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Synthesis and Phosphorus-31 NMR Studies of Tertiary Arylphosphine Complexes of Mercury(II) Halides

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Several new p-alkylphenylphosphines have been synthesized as well as 12 compounds of the type L_2HgX_2 and 17 compounds of the type $L_2Hg_2X_4$ where L is a triarylphosphine and X is Cl, Br, or I. Variable temperature phosphorus-31 NMR spectra are reported. The presence or absence and shape of the mercury-199 satellites in the ^{31}P spectra are a function of the rate of ligand exchange. Qualitatively, the rate of exchange decreases with the increasing basicity of the tertiary phosphine, with decreasing temperature, and with increasing acidity of the mercury species. J_{Hg-P} increases with decreasing temperature for all compounds measured.

Introduction

The original phosphorus-31 nuclear magnetic resonance studies [2–4] of mercuric halide–tertiary phosphine coordination compounds revealed spin coupling of phosphorus with mercury-199 (nuclear spin, ½; isotope abundance, 16.8%) at room temperature. The magnitude of the observed coupling for L_2HgX_2, where L is a tertiary phosphine and X is Cl, Br, or I increases in the order $RPh_2P < R_2PhP < R_3P$ and in the order I < Br < Cl. No mercury-199–phosphorus-31 coupling was observed for triphenylphosphine complexes of the type $(Ph_3P)_2HgX_2$ and $(Ph_3P)_2Hg_2X_4$. Therefore it was not possible to place Ph_3P with certainty in the above series of the other trialkyl- and alkylphenylphosphines. Nor was it clear whether the absence of mercury satellites in the room temperature ^{31}P NMR spectra of the triphenylphosphine complexes is due to lower solubility in dichloromethane so that the low intensity satellites were not discernable or whether the absence of satellites is caused by rapid ligand exchange of the less basic triphenylphosphine. This paper describes further investigations into this problem, as does a very recent publication [5] which has reported phosphorus-31–mercury-199 couplings in triphenylphosphine complexes of mercury(II) salts at reduced temperatures. These data [5] have generally substantiated and complemented the earlier work [2–4] and are in agreement with the results reported here.

Results and Discussion

In order to increase the solubility of the arylphosphine complexes of the mercuric halides without substantially altering the electronic properties of triphenylphosphine, several new triarylphosphines were synthesized with n-alkyl groups substituted in the para position. These include $(4\text{-n-}C_3H_7C_6H_4)_3P$, $(4\text{-n-}C_4H_9C_6H_4)_3P$, and $(4\text{-}RC_6H_4)_n(C_6H_5)_{3-n}P$ were R is n-octyl or n-hexyl and n is 1, 2, or 3. They were prepared by the Friedel Crafts acylation of bromobenzene followed by reduction of the 4-acylbromobenzene to 4-alkylbromobenzene. The Grignard reagent of the 4-alkylbromobenzene was then combined with PCl_3, $C_6H_5PCl_2$, or $(C_6H_5)_2PCl$ to give the respective oily triarylphosphines. Of these, $(4\text{-}C_8H_{17}C_6H_4)(C_6H_5)_2P$ and $(4\text{-}C_6H_{13}C_6H_4)(C_6H_5)_2P$ were used as ligands for the mercury complexes. The *para* substituted n-propyl and n-butylarylphosphine complexes of mercuric halides are only slightly soluble and were not pursued further. In addition, several complexes were also prepared with the ligands $[4\text{-}(CH_3)_3CC_6H_4]_3P$, $[4\text{-}(CH_3)_3SiC_6H_4]_3P$, $(4\text{-}FC_6H_4)_3P$, $(4\text{-}ClC_6H_4)_3P$ and $(4\text{-}CH_3C_6H_4)_3P$. The analytical data and melting points for the compounds are given in Table I. Dimeric complexes, $L_2Hg_2X_4$, were prepared in ethanol from the ligand and mercuric halide in a 1:1 molar ratio. The monomeric compounds, L_2HgX_2 were prepared in ethanol in a reaction ratio of 3:1 (phosphine to mercuric halide). For $(4\text{-}ClC_6H_4)_3P$, only the dimeric compound was isolated by addition of the ligand to the halide. A plausible explanation could be that immediate formation of a very insoluble dimer prevents the formation of monomer. More soluble dimers could dissociate and form monomers with additional ligand.

Phosphorus-31 NMR spectra of the compounds were obtained on dichloromethane solutions,

TABLE I. Analytical Data and Melting Points of Mercury(II) Halide Complexes of *para*-Substituted Arylphosphines.

Compound (L = Ligand)	m.p. (°C)	%C		%H		%P	
		Calcd.	Found	Calcd.	Found	Calcd.	Found
L = $[4\text{-}(CH_3)_3CC_6H_4]_3P$							
L_2HgCl_2	315–318	63.61	63.62	6.88	6.68	5.47	5.48
$L_2Hg_2Cl_4$	339–341	51.33	50.58	5.60	5.69	4.41	4.28
L_2HgBr_2	295–298	58.99	59.40	6.43	6.70	5.07	5.27
$L_2Hg_2Br_4$	345–348	45.55	45.80	4.97	5.20	3.92	4.21
L_2HgI_2	275–277	54.94	53.92	6.06	6.10	4.72	4.61
$L_2Hg_2I_4$	305–308	40.90	40.99	4.46	4.36	3.52	3.55
L = $(4\text{-}FC_6H_4)_3P$							
L_2HgCl_2	247–249	47.82	47.77	2.67	2.40	6.85	6.64
$L_2Hg_2Cl_4$	281–283	36.43	36.60	2.02	2.30	5.22	5.17
L_2HgBr_2	251–253	43.59	43.29	2.42	2.54	6.20	6.50
$L_2Hg_2Br_4$	275–277	31.95	31.96	1.77	1.76	4.57	4.28
L_2HgI_2	192–194	39.78	39.66	2.23	2.17	5.70	5.62
$L_2Hg_2I_4$	225–226	28.05	27.93	1.57	1.46	4.02	4.06
L = $(4\text{-}CH_3C_6H_4)_3P$							
L_2HgCl_2	261–263	57.34	57.86	4.81	5.11	7.04	7.07
$L_2Hg_2Cl_4$	310–314	43.81	43.89	3.67	3.85	5.36	5.25
L_2HgBr_2	285–287	52.08	51.85	4.37	4.58	6.39	6.32
$L_2Hg_2Br_4$	300–302	37.94	38.27	3.18	3.37	4.00	4.40
L_2HgI_2	146–148	47.45	47.20	3.98	3.99	5.83	5.80
$L_2Hg_2I_4$	265–267	33.23	33.51	2.79	2.81	4.08	4.12
L = $[4\text{-}(CH_3)_3SiC_6H_4]_3P$							
L_2HgCl_2	287–289	52.76	52.16	6.39	6.50	5.04	4.80
$L_2Hg_2Cl_4$	325–328	43.21	43.05	5.23	4.96	4.12	3.94
$L_2Hg_2Br_4$	311–313	38.68	38.65	4.69	4.77	3.69	3.82
L = $(4\text{-}ClC_6H_4)_3P$							
$L_2Hg_2Cl_4$	301–302	33.92	34.01	1.88	1.60	4.50	5.16
$L_2Hg_2Br_4$	293–295	29.78	30.19	1.65	1.78	4.26	4.55
$L_2Hg_2I_4$	273–275	26.37	26.46	1.46	1.52	3.78	3.82
L = $(4\text{-}C_8H_{17}C_6H_4)(C_6H_5)_2P$							
L_2HgBr_2	148–150	56.34	56.37	5.64	5.69	5.58	5.60
L_2HgI_2	117–119	51.89	51.87	5.20	5.27	5.15	5.21
$L_2Hg_2Cl_4$	205–207	48.54	48.85	4.83	4.92	4.79	4.56
$L_2Hg_2Br_4$	195–197	42.49	42.95	4.25	4.31	4.21	4.24
L = $(4\text{-}C_6H_{13}C_6H_4)(C_6H_5)_2P$							
$L_2Hg_2Br_4$		40.83	41.09	3.85	4.00	4.38	4.28

although the $(4\text{-}ClC_6H_4)_3P$, $(4\text{-}CH_3C_6H_4)_3P$, and $(4\text{-}FC_6H_4)_3P$ compounds were insufficiently soluble to detect ^{31}P signals. The NMR data are given in Table II. The typical ^{31}P NMR spectrum for a non-labile mercury-phosphorus compound in which there is mercury–phosphorus spin–spin coupling is a 8:84:8 triplet. At room temperature, the soluble $[(4\text{-t-BuC}_6H_4)_3P]_2HgCl_2$ and $[(4\text{-tBuC}_6H_4)_3P]_2HgBr_2$ compounds show this type spectrum although the satellite peaks are broad and weak. The room temperature

TABLE II. Phosphorus NMR Data for L_2HgX_2 and $L_2Hg_2X_4$ Compounds.[a]

L	δ_L (ppm)	L_2HgCl_2		L_2HgBr_2		L_2HgI_2	
		J(Hz)	Δ(ppm)[b]	J(Hz)	Δ(ppm)[b]	J(Hz)	Δ(ppm)[b]
$n\text{-}Bu_3P$[c]	−32.3	5078	61.3	4741	54.9	4110	42.7
$n\text{-}Bu_2PhP$[c]	−26.2	5035	54.8	4629	48.3	3726	32.3
$n\text{-}BuPh_2P$[c]	−16.9	4754	43.3	4216	36.2	–	20.9
$(4\text{-}t\text{-}BuC_6H_4)_3P$	−9.1	4662	34.4	4115	27.5	–	19.2
		$L_2Hg_2Cl_4$		$L_2Hg_2Br_4$		$L_2Hg_2I_4$	
$n\text{-}Bu_3P$[c]	−32.3	7446	66.7	6624	59.9	5127	39.1[d]
						4330	50.3
$n\text{-}Bu_2PhP$[c]	−26.2	7514	62.7	6658	55.2	5020	32.6[d]
						4250	42.6
$n\text{-}BuPh_2P$[c]	−16.9	–	–	6653	43.9	–	–
$(4\text{-}t\text{-}BuC_6H_4)_3P$	−9.1	7548	40.9	6559	34.2	–	14.5
$(4\text{-}C_8H_{17}C_6H_4)Ph_2P$	−6.5	7494	40.4	6427	33.7	–	–
$(4\text{-}Me_3SiC_6H_4)_3P$	−5.8	7426	39.3	6392	32.4	–	–
$(4\text{-}C_6H_{13}C_6H_4)Ph_2P$	−6.2	–	–	6491	33.6	–	–

[a] In CH_2Cl_2 solution. Positive chemical shifts are downfield from the reference. [b] $\Delta(\text{ppm}) = \delta_{\text{complex}} - \delta_{\text{free ligand}}$. [c] Reference 2. [d] See footnote.

coupling constants for the ligand series $n\text{-}Bu_3P$, $n\text{-}Bu_2PhP$, $n\text{-}BuPh_2P$, $(4\text{-}t\text{-}BuC_6H_4)_3P$ are respectively 5078, 5035, 4754, and 4602 Hz for the L_2HgCl_2 series and 4741, 4629, 4216, and 4115 Hz for the L_2HgBr_2 series. Thus, the triarylphosphine fits into the anticipated basicity order of tertiary phosphines and of J_{Hg-P} in $(R_3P)_2HgX_2$. That is, the more basic the ligand, the larger is J_{Hg-P}. This trend is opposite to that observed in $R_3PW(CO)_5$ complexes, where there is an inverse relationship between phosphine basicity and J_{W-P} [6–8]. However, the variable temperature studies (*vide infra*) indicate that the least basic phosphines and least acidic mercury species form the most labile complexes. Thus at any given temperature, the phosphine of lower basicity would be exchanging more rapidly at a mercury site than a more basic phosphine at the same temperature, and the observed coupling constant would be dependent on the inherent coupling constant of the 'frozen out', *i.e.*, inert complex, and also the exchange rate. Since we have not been able to experimentally reach the condition for quenching the exchange, and therefore measure the coupling constant of the inert complex, comparisons of the coupling constants at any given temperature, *e.g.*, room temperature, must be made cautiously.

No mercury satellites were observed at room temperature in the $(Ar_3P)_2HgI_2$ complexes, in which ligand exchange is rapid on the NMR time scale. This phenomenon has been observed earlier by Mann [9] in the case of phosphine complexes of CdI_2, which exhibit no cadmium satellites at room temperature but do exhibit the satellites at −90 °C, and more recently in the case of phosphine-mercury compounds [10]. Upon cooling the $(Ar_3P)_2HgX_2$ compounds in CH_2Cl_2 to −28 °C or lower, the mercury satellite peaks become sharp; the main ^{31}P signal shifts downfield, *i.e.*, a larger coordination shift results; J_{Hg-P} increases substantially; and satellite peaks are observed in the case of the HgI_2 complexes. Most of these observations can be explained by the slowing of the phosphine ligand exchange with decreasing temperature [9, 10] although this area needs further study. Based on the variable temperature studies, the appearance of the mercury satellites, and the sharpness of the satellites, the exchange rate for a given ligand at constant temperature is

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[d] The ^{31}P spectrum of $(n\text{-}Bu_3P)_2Hg_2I_4$ in CH_2Cl_2 solution exhibits two major peaks of unequal intensity, with their respective ^{199}Hg satellites. Professor K. G. Caulton of Indiana University has pointed out in a personal communication that the coupling constants associated with these two peaks were interchanged in the original report (ref. 2). We confirm that this is the case. The correct assignments should be: downfield peak of lesser intensity; δ, 19.4, J, 4358 (ref. 2); δ, 20.5; J, 4379 (Caulton); δ, 18.0; H, 4330 (our recent measurement); upfield major peak; δ, 7.3; J, 5120 (ref. 2); δ, 8.5; J, 5223 (Caulton); δ, 6.8; J, 5127 (our recent measurement). The reported coupling constants for the two principal peaks in $(n\text{-}Bu_2PhP)_2Hg_2I_4$ and $(Et_2PhP)_2Hg_2I_4$ are undoubtedly interchanged in the original report (ref. 2) also.

TABLE III. Temperature Dependence of J_{Hg-P} in $(Ar_3P)_2HgX_2$ and $(Ar_3P)_2Hg_2X_4$.

T (°C)	J(Hz)	δ(ppm)	T (°C)	J(Hz)	δ(ppm)
$[(4\text{-}Me_3SiC_6H_4)_3P]_2Hg_2Cl_4$			$[(4\text{-}t\text{-}BuC_6H_4)_3P]_2HgBr_2$		
25	7546	34.2	25	4115	18.4
−6	7593	33.9	−5	4156	18.9
−20	7612	33.7	−20	4190	19.0
−30	7642	33.5	−40	4228	19.1
−40	7653	33.3	−55	4234	19.2
−64	7696	32.7			
−72	7705	–	$[(4\text{-}C_8H_{17}C_6H_4)(C_6H_5)_2P]_2HgBr_2$		
−78	7733	–			
−92	7747	–	25	–	20.7
			−47	4130	21.8
$[(4\text{-}Me_3SiC_6H_4)_3P]_2Hg_2Br_4$					
			$[(4\text{-}C_8H_{17}C_6H_4)(C_6H_5)_2P]_2HgI_2$		
25	6391	25.6			
20	6411	26.6	25	–	5.5
−7	6470	26.5	−47	–	6.3
−27	6525	26.3			
−40	6547	26.1	$[(4\text{-}Me_3SiC_6H_4)_3P]_2HgCl_2$		
			25	–	26.4
−64	6603	25.9	−47	4653	27.3
−72	6632	25.7			
			$[(4\text{-}C_6H_{13}C_6H_4)(C_6H_5)_2P]_2Hg_2Br_4$		
$[(4\text{-}C_8H_{17}C_6H_4)(C_6H_5)_2P]_2Hg_2Cl_4$					
			25	6491	27.4
25	7491	33.9	−47	6602	27.2
−6	7562	33.8			
−26	7600	33.6	$[(4\text{-}t\text{-}BuC_6H_4)_3P]_2Hg_2I_4$		
−40	7632	33.3			
−47	7649	33.0	25	–	5.4
−55	7666	32.8	−47	4907	3.6
−64	7700	32.5			
−72	7704	–			

observed to increase in the order $L_2HgCl_2 < L_2HgBr_2 < L_2HgI_2$. This is to be expected since the mercury center with the more electronegative halide will be more electron deficient and a stronger Lewis acid.

The dimer complexes, $(Ar_3P)_2Hg_2X_4$, have sharp detectable mercury satellites in the phosphorus-31 NMR spectra except for the iodide complexes, which exhibit broad main peaks and no satellites. Upon cooling these dimer solutions, the mercury satellites appear in the iodide complexes, the ^{31}P chemical shifts moves upfield and J_{Hg-P} increases. Except for the chemical shift change, these observations are similar to the 2:1 complexes. However, the dimer system [11–18] is much more complicated than the monomer system because of additional equilibria and isomer possibilities (symmetrical-*cis*, symmetrical-*trans*, and unsymmetrical dihalo-bridged dimers). For example, the halogen bridge dissociation

$$L_2Hg_2X_4 \rightleftharpoons 2LHgX_2$$

can occur. Since the chemical shift and J_{Hg-P} for the tricoordinated species are not available, the effect of this equilibrium on the observed data is not clear. Further, there is no ^{31}P evidence in the case of the iodide complexes, $(Ar_3P)_2Hg_2I_4$, that there is more than one principal species present as had been observed earlier [2] in the case of $(Bu_3P)_2Hg_2I_4$*.

For several of the complexes, low temperature ^{31}P spectra were observed, although limited solubilities restricted large temperature ranges for most of the complexes (Table III). For $[(4\text{-}Me_3SiC_6H_4)_3P]_2Hg_2Br_4$ and $[(4\text{-}C_8H_{17}C_6H_4)(C_6H_5)_2P]_2Hg_2Cl_4$ there is a linear increase in J_{Hg-P} with decreasing temperature. It was hoped that the exchange would be 'frozen out' and J_{Hg-P} would asymtotically approach a maximum value, however those conditions were not obtained. The linear correlation coefficient is greater than 0.99 for each of these two data sets (Table III). Variable temperature studies of $[(4\text{-}Me_3SiC_6H_4)_3P]_2Hg_2Cl_4$ in dichloroacetonitrile gave results similar to those in CH_2Cl_2 solution, except that J_{Hg-P} is larger in $CHCl_2CN$ by about 75 Hz at each temperature.

Among the triarylphosphine complexes for which the same type compounds have been made, *i.e.*, $L_2Hg_2Cl_4$ and $L_2Hg_2Br_4$, the mercury–phosphorus coupling increases in the order $(4\text{-}Me_3SiC_6H_4)_3P < (4\text{-}C_8H_{17}C_6H_4)(C_6H_5)_2P < (4\text{-t-}BuC_6H_4)_3P$ in each case. This is the order of expected basicities for the compounds and is also the experimental order of basicities for the trimethylsilyl and tert-butyl compounds [19, 20].

In conclusion, twenty-nine compounds of the type L_2HgX_2 and $L_2Hg_2X_4$, where L is a tertiary phosphine and X is Cl, Br or I have been synthesized. Room temperature phosphorus-31 NMR spectra indicate that for L_2HgX_2, J_{Hg-P} increases with increasing basicity of the tertiary phosphine, but that for weaker bases (such as arylphosphines) and weaker Lewis acids (such as mercuric iodide) ligand exchange is often rapid so that mercury–phosphorus coupling is not observed. At low temperatures ligand exchange is slowed so that J_{Hg-P} can be observed. As the temperature decreases, J_{Hg-P} increases.

Experimental

Phosphorus-31 NMR spectra were recorded on a Varian Associates XL-100-12 Fourier Transform Spectrometer operating at 40.5 MHz using 10 mm spinning sample tubes with 85% H_3PO_4 as an external reference. The spectra were taken on CH_2Cl_2 solutions (unless otherwise indicated in the tables) in the Fourier transform mode with protons decoupled. Chemical shifts are reported as positive when down field from H_3PO_4.

Microanalyses were performed by Dr. Franz Kasler, University of Maryland. Melting points were obtained on a Mel-Temp instrument and are reported uncorrected.

The tertiary phosphines, $(4\text{-t-}BuC_6H_4)_3P$, $(4\text{-}Me_3SiC_6H_4)_3P$, $(4\text{-}ClC_6H_4)_3P$, $(4\text{-}CH_3C_6H_4)_3P$ and $(4\text{-}FC_6H_4)_3P$ were prepared as described earlier [21]. The 4-octylphenyl- and 4-hexylphenylphosphines were prepared from the Grignard reagents of the 4-alkylbromobenzenes and PCl_3, $PhPCl_2$ or Ph_2PCl as illustrated below for $(4\text{-}C_8H_{17}C_6H_4)(C_6H_5)_2P$.

1-(4'-Bromophenyl)-1-octanone

This compound, $4\text{-}BrC_6H_4CO(CH_2)_6CH_3$, was prepared by the Friedel-Crafts acylation [22] of bromobenzene with octanoyl chloride to give crystals, m.p. 66–67 °C, in 73% yield (lit. [23], b.p. 142–145 °C/1.5 mm). NMR: 0.88 δ (t), J = 5Hz, $\text{-}CH_3$; 1.1–1.8 δ (m, with very large peak at 1.29), $\text{-}(CH_2)_5\text{-}$; 2.92 δ (t), J = 7 Hz, $\text{-}COCH_2\text{-}$; aromatic AB quartet centered at 7.64 δ, J = 8 Hz (7.51 δ, H *ortho* to Br; 7.78 δ, H *ortho* to C=O). For an analogous spectrum see that of 4-bromoacetophenone [24].

1-Bromo-4-n-octylbenzene

The compound, $4\text{-}BrC_6H_4(CH_2)_7CH_3$, was prepared by a modified Clemmenson reduction [25] of the ketone above, $4\text{-}BrC_6H_4CO(CH_2)_6CH_3$. The product was distilled 144–148°/5 mm (lit. [26], 125–126°/1 mm). NMR: 0.87δ (t), J = 6 Hz, $\text{-}CH_3$; 1.26 δ (br s) $\text{-}(CH_2)_6\text{-}$; 2.15δ (t), J = 7 Hz, CH_2 adjacent to phenyl; aromatic AB quartet centered at 7.12 δ, J = 8 Hz (6.92 δ, H *ortho* to octyl; 7.30 δ, H *ortho* to Br). For an analogous spectrum see that of 1-bromo-4-ethylbenzene [27]. A slight impurity which occurs in the distillation product is n-octylbenzene, which results from partial reduction of the bromine by Zn during the Clemmenson procedure. This is recognized in the ^1H NMR aromatic region by a singlet (7.13 δ) between the middle peaks of the AB quartet. For comparison the aromatic region of n-butylbenzene is a quite sharp singlet at 7.09 δ [28].

Diphenyl-4-octylphenylphosphine

The Grignard reagent of 1-bromo-4-octylbenzene (13.4 g, 0.05 mol) was prepared with Mg (1.2 g, 0.05 mol) turnings in tetrahydrofuran (THF, 500 mL) under N_2. After heating at reflux for 30 min, the Grignard reagent was cooled in an ice bath and Ph_2PCl (8.3 g, 0.04 mol) was added dropwise with rapid stirring. The mixture was heated at reflux for 4 hr, then cooled and hydrolyzed with deoxygenated, saturated, aqueous NH_4Cl. The THF layer was removed, concentrated and chromatographed with an alumina column (125 g) with benzene: cyclohexane (1:10) as the eluent. The oily phosphine was recovered by evaporation of the eluate. The ^{31}P chemical shift for $(4\text{-}C_8H_{17}C_6H_4)(C_6H_5)_2P$ is −6.5 ppm. Other phosphines prepared by this method and their ^{31}P chemical shifts are: $(4\text{-}C_8H_{17}C_6H_4)_2(C_6H_5)P$, −7.0 ppm; $(4\text{-}C_8H_{17}C_6H_4)_3P$, −8.2 ppm; $(4\text{-}C_6H_{13}C_6H_4)(C_6H_5)_2P$, −6.2 ppm; $(4\text{-}C_6H_{13}C_6H_4)_2(C_6H_5)P$, −7.0 ppm; and $(4\text{-}C_6H_{13}C_6H_4)_3P$, −7.7 ppm; $(4\text{-}C_4H_9C_6H_4)(C_6H_5)_2P$, −6.5 ppm; $(4\text{-}C_4H_9C_6H_4)_3P$, −7.6 ppm; and $(4\text{-}C_3H_7C_6H_4)_3P$, −8.2 ppm.

Mercury Halide Complexes

The mercury halide complexes were prepared as described earlier [29]. The L_2HgX_2 complexes were prepared by the addition of the ligand in hot EtOH to a stirring solution of HgX_2 in EtOH in a 3:1 molar ratio (P:Hg). The dimers, $L_2Hg_2X_4$, were prepared similarly in a 1:1 molar ratio of ligand and mercury halide. Melting points and analytical data are given in Table I.

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