

## SHORT COMMUNICATIONS

### ORGANOMERCURY COMPOUNDS\*

#### III.† ACCEPTOR PROPERTIES OF BIS(PENTACHLOROPHENYL)MERCURY

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The recently reported pentachlorophenylmercury compounds<sup>1</sup> have thermal stabilities, and cleavage reactions with hydrogen chloride, similar to those of the corresponding pentafluorophenylmercury compounds.<sup>2</sup> However, in the present study it has been found that the acceptor properties of bispentachlorophenylmercury towards bidentate ligands are very different from those of bispentafluorophenylmercury.<sup>2,3</sup> With 1,2-bisdiphenylphosphinoethane (biphos), 2,2'-bipyridyl (bipy), and 1,10-phenanthroline (phen), bispentafluorophenylmercury gives the complexes  $\text{Hg}(\text{C}_6\text{F}_5)_2$  biphos,  $\text{Hg}(\text{C}_6\text{F}_5)_2$  bipy, and  $\text{Hg}(\text{C}_6\text{F}_5)_2$  phen, respectively. However, from reactions of bispentachlorophenylmercury with 2,2'-bipyridyl and 1,10-phenanthroline, the free mercurial is recovered in high yield even when a 10:1 mole ratio of ligand: $\text{Hg}(\text{C}_6\text{Cl}_5)_2$  is used. Similarly,  $\text{Hg}(\text{C}_6\text{Cl}_5)_2$  is recovered from reaction with 3,4,7,8-tetramethyl-1,10-phenanthroline (tmp) using a 5:1 mole ratio of tmp: $\text{Hg}(\text{C}_6\text{Cl}_5)_2$ , but a solid, approximate composition  $\text{Hg}(\text{C}_6\text{Cl}_5)_2 \cdot 2\text{tmp}$  (A), is obtained when the mole ratio is 10:1. Attempted recrystallization of (A) gives  $\text{Hg}(\text{C}_6\text{Cl}_5)_2$  as excess ligand is not present. By contrast,  $\text{Hg}(\text{C}_6\text{F}_5)_2$  reacts with an equimolar amount of tetramethylphenanthroline to give  $\text{Hg}(\text{C}_6\text{F}_5)_2$  tmp, and this complex can be recrystallized unchanged as can previously reported complexes of this acceptor.

Although the X-ray powder photograph of (A) shows lines indicative of the presence of free ligand, it is definitely different from the powder photograph of a mixture of 3,4,7,8-tetramethyl-1,10-phenanthroline and bispentachlorophenylmercury in a 2:1 mole ratio (B). There are similarities between the powder photograph of (A) and that of an equimolar mixture of tetramethylphenanthroline and  $\text{Hg}(\text{C}_6\text{F}_5)_2$  tmp. Accordingly it is likely that (A) is an approximately equimolar mixture of tetramethylphenanthroline and the 1:1 complex,  $\text{Hg}(\text{C}_6\text{Cl}_5)_2$  tmp. Further evidence for this composition is provided by the infrared spectrum of (A) in the region 880–810  $\text{cm}^{-1}$ . The bands of relevant compounds are listed in Table 1, and for convenience those

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<sup>1</sup> Paulik, F. E., Green, S. I. E., and Dessey, R. E., *J. organomet. Chem.*, 1965, **3**, 229.

<sup>2</sup> Chambers, R. D., Coates, G. E., Livingstone, J. G., and Musgrave, W. K. R., *J. chem. Soc.*, 1962, 4367.

<sup>3</sup> Connett, J. E., Davies, A. G., Deacon, G. B., and Green, J. H. S., *J. chem. Soc. C*, 1966, 106.

of tetramethylphenanthroline are numbered. Ligand absorption in this region has been assigned to C-H out-of-plane deformation modes.<sup>4</sup> Bands (1) and (3) of tetramethylphenanthroline can be identified at similar frequencies in the spectrum of the mixture (B), but in  $\text{Hg}(\text{C}_6\text{F}_5)_2$  tmp (1) is shifted to higher and (3) to lower frequencies. The second band coincides with strong absorption of  $\text{Hg}(\text{C}_6\text{Cl}_5)_2$  at  $853\text{ cm}^{-1}$  and is only slightly displaced in  $\text{Hg}(\text{C}_6\text{F}_5)_2$  tmp. In the spectrum of (A), absorption is found both at frequencies corresponding to the free ligand values of (1) and (3) and also at frequencies corresponding to the values of (1) and (3) in  $\text{Hg}(\text{C}_6\text{F}_5)_2$  tmp. This observation is consistent with the formulation of (A) as an approximately equimolar mixture of the complex  $\text{Hg}(\text{C}_6\text{Cl}_5)_2$  tmp and free tetramethylphenanthroline. An attempt to remove the free ligand by washing (A) with boiling methanol gave bispentachlorophenylmercury.

The main factor inhibiting isolation of complexes of bispentachlorophenylmercury with bidentate ligands is the low solubility of the mercurial. (The only satisfactory solvent is hot nitrobenzene.) Thus unless it forms stable complexes or unless the dissociation of the complexes can be suppressed by the addition of excess ligand, crystallization of the mercurial is favoured. By contrast,  $\text{Hg}(\text{C}_6\text{F}_5)_2$ -biphos and  $\text{Hg}(\text{C}_6\text{H}_5)_2$  bipy can be crystallized even though dissociation into free ligand and mercurial is nearly complete in acetone or benzene.<sup>3</sup> A further factor which may inhibit complex formation by  $\text{Hg}(\text{C}_6\text{Cl}_5)_2$  is steric repulsion between chlorine atoms *ortho* to mercury and the donor atoms of the ligand molecule, and similar interactions may impede solvation of the mercurial and contribute to the low solubility.

### Experimental

Microanalyses were carried out by the Australian Microanalytical Service, Melbourne. Melting points are uncorrected. Those of derivatives of 3,4,7,8-tetramethyl-1,10-phenanthroline are somewhat dependent on the rate of heating, probably owing to decomposition, and hence are approximate. Molecular weights in AnalaR benzene at  $25^\circ$  were measured with a Mechrolab 301A vapour pressure osmometer. Infrared spectra ( $1800\text{--}600\text{ cm}^{-1}$ ) of compounds as Nujol and hexachlorobutadiene mulls were recorded with a Perkin-Elmer 521 spectrophotometer. X-ray powder photographs were obtained with a Philips-Debye-Scherrer 114.6-mm powder camera using nickel filtered Cu K $\alpha$  radiation, and were examined with a double-beam microdensitometer.

### Reagents

*Bispentachlorophenylmercury*, m.p.  $>300^\circ$  (lit.<sup>1</sup>  $383^\circ$ ) (Found: C, 20.5; Cl, 50.2. Calc. for  $\text{C}_{12}\text{Cl}_{10}\text{Hg}$ : C, 20.6; Cl, 50.7%) was prepared and purified by the reported method,<sup>1</sup> and was further characterized by conversion into pentachlorophenylmercuric chloride, m.p.  $260^\circ$  (lit.<sup>1</sup>  $264^\circ$ ) (Found: C, 15.4; Cl, 43.7. Calc. for  $\text{C}_6\text{Cl}_5\text{Hg}$ : C, 14.85; Cl, 43.8%).

*Bispentafluorophenylmercury*.—The preparation has been reported.<sup>3</sup>

*3,4,7,8-Tetramethyl-1,10-phenanthroline* (Monsanto) was recrystallized several times from methanol (Found: C, 80.9; H, 6.9; N, 11.9. Calc. for  $\text{C}_{18}\text{H}_{16}\text{N}_2$ : C, 81.35; H, 6.8; N, 11.9%).

### Reactions of Bispentachlorophenylmercury with Bidentate Ligands

*With 2,2'-bipyridyl*.—Bispentachlorophenylmercury (0.35 g, 0.50 mmole) and 2,2'-bipyridyl (0.80 g, 5.00 mmole) were refluxed in boiling nitrobenzene (35 ml). On cooling, the solution deposited white crystals, which were filtered off, washed with nitrobenzene, benzene, and light petroleum (b.p.  $30\text{--}40^\circ$ ), and dried at  $130^\circ$ . They were identified as  $\text{Hg}(\text{C}_6\text{Cl}_5)_2$  (0.33 g, 0.47 mmole, 94%) by infrared spectroscopy.

<sup>4</sup> Grigg, E. C. M., and Hall, J. R., *Aust. J. Chem.*, 1962, **15**, 864.

With 1,10-phenanthroline.—From a similar experiment with a phen : Hg(C<sub>6</sub>Cl<sub>5</sub>)<sub>2</sub> mole ratio of 10 : 1, the mercurial was recovered in 87% yield.

With 3,4,7,8-tetramethyl-1,10-phenanthroline.—From a similar experiment with a tmp : Hg(C<sub>6</sub>Cl<sub>5</sub>)<sub>2</sub> mole ratio of 5 : 1, the mercurial was recovered in 90% yield.

From a similar reaction between bispentachlorophenylmercury (0.20 g, 0.29 mmole) and tetramethylphenanthroline (0.69 g, 2.92 mmole) in nitrobenzene (25 ml), a white crystalline solid (A) (0.25 g), m.p. c. 243° (dec.) (Found: C, 43.5; H, 3.0; Cl, 31.1; N, 5.1. Calc. for C<sub>44</sub>H<sub>32</sub>Cl<sub>10</sub>HgN<sub>4</sub> [Hg(C<sub>6</sub>Cl<sub>5</sub>)<sub>2</sub>,2tmp]: C, 45.05; H, 2.7; Cl, 30.3; N, 4.8. Calc. for C<sub>28</sub>H<sub>16</sub>Cl<sub>10</sub>HgN<sub>2</sub>·[Hg(C<sub>6</sub>Cl<sub>5</sub>)<sub>2</sub>,tmp]: C, 35.9; H, 1.9; Cl, 37.9; N, 3.0%) was obtained. Infrared absorption: 1612w (br), 1573w, 1518s, 1424s, 1381m, 1369sh, 1325vs, 1296s, 1275sh, 1268sh, 1237m, 1197m, 1165w (br), 1145sh, 1078w, c. 1007vw(br), 947w, 923w, 875w, 865vw, 857sh, 849s, 828w, 813w, 735sh, 728s, 714vw, 678vs, 608vw. Additional weak absorption at 1533, 1349, and 704 cm<sup>-1</sup> indicated a trace of nitrobenzene,<sup>5</sup> which could not be removed by drying at 130°. The mixture (B) has similar infrared absorption, except in the 880–810 cm<sup>-1</sup> region (Table 1) and the band at 683 cm<sup>-1</sup> has only medium intensity (cf. 678vs for (A)). Recrystallization of (A) (0.07 g) from nitrobenzene gave bispentachlorophenylmercury (0.03 g, 70%), identified by the infrared spectrum. Washing of (A) (0.07 g) with 100 ml of boiling methanol also gave Hg(C<sub>6</sub>Cl<sub>5</sub>)<sub>2</sub>.

TABLE I  
INFRARED ABSORPTION BANDS (880–810 cm<sup>-1</sup>)

tmp <sup>a</sup>	Mixture (B)	Hg(C <sub>6</sub> F <sub>5</sub> ) <sub>2</sub> tmp	Product (A)
		875m	875w
(1) 866m	864sh		865vw
		856w	857sh
(2) 852s	851s <sup>b</sup>		849s <sup>b</sup>
(3) 829s	827m		828w
		814w	813w

<sup>a</sup> Reported<sup>4</sup> values 861m, 847m, 823s.

<sup>b</sup> Hg(C<sub>6</sub>Cl<sub>5</sub>)<sub>2</sub> has strong absorption at 853 cm<sup>-1</sup>.

#### Bispentafluorophenyl-3,4,7,8-tetramethyl-1,10-phenanthroline-mercury

Bispentafluorophenylmercury (0.27 g, 0.50 mmole) and 3,4,7,8-tetramethyl-1,10-phenanthroline (0.12 g, 0.50 mmole) were dissolved in boiling benzene (20 ml). After evaporation to 5 ml, boiling hexane (35 ml) was added, and the required compound crystallized on cooling. Recrystallized from benzene/hexane, the complex (0.27 g, 0.35 mmole, 70%) had m.p. c. 214° (dec.) (Found: C, 44.1; H, 2.1; F, 25.3; N, 3.7; mol. wt., 730 (1.17% w/v); mol. wt., 708 (0.80% w/v). Calc. for C<sub>28</sub>H<sub>16</sub>F<sub>10</sub>HgN<sub>2</sub>: C, 43.6; H, 2.1; F, 24.7; N, 3.7%; mol. wt., 771). Infrared absorption: 1764w, 1636m, 1615w, 1582sh, 1576w, 1521sh, 1510vs, 1462vs (br), 1431s, 1378s, 1364s, 1271m, 1244m, 1198m, 1078s, 1062s, 1015m, 966vs, 927m (br), 875m, 856w, 814w, 796m, 728s, 722sh, 638vw (br), 611m.

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<sup>5</sup> Kross, R. D., and Fassel, V. A., *J. Am. chem. Soc.*, 1956, 78, 4225.