13}AsN$	7.35 (s), 6 H, NMe_2; 7.8 (s), 9 H, $AsMe_3$
(6) *o*-$C_6H_4(NMe_2)(SbMe_2)$	82, 1	7.4 (s), 6 H, NMe_2; 9.2 (s), 6 H, $SbMe_2$		271 (6.5)	120 (100)	$C_8H_{10}N$	7.3 (s), 6 H, NMe_2; 8.2 (s), 9 H, $SbMe_3$
(7) *o*-$C_6H_4(PMe_2)(AsMe_2)$	92, 1	8.95 (d) (3.5), 6 H, PMe_2; 8.9 (s), 6 H, $AsMe_2$	+54.5 (*ca.* 4)	242 (11)	227 (100)	$C_9H_{13}AsP$	7.5 (d) (13.5), 9 H, PMe_3; 8.65 (s), 6 H, $AsMe_2$
(8) *o*-$C_6H_4(PMe_2)(SbMe_2)$	98, 1	8.75 (d) (3.0), 6 H, PMe_2; 9.1 (s), 6 H, $SbMe_2$	+56.0 (*ca.* 4)	288 (15)	273 (100)	$C_9H_{13}PSb$	7.7 (d) (15), 9 H, PMe_3; 8.95, 6 H, $SbMe_2$
(9) *o*-$C_6H_4(AsMe_2)(SbMe_2)$	98—100, 0.5	8.9 (s), 6 H, $AsMe_2$; 9.05 (s), 6 H, $SbMe_2$		332 (8)	317 (100)	$C_9H_{13}AsSb$	7.65 (s), 9 H, $AsMe_3$; 8.7 (s), 6 H, $SbMe_2$
o-$C_6H_4(PMe_2)(OMe)$	70—72, 2	6.3 (s), 3 H, OMe; 8.8 (d) (3.5), 6 H, PMe_2	+53.5 (3.5)	168 (100)		$C_9H_{13}OP$	6.02 (s), 3 H, OMe; 7.84 (d) (15.3), 9 H, PMe_3
o-$C_6H_4(PMe_2)(SMe)$	68—70, 1	7.6 (s), 3 H, SMe; 8.5 (d), 8.7 (d) (4), 3 H, 3 H, PMe_2	+46.7				7.65 (s), 3 H, SMe; 7.35 (d) (15), 9 H, PMe_3 [e]

[a] Relative intensities in parentheses. For polyisotopic species the *m/e* quoted corresponds to the lightest isotope (*i.e.* ^{79}Br, ^{121}Sb, ^{35}Cl) and intensities are uncorrected. [b] In $CDCl_3$ solution, τ relative to internal $SiMe_4$ ($\tau = 10$); J(PH) in Hz given in parentheses. All compounds show complex multiplets at τ *ca.* 2.7—3.2 due to the aromatic protons (4 H). [c] In *ca.* 50% solution in benzene, referenced to 85% H_3PO_4; J(PH) in parentheses. [d] In $S(CD_3)_2O$ relative to internal $SiMe_4$ ($\tau = 10$); J(PH) in parentheses. Also aromatic multiplet at τ *ca.* 2.3—3.0 (4 H). [e] Not isolated pure (see text). [f] When ^{123}Sb also considered, base is $C_9H_{13}Sb_2$.

(PhOMe) is rapidly dealkylated by $Li[PPh_2]$ forming $PMePh_2$ and PhOH. In the present synthesis, the $Li[PMe_2]$ was added to cooled (*ca.* 0 °C) *o*-bromoanisole so that a large excess of nucleophile was not present at any time. The good yield of the ligand *o*-$C_6H_4(PMe_2)$(OMe) (*ca.* 53%) and the absence of large amounts of trimethylphosphine indicates that, under these conditions at least, the $[PMe_2]^-$ ion attacks the C–Br bond more readily than the O–Me. The new ligand (*o*-methylthiophenyl)dimethylphosphine was produced similarly from $Li[PMe_2]$ and *o*-bromophenyl methyl sulphide.

Properties. All of the ligands are foul-smelling air-sensitive liquids. The ^1H n.m.r. spectra (Table) are generally as expected exhibiting sharp singlets at τ *ca.* 7.3 (NMe_2), *ca.* 8.9 ($AsMe_2$), *ca.* 9.1 ($SbMe_2$), and doublets *ca.* 8.8 (PMe_2), $^2J(PH) \approx 4$ Hz. The only exception is the diphosphine (2), where the methyl resonances occur as an apparent triplet at τ 8.8 [$^2J(PH) + {}^5J(PH) \approx 4$ Hz]. The ^{31}P n.m.r. spectra show absorptions in the range 44—54 p.p.m. consistent with (aryl) PMe_2 groups (*cf.* PMe_2Ph, 47 p.p.m.),[28] which under high resolution are multiplets with $^2J(PH) \approx 4$ Hz. The ^1H n.m.r. spectrum of *o*-$C_6H_4(PMe_2)(SMe)$ contains two methyl doublets at τ 8.5, 8.7 (integral 1 : 1) indicating that the PMe protons are diastereotopic. The compound *o*-$C_6H_4(PMe_2)$(OMe) exhibits only a single PMe doublet since inversion at oxygen is fast on the n.m.r. time scale.

Quaternisation of all the ligands occurred easily on treatment with iodomethane. In all cases monomethiodides were formed, although the use of more forcing conditions which may have yielded dimethiodides [29] were not tried. Analytical data of these derivatives are reported in the Experimental section and ^1H n.m.r. data in the Table. The methyl resonance of the $[EMe_3]^+$ group is downfield from that of EMe_2; the unquaternised EMe_2 group shifts downfield slightly in the monomethiodides due to inductive effects. In the cases of the unsymmetrical ligands *o*-$C_6H_4(EMe_2)(E'Me_2)$, the ^1H n.m.r. spectra indicate that quaternisation occurs preferentially in the order P > As > Sb > N. In contrast to the free ligand, the ^1H n.m.r. spectrum of [*o*-$C_6H_4(PMe_2)(PMe_3)$]I shows doublets at τ 7.4 [$^2J(PH)$ 14 Hz] and 8.75 [$^2J(PH)$ 3.5 Hz] due to $[PMe_3]^+$ and PMe_2 respectively; at 60 MHz there is little evidence for coupling to the second phosphorus atom.

Mass spectra of the ligands were recorded to provide confirmation of the identity and structure; the parent and base peaks and relative intensities are given in the Table. In general the fragmentation patterns were very complicated, more so than those of either analogues containing alkane backbones,[30] or the aryls *o*-$C_6H_4(EPh_2)_2$.[10] For all except the diamine *o*-$C_6H_4(NMe_2)_2$ and *o*-$C_6H_4(PMe_2)$(OMe) for which the parent is also the base peak, the base peak is $[P - Me]^+$. Our spectra are in good agreement with the published data for (1), (4), and (6).[31] One curious result was that the spectra of the arsine–stibine (9) and the phosphine–stibine (8) both showed ions corresponding to the symmetrical analogues ligands (1) + (3) and (2) + (3) respectively. From the method of preparation the presence of the lighter ligand might be explained, but the presence of the distibine (3) is difficult to account for. Moreover, for the nitrogen-containing ligands and the phosphine–arsine (7) the spectra show no evidence of the presence of the symmetrical analogues. Several samples of ligand (9) from different preparations were examined and all were found to give ions in the mass spectra corresponding to (1), (3), and (9). This suggests that in fact rather than the symmetrical analogues being an impurity in (9) and (8) they may be formed by rearrangement in the mass spectrometer. Similar rearrangements of unidentate alkyl(phenyl)stibines have been recorded.[32]

The mechanism of the formation of *o*-phenylene ligands from *o*-$C_6H_4X_2$ or *o*-$C_6H_4X(EMe_2)$ and $Na[E'Me_2]$ is unknown, but is almost certainly more complicated than straightforward nucleophilic substitution. A more detailed examination [33,34] of the reaction of *o*-$C_6H_4Cl_2$ with $Na[AsMe_2]$ or Na[AsMePh] revealed a large number of by-products. In the present study we observed that the bidentate *o*-$C_6H_4(EMe_2)_2$ was invariably accompanied by the unidentate analogues EMe_2Ph, but no attempt was made to systematically identify other by-products, an extremely long, and from the point of view of the present study (aimed at devising syntheses which allowed the co-ordination chemistry of the ligands to be developed), unnecessary, procedure. Many of the ligands described here have been further characterised by the preparation of transition-metal derivatives, details of which will be published elsewhere.

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