ORGANOMERCURY COMPOUNDS

XV*. THE ACCEPTOR PROPERTIES OF DIPHENYLMERCURY

A. J. CANTY** and G. B. DEACON

Chemistry Department, Monash University, Clayton, Vic. 3168 (Australia)

SUMMARY

Crystalline adducts, $Ph_2Hg \cdot 2L$ (L = 1,10-phenanthroline, 2,9-dimethyl-1,10-phenanthroline, and 2,4,7,9-tetramethyl-1,10-phenanthroline), have been prepared by reaction of diphenylmercury and the appropriate ligands in hexane, but derivatives of the mercurial with a range of ligands having nitrogen, phosphorus, arsenic and oxygen donor atoms could not be prepared. No definite evidence for coordination of the phenanthroline ligands in the solid adducts could be obtained by infrared or ultraviolet spectroscopy. Molecular weights of the adducts in benzene or chloroform showed them to be completely dissociated in solution. Similar measurements for mixtures of the mercurial and a range of ligands in benzene showed no evidence for complex formation. Thus, any acceptor properties of diphenylmercury appear to be very weak.

INTRODUCTION

Isolable complexes of diorganomercurials, R_2Hg, are restricted to mercurials in which the organic groups contain highly electronegative substituents[2–10]. Unsuccessful attempts to prepare complexes between diphenylmercury and 2,2'-bipyridine[3] or ethylenediamine[11] have been reported. On the other hand, end points in oscillometric titrations of diphenylmercury with ligands (*e.g.* pyridine or triphenylphosphine) in benzene have been interpreted as indicating complex formation[12], and PMR data suggest that solvation of dimethylmercury and dibenzylmercury by polar solvents may involve a weak donor–acceptor interaction[13]. In the present investigation, we have examined the possibility of preparing complexes of diphenylmercury with a range of ligands, and have studied possible complex formation between this mercurial and ligands in benzene by molecular weight measurements.

RESULTS AND DISCUSSION

(a). Attempted syntheses of complexes of diphenylmercury

The adducts, $Ph_2Hg \cdot 2L\star$ [L=2,9-dimethyl-1,10-phenanthroline (Dmp), 1,10-phenanthroline (Phen), or 2,4,7,9-tetramethyl-1,10-phenanthroline (2-Tmp)] were precipitated on mixing hexane solutions of the mercurial and ligand or ligand hydrate in mole ratios of 1/2 or 1/1. However, similar attempts to prepare derivatives with 3,4,7,8-tetramethyl-1,10-phenanthroline (3-Tmp), 2,2'-bipyridine (Bipy), 4,4'-dimethyl-2,2'-bipyridine (Me₂Bipy), 2,2'-biquinoline (Biqy), 2,2'-6',2''-terpyridine (Terpy), ethylenediamine, o-phenylenediamine (Opd), di-2-pyridylamine (Dpa), pyridine, 4-cyanopyridine (Cpy), diphenylamine, triphenylphosphine, triphenylphosphine oxide, triphenylarsine, bis(diphenylphosphino)methane, bis(diphenylarsino)methane, 1,2-bis(diphenylphosphino)ethane, or 1,2-bis(diphenylarsino)ethane, were unsuccessful, whereas bis(pentafluorophenyl)mercury gives complexes with all ligands except triphenylarsine[3,4,7,10]. The absence of an adduct with 3-Tmp in contrast to the other 1,10-phenanthrolines may be attributed to its low solubility. The failure to isolate derivatives with pyridine, triphenylphosphine, and triphenylarsine from hexane, may be contrasted with the detection, by oscillometry[12], of interactions between the mercurial and these ligands in the more polar solvent, benzene.

(b). Properties of the adducts, $Ph_2Hg \cdot 2L$

X-ray powder photography established that the adducts are not mixtures of crystals of diphenylmercury and ligands or ligand hydrates. The infrared spectra of the adducts (Experimental section) confirm the absence of ligand hydrates, but show no features indicative of coordination of the phenanthroline ligands in the region 1650–400 cm⁻¹ [cf. $(C_6F_5)_2HgPhen$ or $(C_6F_5)_2Hg(2\text{-Tmp})^{10}$]. In the far infrared spectrum (400–70 cm⁻¹) of $Ph_2Hg \cdot 2Dmp$, the absorption near 250 cm⁻¹, attributable[14] to the "X-sensitive" mode *t* of the PhHg group, differs slightly from that of the free mercurial (258 s, 252 s, and 248 (sh) cm⁻¹), and the "X-sensitive" mode *u*, at 207 cm⁻¹ in Ph_2Hg^{14}, is split into two components (216 and 205 cm⁻¹). These changes indicate an alteration in the environment of diphenylmercury, though not necessarily due to coordination. No absorption attributable to mercury–nitrogen stretching is observed. Assignment of one of the bands at 216 and 205 cm⁻¹ to this mode is ruled out, because $v(M–N)$ of four- and six-coordinate pyridine and quinoline complexes of divalent zinc and first row transition elements, are at comparable or only slightly higher frequencies[15].

The ultraviolet absorption bands of $Ph_2Hg \cdot 2Phen$ (Table 1) do not show the shifts to longer wavelengths from free ligand values, often observed for 1,10-phenanthroline complexes[16], nor are corresponding shifts obtained for $Ph_2Hg \cdot 2Dmp$ or $Ph_2Hg \cdot 2(2\text{-Tmp})$. Nevertheless, this is not unequivocal evidence against complex formation, since the corresponding $(C_6F_5)_2HgL$ complexes do not show significant shifts apart from the highest wavelength band of $(C_6F_5)_2HgDmp$ (Table 1).

Molecular weights of $Ph_2Hg \cdot 2(2\text{-Tmp})$ in chloroform indicate that complete dissociation into diphenylmercury and free ligand occurs in solution. Values for

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    * The term "adduct" and the representation $R_2Hg \cdot xL$, in contrast with "complexes" and R_2HgL_x, is used for compounds in which the ligand is not coordinated, or in which the role of the ligand is uncertain.

TABLE 1

ULTRAVIOLET ABSORPTIONS (225–400 nm) OF ADDUCTS OF DIPHENYLMERCURY AND CORRESPONDING COMPLEXES OF BIS(PENTAFLUOROPHENYL)MERCURY[a]

| Ligand (L)[b]		$Ph_2Hg \cdot 2L$	$(C_6F_5)_2HgL$
Phen	228, 233, 267	227, 233, 265	227, 234, 267
Dmp	229, 235, 270, 281(sh)	230, 235, 271, 281(sh)	229, 236, 274, 295(sh)
2-Tmp	235, 242, 271, 304	234, 241, 270, 307	234, 241, 275, 308

[a] Compounds examined as Nujol mulls. [b] Phen · H$_2$O and Dmp · 0.5 H$_2$O used.

$Ph_2Hg \cdot 2Dmp$ and $Ph_2Hg \cdot 2Phen$ in benzene (Experimental section) are consistent with the formation of less than three particles per molecule of adduct by a small (5–13 %) but significant amount (experimental error 3 %), suggesting some complex formation in solution. However, if moisture is rigorously excluded, molecular weights of $Ph_2Hg \cdot 2Dmp$ indicate complete dissociation. Apparently, if some water is present in the solvent, its removal by the formation of ligand hydrate (solid Dmp · 0.5H$_2$O and Dmp · 2H$_2$O are known)[17], slightly reduces the overall number of particles from

$$Ph_2Hg \cdot 2Dmp \rightarrow Ph_2Hg + 2Dmp$$

$$Dmp + nH_2O \rightleftharpoons Dmp \cdot nH_2O$$
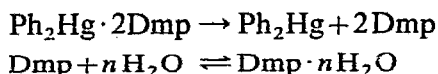
that expected for complete dissociation of the adduct. The infrared spectrum of Dmp · 0.5H$_2$O (0.076 mol · dm^{-3}) in benzene shows very broad absorption due to hydrogen-bonded water at 3420 cm^{-1} [cf. 3450 m, 3300 w for solid Dmp · 0.5H$_2$O and 3420 s, 3260 w for solid Dmp · 2H$_2$O][17], confirming that some hydration of 2,9-dimethyl-1,10-phenanthroline is possible in this solvent. The molecular weight data for $Ph_2Hg \cdot 2Phen$ can be similarly explained, and partial hydration of 1,10-phenanthroline in benzene has been demonstrated[18].

Thus, spectroscopic and molecular weight data provide no definite evidence for coordination of the phenanthroline ligands, indicating either that coordination is very weak, or that the adducts are inclusion compounds like $Et_2Hg \cdot 5.43(NH_2-CONH_2)$[19]. Investigation of the crystal structures of $Ph_2Hg \cdot 2Dmp$ and $Ph_2Hg \cdot 2(2-Tmp)$ has not unequivocally established the role of the phenanthroline ligands, since the structures could not be refined owing to disorder[20]. In the adducts, the ligand molecules lie in parallel planes, perpendicular to the linear C–Hg–C units of the Ph_2-Hg moieties, each of which has one adjacent ligand molecule (I), and one half of the

(I)

R = Me or H
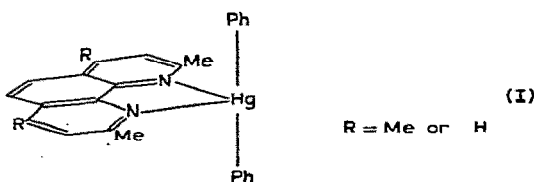
ligand molecules do not have adjacent mercury atoms. The mercury–nitrogen distances in (I) are in the range 2.8–3.0 Å (cf. 2.60 Å for Py_2HgCl_2[21]; 2.80 Å for ClHgSCN[22]; 3.00 Å or possibly 3.23 Å for the sum of the appropriate Van der Waals

radii[22]). Because the errors are unknown, it is not clear whether the mercury–nitrogen distance is slightly less than the sum of the Van der Waals' radii, as expected[22] for very weak N–Hg coordination. We consider that some weak coordination probably occurs because each mercury is adjacent to and approximately equidistant from two nitrogen atoms, and because it accounts for two different types of phenanthroline molecule in the adducts.

(c). *Molecular weights of mixtures of diphenylmercury and ligands*

Molecular weights of mixtures of diphenylmercury and fourteen ligands in benzene (Table 2) show no evidence for complex formation (*cf.* oscillometric titration data for Ph_3P and Ph_3As[12]). Some mixtures of diphenylmercury and 4-cyanopyridine or di-2-pyridylamine give molecular weights which exceed the values for no complex formation by an amount (3–5%) slightly greater than experimental error, but this is due to slight ligand association (see Table 2 for data for Dpa, and ref. 10 for Cpy).

TABLE 2

MOLECULAR WEIGHT DATA FOR MIXTURES OF LIGANDS AND DIPHENYLMERCURY IN BENZENE

Composition of mixture $Ph_2Hg + x L$	Mol. wt. calcd. for no complex formed	Mol. wt. observed	% w/v[a]	Mol. wt. observed	% w/v[a]
$Ph_2Hg + 1$ Bipy	256	254	0.63	249	0.99
$Ph_2Hg + 2$ Bipy	222	216	0.81	224	0.87
$Ph_2Hg + 2$ Me_2 Bipy	241	238	0.77	242	0.85
$Ph_2Hg + 2$ Terpy	274	274	1.10	269	1.34
$Ph_2Hg + 2$ Bipy	289	288	0.55	294	0.76
$Ph_2Hg + 1$ Cpy	229	240	0.97	242	1.17
$Ph_2Hg + 1$ Ph_2NH	262	260	0.68	263	1.04
$Ph_2Hg + 1$ Ph_3PO	317	324	1.26	323	1.61
$Ph_2Hg + 4$ Ph_3PO	294	295	1.17	294	1.58
$Ph_2Hg + 1$ Ph_3P	309	307	0.76	301	1.20
$Ph_2Hg + 2$ Ph_3P	293	287	1.05	289	1.18
$Ph_2Hg + 4$ Ph_3P	281	275	1.00	282	1.19
$Ph_2Hg + 2$ $(Ph_2P)_2CH_2$	375	370	1.33	365	1.56
$Ph_2Hg + 2(Ph_2PCH_2)_2$	384	380	1.09	385	1.25
$Ph_2Hg + 4$ Ph_3As	316	317	1.27	311	1.40
$Ph_2Hg + 2(Ph_2As)_2CH_2$	433	431	1.51	425	1.90
$Ph_2Hg + 2(Ph_2AsCH_2$	442	434	1.53	431	1.82
$Ph_2Hg + 2$ Dpa	232	241	0.95	239	0.97
Dpa	171	187	0.29	188	0.47

[a] % (Total weight of reactants)/v

(d). *Conclusions*

Attempted preparations, structural data, and molecular weights in benzene [Sections (a)–(c)] show that the acceptor properties of diphenylmercury are very weak. The apparent difference between these results and the earlier detection of Ph_2HgL_n ($n = 1$ or 2; L = Ph_3P, Ph_3As, Py, Me_2CO, or EtOH) complexes by oscillometric titrations[12] requires further comment. The significance of interactions detected by

oscillometry is hard to evaluate, since its provides no indication of absolute or relative stabilities[12]. Indeed some results, e.g. detection of $Ph_2HgAsPh_3$ but not of $(CF_3)_2$-$HgAsPh_3$, are at variance with known stability trends, e.g. $(CF_3)_2HgPhen$ is monomeric[5], and $Ph_2Hg \cdot 2Phen$ dissociated in benzene (see above). The present study cannot provide specific stability data, as no complexes have been detected in benzene. Upper limits for stability constants (K) of possible Ph_2HgL complexes in benzene in terms of the reaction, $Ph_2Hg + L \rightleftharpoons Ph_2HgL$, can be calculated from observed molecular weights plus experimental error (3 %), except for cases where ligand hydration or association occurs, and indicate $K < 10$ for all complexes, and $K < 5$ for most, including Ph_2HgPPh_3 and $Ph_2HgAsPh_3$. However, these limits may be more a reflection of experimental error than a guide to actual stabilities. Certainly many stabilities must be much lower than these limits, e.g. for Ph_2HgL [L = Ph_2NH, Ph_3P, $(Ph_2$-$PCH_2)_2$, or $(Ph_2AsCH_2)_2$] complexes, since the corresponding $(C_6F_5)_2HgL$ derivatives have $K < 4$* and complexes of $(C_6F_5)_2Hg$ are much more stable than those of Ph_2Hg, e.g. $K < 10$ for Ph_2HgDmp in benzene, but $K \approx 1200$* for $(C_6F_5)_2HgDmp$ in the more polar acetone. Low stabilities are also indicated by the general failure to prepare complexes in hexane, which is satisfactory for syntheses of the less stable ($K < 4$) complexes of bis(pentafluorophenyl)mercury[10]. Accordingly, we consider that interactions between diphenylmercury and ligands detected by oscillometry probably involve very weak metal–ligand contacts near the sum of the appropriate Van der Waals' radii, as in $Ph_2Hg \cdot 2L$ adducts. Weak solvation of dimethylmercury and dibenzylmercury in polar solvents, detected by small shifts in mercury–proton coupling constants, has been attributed to very weak bonding involving ligand lone pairs and empty p orbitals of a linear sp hybridized mercury atom[13]. Such a model also accommodates interactions between diphenylmercury and ligands, observed by oscillometry, and mercury–nitrogen interactions in $Ph_2Hg \cdot 2L$ adducts.

EXPERIMENTAL

Microanalyses were by the Australian Microanalytical Service, Melbourne. Molecular weights were determined in AnalaR benzene or chloroform at 25° with a Hewlett–Packard 302 osmometer. Concentrations of adducts are given as %w/v. Two determinations of the molecular weight of $Ph_2Hg \cdot 2Dmp$ were carried out in sodium-dried benzene under dry nitrogen as described previously[23]. Far-infrared spectra (400–70 cm^{-1}) of compounds as vaseline mulls were recorded with a Perkin–Elmer 301 spectrophotometer. A description of the other techniques has been given[10].

Reagents

Diphenylmercury (K & K) was recrystallized from hexane, and had infrared absorption in agreement with that reported[14]. The sources and purification of the ligands and the preparation of complexes of bis(pentafluorophenyl)mercury have been reported[10].

Preparations of adducts of diphenylmercury

With 2,9-dimethyl-1,10-phenanthroline. On addition of a solution of 2,9-dimethyl-1,10-phenantrholine hemihydrate (0.59 mmol) in boiling hexane (70 ml)

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* Stability constants or their upper limits for the complexes $(C_6F_5)_2HgL$ were calculated from reported molecular weight data[7,10].

to a solution of diphenylmercury (0.29 mmol) in boiling hexane (26 ml), a fine white precipitate of $Ph_2Hg \cdot 2Dmp$ (nc) was obtained and was washed with boiling hexane, yield 35%, m.p. 202°. [Found: C, 61.5; H, 4.4; N, 7.25; mol. wt. (in benzene), 274 (0.47%), n (no. of particles/molecule of adduct), 2.81; 297 (1.02%), n, 2.60; (in dry benzene under nitrogen), 263 (0.55%), n, 2.93; 249 (0.74%), n, 3.10. $C_{40}H_{34}HgN_4$ calcd.: C, 62.3; H, 4.4; N, 7.3%; mol. wt., 771.] Infrared absorption (4000–70 cm^{-1}): 3059 w, 3046 w, 1609 w(br), 1587 m(br), 1576 w, 1558 vw, 1547 w(br), 1496 m(br), 1476 w(br), 1442 w(br), 1420 w, 1401 vw, 1376 vw, 1355 vw, 1297 w(br), 1278 w(br), 1259 vw(br), 1240 w(br), 1222 w, 1204 w, 1144 m, 1080 w, 1030 w(br), 996 vw, 850 s, 738 s and 730 m, 704 m, 546 w, 463 w, 384 w, 315 w, 292 w, 254 s, 247 s, 216 m, 205 m, 161 m, and 113 s cm^{-1} (cf. $Dmp \cdot 0.5H_2O$ (400–70 cm^{-1}): 382 w, 329 vw, 298 s, 252 w, 234 w, 158 m and 123 s cm^{-1}). d spacings (Å): 7.23 m, 7.14 m, 5.88 s, 4.83 m, 4.08 m, 3.55 vs, 3.41 w, 2.86 w, 2.78 m, 2.50 vw, 2.41 vw, 2.31 w, 2.22 vw, 2.16 w, 1.86 w, and 1.41 w. Use of equimolar amounts of the reactants gave the same adduct, m.p. 202° (Found: C, 62.1; H, 4.55; N, 7.3%.), as also did a mole ratio of ligand to mercurial of 5/1 (IR identification).

With 1,10-phenanthroline. After addition of a solution of diphenylmercury (0.39 mmol) in hot hexane (15 ml) to a solution of 1,10-phenanthroline hydrate (0.79 mmol) in hot hexane (100 ml), the adduct $Ph_2Hg \cdot 2Phen$ (nc) crystallized on cooling, yield 14%, m.p. 121°. [Found: C, 60.1; H, 3.6; Hg, 27.2; N, 7.85; mol. wt. (in benzene), 250 (0.43%), n, 2.85; 255 (0.80%), n, 2.80. $C_{36}H_{26}HgN_4$ calcd.: C, 60.5; H, 3.7; Hg, 28.0; N, 7.8%; mol. wt., 715.] Infrared absorption (4000–400 cm^{-1}): 3044 w(br), 1617 m, 1590 w, 1562 m, 1556 m, 1504 s, 1479 m, 1419 vs, 1156 w, 1138 m, 1093 w, 1082 m, 1030 w, 998 w, 855 m, 840 s, 763 m, 737 and 732 vs, 705 s, 626 m, and 461 s cm^{-1}. d spacings (Å): 9.68 m(br), 8.17 w(br), 7.16 w(br), 5.84 m(br), 5.25 m(br), 4.85 w(br), 4.58 m(br), 4.41 m(br), 3.54 vs(br), 3.07 vw(br), 2.96 vw(br), 2.82 vw(br), and 2.30 w(br). Use of equimolar amounts of diphenylmercury and ligand gave the same adduct, m.p. 121°. (Found: C, 60.0; H, 3.7; Hg, 27.3; N, 7.85%.)

With 2,4,7,9-tetramethyl-1,10-phenanthroline. On addition of diphenylmercury (0.29 mmol) in hot hexane (6 ml) to 2,4,7,9-tetramethyl-1,10-phenanthroline (0.29 mmol) in hot hexane (26 ml), white microcrystals of $Ph_2Hg \cdot 2(2\text{-}Tmp)$ (nc) deposited immediately, yield 73%, m.p. 230–233° (dec.). [Found: C, 64.6; H, 5.3; Hg, 23.5; mol. wt. (in chloroform), 276 (0.32%), n, 3.00; 265 (0.62%), n, 3.12. $C_{44}H_{42}HgN_4$ calcd.: C, 63.9; H, 5.1; Hg, 24.2%; mol. wt., 827.] The compound was insufficiently soluble for molecular weight measurements in benzene. Infrared absorption (4000–400 cm^{-1}): 1617 w(br), 1582 m, 1552 w and 1538 w, 1479 m, 1474 vw(br), 1439 m(br), 1420 vw(br), 1379 w, 1363 w, 1349 vw(br), 1333 w, 1078 w, 1035 w(br), 960 w(br), 884 m, 808 m, 738 s, 723 m, 705 m, 682 w, 566 w, 533 w, 510 m, and 462 m cm^{-1}. d spacings (Å): 7.92 vw, 6.76 s, 5.73 s, 5.10 m, 4.71 w, 4.23 m, 3.63 w, 3.38 vs, 3.25 w, 2.74 w, 2.62 w, 2.54 w, 2.29 vw, 2.20 w, 2.13 vw, 2.09 vw, 1.88 vw, and 1.68 w. Use of a ratio of two moles of ligand to one of diphenylmercury yielded the same adduct, m.p. 230–233° (dec.) (IR identification).

Attempted preparations of other adducts. Mixtures of reactants were dissolved in hexane and the solution was evaporated to crystallization at room temperature, unless indicated otherwise. For the ligands, Bipy (mole ratio Ph_2Hg/ligand 1/2), Me_2Bipy (1/2 and 1/1), 3-Tmp (1/2 in benzene; 1/1 in hot hexane), Biqy (1/2), Cpy (1/1), Opd (1/1), Ph_2NH (1/1), Ph_3P (1/1), Ph_3PO (2/1 because of low ligand solubility),

Ph$_3$As (1/4), (Ph$_2$P)$_2$CH$_2$ (2/1), (Ph$_2$As)$_2$CH$_2$ (2/1), (Ph$_2$PCH$_2$)$_2$ (1/1 in benzene/ hexane), (Ph$_2$AsCH$_2$)$_2$ (1/2), either fractional crystallization of ligand and diphenyl-mercury occurred or manual separation of the reactants from the crystalline product was possible (m.p. and/or IR identification). With Terpy (1/2), a mixture of ligand and mercurial was deposited (IR and m.p. identification) and could not be separated manually. Diphenylmercury crystallized from solutions in petrol (b.p. 40–60°) containing an excess of pyridine or ethylenediamine. Evaporation of hexane solutions of diphenylmercury and di-2-pyridylamine gave either the usual form of the ligand [IR absorption (4000–625 cm^{-1}); 3236 m(br), 3152 m(br), 3082 m, 1603 vs(br), 1593 s, 1585 s, 1565 s, 1527 s(br), 1480 m, 1463 m. 1439 m, 1343 m, 1332 m, 1312 s, 1275 w, 1147 m, 1049 w (br), 997 m, 990 m, 909 w, 875 w (br), 768 vs, and 735 m(vbr) cm^{-1}], or a less usual form [m.p. 93.5–95.5°, mixed m.p. (with the normal form, m.p. 95.5–96.5°), 95.5°. Infrared absorption (4000–625 cm^{-1}, Nujol only): 3256 m(br), 3166 m(br), 3082 w, 1569 s(vbr), 1568 m, 1531 m, 1350 m, 1316 m, 1235 w, 1146 m, 1097 w, 1058 w, 1000 w, 992 m, 915 w, 835 w, 762 vs, 729 s, and 673 w cm^{-1}], or mixtures of the mercurial with either form.

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