Journal of Organometallic Chemistry, 88 (1975) 171—174

BIDENTATE GROUP VB CHELATES

XVI*. THE PREPARATION OF *o*-PHENYLENEBIS(DIPHENYLSTIBINE) AND ATTEMPTS TO PREPARE *cis*- AND *trans*-1,2-BIS(DIPHENYLSTIBINO)-ETHYLENE

W. LEVASON, C.A. McAULIFFE** and S.G. MURRAY

Department of Chemistry, University of Manchester Institute of Science and Technology, Manchester M60 1QD (Great Britain)

(Received October 22nd, 1974)

Summary

o-Phenylenebis(diphenylstibine) (sbsb) has been obtained from sodium diphenylstibide and *o*-bromophenyldiphenylstibine. The failure of other routes to this compound, and of attempts to prepare ethylenic distibines, are discussed.

The coordination chemistry of antimony donor ligands has received considerably less attention than that of the corresponding phosphines and arsines. Few chelating agents containing antimony donors are known, e.g. $Ph_2SbCH_2SbPh_2$ [2], $Ph_2SbCH_2CH_2CH_2SbPh_2$ [3], o-$C_6H_4(SbMe_2)(AsMe_2)$ [4], o-$C_6H_4(PPh_2)(SbPh_2)$ [5], o-$C_6H_4(SbPh_2)(AsPh_2)$ [5], and o-$C_6H_4(SbMe_2)_2$ [6].

Here we report the synthesis of *o*-phenylenebis(diphenylstibine) (sbsb) and some metal complexes, and describe some unsuccessful attempts to prepare analogues with alkene backbones.

Experimental

Physical measurements [7] and mass spectra [8] were obtained as described previously. All reactions were performed under dry nitrogen.

---

* For Part XV see ref. 1.

** For correspondence.

o-Phenylenebis(diphenylstibine) (sbsb)

(i). *o*-Bromophenyldichlorostibine [4] was treated with two equivalents of phenylmagnesium bromide to yield *o*-bromophenyldiphenylstibine, m.p. 59°. (Found, C, 50.0; H, 3.6. $C_{18}H_{14}SbBr$ calc.: C, 50.0; H, 3.3%).

A solution of sodium diphenylstibine in liquid ammonia was prepared from diphenylchlorostibine [9] (18.3 g, 0.06 mol) and sodium (2.7 g, 0.12 mol). The dark red stibide solution was added dropwise with rapid stirring to *o*-bromophenyldiphenylstibine (25.0 g, 0.058 mol) in dry THF (200 ml) at —78°. During the course of the reaction the solution was allowed to warm to —33°. When reaction was complete the ammonia was evaporated, the milky suspension was hydrolysed with aqueous ammonium chloride, and the ether layer dried over sodium sulphate. Evaporation and recrystallisation from methanol, and drying at 100°/1 Torr, produced a white powder. Yield 26%. (Found: C, 57.0; H, 3.7. $C_{30}H_{24}Sb_2$ calc.: C, 57.4; H, 3.8%).

(ii). The preparation was also attempted from *o*-bromophenyldiphenylstibine, butyllithium, and diphenylchlorostibine, by a method similar to that used to obtain *o*-diphenylarsinophenyldiphenylstibine [5]. A considerable quantity of insoluble grey solid was obtained, whilst evaporation of the ether extract yielded a white solid (≈ 1 g). (Found: C, 49.8; H, 3.4%. M.p. 58°.)

(iii). The reaction of *o*-dichlorobenzene and sodium diphenylstibide in THF/liquid ammonia solution was conducted in a similar manner to the preparation of $Ph_2SbCH_2SbPh_2$ [2]. The reaction is very slow; when carried out on a 0.2 molar scale taking ≈ 20 h for completion. Work up yielded a white powder (Table 1).

Attempted preparation of cis- and trans-1,2-bis(diphenylstibino)ethylene

These reactions were conducted as described in (*iii*) above, but with *cis*- or *trans*-1,2-dichloroethylene in place of the *o*-dichlorobenzene. The products obtained are listed in Table 1.

Results and discussion

o-Phenylenebis(diphenylstibine) (sbsb) was prepared in relatively low yield (26%) from sodium diphenylstibide and *o*-bromophenyldiphenylstibine,

TABLE 1

REACTIONS ATTEMPTED

Reaction	Product analysis (%)		M.p. (°C)	Identity
	C	H		
o-$C_6H_4Br(SbPh_2) + NaSbPh_2$	57.0	3.7	198-200	*o*-$C_6H_4(SbPh_2)_2$
o-$C_6H_4Br(SbPh_2) + BuLi + Ph_2SbCl$	50.4	3.7	58	*o*-$C_6H_4Br(SbPh_2)$ [c]
o-$C_6H_4Cl_2 + 2NaSbPh_2$ [a]	50.6	3.7	79-81	$Ph_2SbOSbPh_2$ [d]
o-$C_6H_4Cl_2 + 2NaSbPh_2$ [b]	50.7	3.6	79-81	$Ph_2SbOSbPh_2$
cis-$ClCHCHCl + 2NaSbPh_2$	50.4	3.7	79	$Ph_2SbOSbPh_2$
trans-$ClCH_2CH_2Cl + 2NaSbPh_2$	50.1	3.7	80-81	$Ph_2SbOSbPh_2$
$ClCH_2CH_2Cl + 2NaSbPh_2$	50.8	3.5	79-81	$Ph_2SbOSbPh_2$

[a] *o*-$C_6H_4Cl_2$ added to stibide solution. [b] Inverse addition. [c] Small quantity of unreacted starting materials. [d] Lit. [9] m.p. 82°. Calc. C, 50.7; H, 3.5%.

TABLE 2

MASS SPECTRAL AND INFRARED DATA

o-$C_6H_4(SbPh_2)_2$			$Pb_2SbOSbPh_2$		
m/e[a]	*I* (%)	Fragment	*m/e*	*I* (%)	Fragment
626	14	$C_{30}H_{24}Sb_2$	566	1	$C_{24}H_{20}Sb_2O$
549	23	$C_{24}H_{19}Sb_2$	489	0.4	$C_{18}H_{15}Sb_2O$
352	11	$C_{18}H_{15}Sb$	412	3.5	$C_{12}H_{10}Sb_2O$
351	4	$C_{18}H_{14}Sb$	352	3.5	$C_{18}H_{15}Sb$
275	64.5	$C_{12}H_{10}Sb$	275	15	$C_{12}H_{10}Sb$
273	61.5	$C_{12}H_8Sb$	273	8	$C_{12}H_8Sb$
198	78	C_6H_5Sb	198	51	C_6H_5Sb
197	14	C_6H_4Sb	197	9	C_6H_4Sb
154	100	$C_{12}H_{10}$	154	100	$C_{12}H_{10}$
153	28	$C_{12}H_9$	153	19	$C_{12}H_9$
152	39	$C_{12}H_8$	152	14	$C_{12}H_8$
121	2	Sb	121	2.5	Sb

o-$C_6H_4(SbPh_2)_2$	$Pb_2SbOSbPh_2$
3050 m, 1575 w, 1480 s, 1440 s, 1250 s, 1170 m, 1150 m, 1065, 1045 w, 1000 w, 780 s, 740 s, 730 s, 695 s, 680 s, 605 m, 545 m, 510 m, 450 s, 410 m, 360 w, 340 w, 250 m	3050 s, 1470 s, 1433 m, 1427 s, 1325 w, 1300 w, 1170 m, 1065, 1058 w, 1020 m, 995 m, 740 s, 730 s, 695 s, 660 s, 630 s, 510 s, 475 s, 440 s, 315 s, 275 w, 236 m

[a] Only ^{121}Sb peaks listed.

and was identified by analysis and mass spectrometry*. The major fragments in the mass spectrum are listed in Table 2. An alternative preparation from o-bromophenyldiphenylstibine, butyllithium, and diphenylchlorostibine, which is an analogous method to that used [5] to prepare other o-$C_6H_4(EPh_2)(E'Ph_2)$ (E, E' = P, As, Sb) compounds failed. The only solid obtained from the ether extract was a small quantity of unreacted starting material; the major product appeared to be an insoluble grey powder. The failure of this reaction is probably attributable to the fission of C—Sb bonds by the butyllithium, a reaction known to occur in other systems [11, 12]. The most direct potential synthesis from o-dichlorobenzene and sodium diphenylstibide was examined, both by addition of the stibide solution to the dichlorobenzene and by addition in the reverse order. This procedure was adopted since previous work has shown that excess nucleophile causes appreciable decomposition of o-$C_6H_4Br(SbMe_2)$ [6]. In fact, the same product was isolated irrespective of the mode of mixing and was identified by analysis and mass spectrometry as $Ph_2SbOSbPh_2$, bis(diphenylstibine)-oxide. The most likely source of the latter appeared to be reaction of the dichlorobenzene with sodium diphenylstibide to yield tetraphenyldistibine, which oxidises to $Ph_2SbOSbPh_2$ during workup. In order to confirm this, the reaction of 1,2-dichloroethane with sodium diphenylstibide, which is known

---

* o-Phenylenebis(dimethylstibine) can be obtained analogously in 30% yield.

[9, 13] to yield $Ph_2SbSbPh_2$, was performed in the same way and, as expected, yielded bis(diphenylstibine)oxide*.

The reaction of *cis*- and *trans*-1,2-dichloroethylene was examined in order to (a) attempt to prepare distibines with ethylenic backbones, and (b) determine if the reaction is stereospecific, as are the corresponding reactions with diphenylphosphide and -arsenide ions [14, 15]. In fact, both reactions yielded bis(diphenylstibine)oxide, probably via tetraphenyldistibine. Thus we conclude that, like 1,2-dichloroethane [12], the dichloroethylenes undergo elimination rather than substitution. Since little spectroscopic information is available on bis(diphenylstibine)oxide we list the mass spectral and infrared absorptions in Table 2. The proton NMR spectrum shows a broad phenyl multiplet at τ 2.4 (CCl_4 solution).

Metal complexes. The ligand sbsb exhibits no reaction with nickel(II) or cobalt(II) salts, even in solvents of very weak donor power (e.g. dichloromethane), as expected by extrapolation from the properties of o-$C_6H_4(AsPh_2)(SbPh_2)$ or $Ph_2SbCH_2SbPh_2$ [5]. The only palladium(II) complexes formed, even in the presence of a considerable excess of ligand, are the 1/1 $Pd(sbsb)X_2$ (X = Cl, Br, I, SCN) species [16], which are planar Sb_2X_2 chromophores.

Acknowledgements

WL and SGM are grateful to The Science Research Council for the award of Research Studentships, and to Dr. R.D. Sedgwick for obtaining mass spectra.

References

1 W. Levason and C.A. McAuliffe, Inorg. Chim. Acta, submitted.
2 Y. Matsumura and R. Okawara, J. Organometal. Chem., 25 (1970) 439.
3 S. Sato, Y. Matsumura, and R. Okawara, J. Organometal. Chem., 43 (1972) 333.
4 B.R. Cook, C.A. McAuliffe and D.W. Meek, Inorg. Chem., 10 (1971) 2676 and refs. therein.
5 W. Levason and C.A. McAuliffe, Inorg. Chim. Acta, 11 (1974) 33.
6 E. Schewchuk and S.B. Wild, J. Organometal. Chem., 71 (1974) C1.
7 L. Baracco and C.A. McAuliffe, J. Chem. Soc. Dalton Trans., (1972) 948.
8 W. Levason, C.A. McAuliffe and R.D. Sedgwick, J. Organometal. Chem., 84 (1975) 239.
9 K. Isslieb and B. Hamaan, Z. Anorg. Allg. Chem., 343 (1966) 196.
10 H.H. Jaffé and G.O. Doak, J. Amer. Chem. Soc., 72 (1950) 3027.
11 L.A. Woods, Iowa State Coll. J. Sci., 19 (1944) 61.
12 L.A. Woods and H. Gilman, Proc. Iowa Acad. Sci., 48 (1941) 251.
13 W. Hewertson and H.R. Watson, J. Chem. Soc., (1962) 1490.
14 A.M. Aguiar and D. Daigle, J. Amer. Chem. Soc., 86 (1964) 2299.
15 K.K. Chow, Ph. D. Thesis, University of Manchester, 1972.
16 W. Levason, C.A. McAuliffe and S.G. Murray, unpublished results.

---

* The workup procedure used here has been successfully used to prepare numerous phosphine and arsine ligands, as well as bis(diphenylstibino)alkanes, although clearly it is not sufficiently anaerobic to handle a compound as air-sensitive as Ph_4Sb_2.