$$OH + O + M \rightarrow HO_2 + M \tag{7}$$

$$OH + OH + M \rightarrow H_2O_2 + M \tag{8}$$

$$OH, BH_3, BH_2, \text{etc.} \rightarrow \text{wall termination} \tag{9}$$

Although we were unable to obtain mass spectral confirmation of the presence of OH as an intermediate, the results of Carabine and Norrish[10] demonstrate its presence in the flash photolysis of $O_2 + B_2H_6$ mixtures; it is unlikely that OH is absent from the reaction under the conditions of the present study.

The observed chemiluminescence requires that BO be produced with some 85-kcal excitation above the ground state. Reactions 10 and 11 fulfill this condition.

$$BH_2 + O \rightarrow BO + H_2 \qquad -108 \pm 15 \text{ kcal/mol} \tag{10}$$

$$BH_2 + O_2 \rightarrow BO + H_2O \qquad -106 \pm 15 \text{ kcal/mol} \tag{11}$$

The observed species BH_2O_2 could arise from either or both of the metatheses

$$BH_3O + O \rightarrow BH_2O_2 + H \qquad -52 \pm 15 \text{ kcal/mol} \tag{12}$$

$$BH_3 + O_2 \rightarrow BH_2O_2 + H \qquad -87 \pm 18 \text{ kcal/mol} \tag{13}$$

while the possible intermediate BOH_2 could be the result of several reactions

$$O + BH_2O_2 \rightarrow BH_2O + O_2 \tag{14}$$

$$O + BH_3O \rightarrow BH_2O + OH \tag{15}$$

etc., among which there is at present very little basis for preference.

When the reaction takes place with little B_2H_6 present, it is much slower, which is nonetheless consistent with the chain mechanism given above. Unless a reasonable amount of B_2H_6 is present, the propagation steps, specifically reaction 5, cannot compete with the termination steps 6-9. The reaction can then be described more simply by reaction 2, followed by numerous steps involving various [B, H, O] species consuming O atoms and each other, but consuming little, if any, diborane. Under these conditions our measured rate constant, which describes the disappearance of B_2H_6, is the true bimolecular rate constant for reaction 2.

The only additional observation which must be accounted for is the greater consumption of O atoms relative to B_2H_6, under conditions of excess atoms. The fact that this consumption ratio is large (*ca.* 10) and not very reproducible (*vide supra*) is indicative of another chain mechanism which consumes O atoms but not B_2H_6, *i.e*, a B_2H_6-catalyzed disappearance of O atoms. A possible reaction sequence is

$$O + B_2H_6 \rightarrow BH_3 + BH_3O \tag{2}$$

$$O + BH_3O \rightarrow O_2 + BH_3 \tag{16}$$

$$BH_3 + BH_3 + M \rightarrow B_2H_6 + M \tag{6}$$

for which the overall reaction is simply

$$2O \rightarrow O_2$$

Acknowledgment. We thank the University Research Committee for a Grant-in-Aid to C. W. H.

Registry No. Atomic oxygen, 17778-80-2; diborane(6), 19287-45-7.

Contribution from the Department of Chemistry,
University of Maryland, College Park, Maryland 20742

Phosphorus-31 Nuclear Magnetic Resonance Study of Tertiary Phosphine-Mercury(II) Halide Complexes[1a]

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Phosphorus-31 nmr results are presented for compounds of the types L_2HgX_2 and $L_2Hg_2X_4$, where L is tributylphosphine, dibutylphenylphosphine, butyldiphenylphosphine, and in several cases diethylphenylphosphine; and X is chloride, bromide, and iodide. Phosphorus-31–mercury-199 coupling constants are reported. They generally increase with the electronegativity of the halogen attached to mercury and in the order of the basicity of the phosphine, *i.e.*, $(n\text{-}C_4H_9)_3P > (n\text{-}C_4H_9)_2(C_6H_5)P > (n\text{-}C_4H_9)(C_6H_5)_2P$. For a particular phosphine, J_{P-Hg} is considerably larger in the halogen-bridged dimer $L_2Hg_2X_4$ than in the corresponding monomeric compound L_2HgX_2. J_{P-Hg} is also generally larger as the downfield coordination chemical shift increases.

Introduction

Phosphorus-31 nuclear magnetic resonance spectroscopy has been used extensively in recent years for the study of coordination compounds.[2,3] Lewis acids which have a spin = $^1/_2$ isotope of reasonable abundance (*e.g.*, ^{199}Pt, ^{183}W, ^{103}Rh, ^{111}Cd, ^{113}Cd, etc.) are often most interesting because of the possibility of phosphorus-metal spin-spin coupling which is generally observable for relatively inert complexes.[4-7] We report here a study of tertiary phosphine complexes of mercury(II) halides. Complexes of this type were definitively studied many years ago by Evans, Mann, Peiser, and Purdie,[8] followed by additional synthetic and physical studies.[9,10]

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(1) (a) Reported at the XIIth International Conference on Coordination Chemistry, Sydney; see Abstracts of Proceedings, p 39, 1969. (b) Taken in part from the M.S. thesis of P. J. Lui, University of Maryland, 1970.

(2) J. F. Nixon and A. Pidcock, *Annu. Rev. NMR* (*Nucl. Magn. Resonance*) *Spectrosc.*, 2, 345 (1969).

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Table I. Preparative and Analytical Data for Mercury-Phosphine Complexes

				% C		% H	
Compd	Mp, °C	Crystallizn solvent	Yield, %	Calcd	Found	Calcd	Found
$(Bu_3P)_2HgCl_2$	93-95.5	Pentane	50	42.64	43.06	8.05	7.99
$(Bu_3P)_2HgBr_2$	84.5-86.5	Pentane	59	37.68	37.81	7.11	7.35
$(Bu_3P)_2HgI_2$	58-59.5	Pentane	56	33.59	33.30	6.29	6.52
$(Bu_2PhP)_2HgCl_2$	Oil	Benzene	50				
$(Bu_2PhP)_2HgBr_2$	150-151	Benzene	65	41,77	41.88	5.80	5.90
$(Bu_2PhP)_2HgI_2$	146-147	Ethanol	78	37.37	38.31	5.12	5.13
$(BuPh_2P)_2HgCl_2$	161-163	Benzene	73	50.79	50.94	5.03	5.00
$(BuPh_2P)_2HgBr_2$	194-195	Benzene	70	45.48	45.40	4.53	4.44
$(BuPh_2P)_2HgI_2$	105-108	Ethanol	75	40.93	41.14	4.08	4.16
$(Ph_3P)_2HgBr_2$	265-270 (258-259)[a]		80	48.85	48.83	3.42	3.50
$(Bu_3P)_2Hg_2Cl_4$	69-70	Pentane-ethanol	48	30.41	30.19	5.70	5.88
$(Bu_3P)_2Hg_2Br_4$	116-117 (116)[b]	Ethanol	79				
$(Bu_3P)_2Hg_2I_4$[c]	85.5-86.5 (85-86)[b]	Ethanol-acetone	75	21.93	21.96	4.12	4.44
$(Bu_2PhP)_2Hg_2Cl_4$	161-162	Benzene	75	34.04	34.99	4.66	4.65
$(Bu_2PhP)_2Hg_2Br_4$	145-146	Benzene	58	28.86	29.00	3.98	3.98
$(Bu_2PhP)_2Hg_2I_4$[d]	112-113	Benzene	50	24.84	24.55	3.40	3.34
$(BuPh_2P)_2Hg_2Br_4$	150-151	Benzene	60	31.88	31.85	3.17	3.30
$(Ph_3P)_2Hg_2Br_4$	252-255 (251-252)[a]		75	34.73	34.55	2.43	2.36
$(Et_2PhP)_2Hg_2Cl_4$	138-139.5	Ethyl acetate	80	27.40	27.57	3.43	3.38
$(Et_2PhP)_2Hg_2Br_4$	117-118 (120-121)[e]	Ethanol-chloroform	80	22.79	22.60	2.84	2.80
$(Et_2PhP)_2Hg_2I_4$	94.5-95.5	Benzene	85	19.33	17.02	2.42	2.36

[a] Reference 10. [b] Reference 8. [c] Calcd: I, 38.67; mol wt 1313. Found: I, 38.80; mol wt 1285. [d] Calcd: I, 37.48; mol wt 1353. Found: I, 36.39; mol wt 1270. [e] Reference 9.

More recent physical studies have utilized infrared[11-13] and nmr[6,14] techniques.

Experimental Section

Microanalyses were performed by Dr. Franz Kasler of this department and by Galbraith Laboratories, Knoxville, Tenn.

Melting points were determined on a Mel-Temp apparatus.

Phosphorus-31 nmr spectra were measured with a Varian Associates DP-60 spectrometer at 24.3 MHz on concentrated dichloromethane solutions in 15-mm tubes. The reference (85% H_3PO_4) was sealed in a 3-mm tube and placed concentrically into the large sample tube through a serum stopper. Chemical shifts and coupling constants were calculated by interpolation between side bands which were generated from the signal of the reference compound. Generally, each spectrum was recorded six times: three times in the direction of increasing field and three times in the direction of decreasing field. The six values were then averaged.

All tertiary phosphines, except commercially available $(C_4H_9)_3P$ and $(C_6H_5)_3P$, were prepared by the Grignard method with $C_6H_5PCl_2$ and $(C_6H_5)_2PCl$.

The preparation of the complexes followed generally the published method.[8-10] The mercuric halide was introduced in a round-bottom flask with approximately 100 ml of absolute ethanol. The whole system was flushed with nitrogen gas for about 10 min. The freshly distilled tertiary phosphine in 100 ml of absolute ethanol was added dropwise from an additional funnel with magnetic stirring. A hot water bath was applied to melt the mercuric halide when it was needed.

In the case of the dimers, the phosphine to mercuric halide molar ratio was 1:1; in the case of the monomers, it was 2:1. The crude product was recrystallized from an appropriate solvent mixture. Preparative and analytical data are given in Table I.

In several cases the compounds were not soluble enough in methylene chloride (and all other solvents tried) in order for the phosphorus nmr spectrum to be determined. In order to get some idea of the solubility necessary for detection of the satellite peaks the solubility of the compounds listed in Table II were determined. Saturated solutions were weighed and allowed to evaporate in an oven at 40°. After 1 week, the residues reached constant weight. The weight of the methylene chloride was obtained by difference. The solubilities are given in Table II.

Table II. Solubilities of Some Phosphine-Mercury Compounds in Methylene Chloride

Compd	g of compd/100 g of CH_2Cl_2	m
$(Bu_3P)_2Hg_2Cl_4$	49.6	0.52
$(Bu_3P)_2Hg_2Br_4$	91.3	0.81
$(Bu_3P)_2Hg_2I_4$	274.5	2.08
$(Et_2PhP)_2Hg_2Cl_4$	10.9	0.12
$(Et_2PhP)_2Hg_2Br_4$	34.6	0.33
$(Et_2PhP)_2Hg_2I_4$	139.2	1.12

Discussion

Most of the compounds listed in Table I are previously unreported. Originally the $(Bu_3P)_2HgX_2$ compounds were reported[8] not to have formed. They have been reported recently but without analytical data or melting points. We have obtained them as crystalline solids from pentane solution.

Phosphorus-31 nuclear magnetic resonance data are given in Table III. The ^{31}P spectrum in the usual case (several exceptions are discussed later) is a triplet of relative intensity of approximately 8:84:8. The major peak arises from those molecules containing spin $\neq {}^1/_2$ nuclei whereas the two small satellite peaks arise from those molecules containing mercury-199 (16.84% natural abundance) which has a nuclear spin of $^1/_2$ and causes spin-spin coupling in the phosphorus spectrum. The magnitude of separation between these satellite peaks is J_{Hg-P}. No splitting was observed for mercury-201 (nuclear spin $^3/_2$; natural abundance 13.2%).

The triphenylphosphine complexes, *viz.*, $(Ph_3P)_2HgBr_2$ and $(Ph_3P)_2Hg_2Br_4$, were not soluble enough to detect any ^{31}P signal. The tetrachlorobis(diethylphenylphosphine)dimercury was too insoluble to detect the satellite peaks although the main peak was observed. In order to determine this limiting value for observing the complete spectrum some solubilities were determined and are listed in Table II. The trend for these dimers is that both weight-wise and molewise the iodides are considerably more soluble in methylene chloride than the bromides, which are in turn more soluble than the chlorides. The molality of a saturated solution of

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Table III. Phosphorus-31 Nmr Data for Mercury–Phosphine Complexes

Compd	Chem shift, ppm		Coordination chem shift,[a] ppm	$J_{^{199}Hg-^{31}P}$, Hz
	Ligand	Complex		
$(Bu_3P)_2HgCl_2$	32.3	−29.0 (−31.0)[b]	−61.3	5078 (5100)[b]
$(Bu_3P)_2HgBr_2$	32.3	−22.6 (−23.0)[b]	−54.9	4741 (5780)[b]
$(Bu_3P)_2HgI_2$	32.3	−10.4 (−10.5)[b]	−42.7	4100 (4040)[b]
$(Bu_2PhP)_2HgCl_2$	26.2	−28.6	−54.8	5035
$(Bu_2PhP)_2HgBr_2$	26.2	−22.1	−48.3	4629
$(Bu_2PhP)_2HgI_2$	26.2	−6.1	−32.3	3726
$(BuPh_2P)_2HgCl_2$	16.9	−26.4	−43.3	4754
$(BuPh_2P)_2HgBr_2$	16.9	−19.3	−36.2	4216
$(BuPh_2P)_2HgI_2$	16.9	−4.0	−20.9	
$(Bu_3P)_2Hg_2Cl_4$	32.3	−34.4 (−34.5)[b]	−66.7	7446 (7480)[b]
$(Bu_3P)_2Hg_2Br_4$	32.3	−27.6 (−28.5)[b]	−59.9	6624 (6680)[b]
$(Bu_3P)_2Hg_2I_4$	32.3	−7.3	−39.6	4358
	32.3	−19.4 (−16.5)[b]	−51.7	5120 (5440)[b]
$(Bu_2PhP)_2Hg_2Cl_4$	26.2	−36.5	−62.7	7514
$(Bu_2PhP)_2Hg_2Br_4$[a]	26.2	−29.0	−55.2	6658
$(Bu_2PhP)_2Hg_2I_4$	26.2	−6.4	−32.6	4250
	26.2	−16.4	−42.6	5020
$(BuPh_2P)_2Hg_2Br_4$	16.9	−27.0	−43.9	6553
$(Et_2PhP)_2Hg_2Cl_4$	17.1	−43.2	−60.3	
$(Et_2PhP)_2Hg_2Br_4$	17.1	−35.6	−52.7	6627
$(Et_2PhP)_2Hg_2I_4$	17.1	−12.2	−29.3	4192
		−21.5	−38.6	4985

[a] $\delta_{complex} - \delta_{ligand}$. [b] Reference 14.

$(Et_2PhP)_2Hg_2Cl_4$ is 0.12 *m* (or 0.24 *m* in phosphorus, since there are two phosphorus atoms per molecule), which allows detection of the main peak but not the satellites. The complete spectrum was observed for a saturated CH_2Cl_2 solution of $(Et_2PhP)_2Hg_2Br_4$, which was 0.33 *m*.

The spectrum of diiodobis(butyldiphenylphosphine)mercury is interesting in this respect, since the satellite peaks were not observed, although they were observed in the less soluble dichlorobis(butyldiphenylphosphine)mercury and dibromobis(butyldiphenylphosphine)mercury. This probably means that there is ligand dissociation which is rapid on the nmr time scale. This is a common phenomenon for labile complexes and has been noted in particular for tertiary phosphine–cadmium(II) complexes at room temperature.[15] A variable-temperature study was not done for lack of a variable-temperature phosphorus probe. Also, no variable concentration study of these compounds was made to investigate this further, since addition of excess ligand or excess mercuric halide can change the stoichiometry of the species in solution so that any resultant measurements would be difficult to interpret.

Several trends are observed. First, for a particular phosphine, J_{Hg-P} increases in the order of the electronegativity of the halogen ligand, *i.e.*, I < Br < Cl (see Figure 1). This is consistent with the fact that the greater the electron-withdrawing power of the ligands attached to mercury, the greater would be the electron deficiency of mercury, and the greater the σ donation of the tertiary phosphine. Greater σ bonding would result in greater spin interaction and larger couplings.

Second, related to this observation is the trend of larger J_{Hg-P} for the dimers $L_2Hg_2X_4$ than for the monomers L_2HgX_2, when L and X are identical. In the dimer case each mercury is attached to three electronegative halogens and one phosphine, so that the mercury is more electron deficient than in the monomer case, in which mercury is attached to only two electronegative halogens and two phosphines. As a result there is greater σ interaction and larger J_{Hg-P}'s in the dimer series.

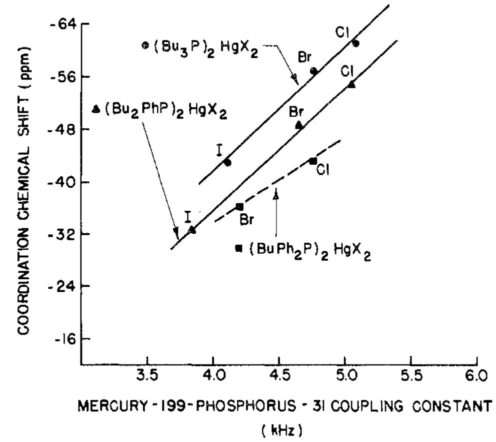

Figure 1. Variation of J_{Hg-P} and ^{31}P coordination chemical shift with halogen.

Third, for the above cases the magnitude of the downfield shift on coordination, *i.e.*, the absolute value of the coordination chemical shift, is larger for those cases which have the larger coupling constants (see Figure 1). This is intuitively reasonable since the phosphorus ligand which is the better σ donor will give up more of its electronic charge and therefore should be less shielded. It also would form the better bond and have the greater spin interaction. These arguments are made on the assumption that there is little or no π bonding. However, it is well documented[16] that paramagnetic effects and not simple diamagnetic shielding parameters predominate for ^{31}P chemical shifts, so the above explanation might be too simplistic. Nevertheless, with many of the variables such as stereochemistry, metal, oxidation state, other ligands, and bond angles remaining constant, it is possible that the σ-bond strength and resulting charge density could determine the chemical shift differences.

Fourth, and perhaps the most interesting observation, is that as the butyl groups are replaced by phenyl groups in each series $(Bu_3P)_2HgX_2$, $(Bu_2PhP)_2HgX_2$, and $(BuPh_2P)_2HgX_2$, where X = Cl, Br, and I [except for $(BuPh_2P)_2HgI_2$, which was discussed above and for which no satellites were

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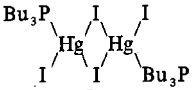
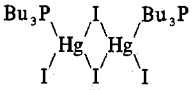
observed], the coupling constant decreases. In each case there is a much larger difference between the last two than between the first two of the three-membered series. The triphenylphosphine complex would be of great interest here but it was too insoluble to detect any signal. This order corresponds to the order of basicity of the phosphines, *i.e,* the most basic phosphine has the largest coupling constant. The same order of phosphorus-heavy metal coupling constants has been observed for tertiary phosphine complexes of cadmium halides [tetrahedral Cd(II)][15] and tin halides [octahedral Sn(IV)].[17]

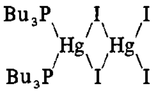
The order is opposite to that found in tungsten carbonyl derivatives [octahedral W(0)],[18] platinum(II) compounds [square-planar Pt(II)],[19] iron carbonyl complexes [trigonal-bipyramidal Fe(0)],[20] and rhodium chloride compounds [octahedral Rh(III)].[21] The former group (Hg, Cd, Sn) has oxidation states and/or stereochemistries which are not particularly amenable to metal-ligand back-bonding, and the results of larger $J_{\mathrm{M-P}}$ for the better σ donor (*i.e.*, more basic phosphine) seem quite reasonable. Likewise, the latter group (W, Fe, Pt, and, to a lesser extent, Rh) has low oxidation states and/or favorable stereochemistries for which metal-phosphorus π bonding has often been invoked. In these, the variation of basicity and $J_{\mathrm{M-P}}$ is inverse. The sign of the metal-phosphorus coupling constant may be important in this respect, but to date only the signs of a few W-P couplings have been determined.[22] Signs of other metal-phosphorus coupling constants would certainly be worthwhile measuring.

The basicity-coupling constant trend is not as clear in the dimer series. The coupling in $(\mathrm{Bu_3P})_2\mathrm{Hg_2Br_4}$ and $(\mathrm{Bu_2PhP})_2\mathrm{Hg_2Br_4}$ is about the same within experimental error, but the trend does become more evident in the third member of the series, $(\mathrm{BuPh_2P})_2\mathrm{Hg_2Br_4}$, which has a considerably smaller coupling constant. A similar slight inversion in $J_{\mathrm{Rh-P}}$ appears to occur also for the middle member of the series: *mer*-$(\mathrm{Et_3P})_3\mathrm{RhCl_2}$, *mer*-$(\mathrm{Et_2PhP})_3\mathrm{RhCl_3}$, *mer*-$(\mathrm{EtPh_2P})_3\mathrm{RhCl_3}$.[21,23]

The fifth observation is that the pure solids $(\mathrm{Bu_3P})_2\mathrm{Hg_2I_4}$, $(\mathrm{Bu_2PhP})_2\mathrm{Hg_2I_4}$, and $(\mathrm{Et_2PhP})_2\mathrm{Hg_2I_4}$, which have sharp melting points, good microanalyses, and acceptable molecular weight determinations, give two main phosphorus nmr peaks of unequal intensity (*ca.* 60:40) with their corresponding satellites in methylene chloride solution. The three possible structures for complexes of their stoichiometry are shown by Ia–c.


Ia
trans symmetrical


Ib
cis symmetrical


Ic
unsymmetrical

All evidence previously presented in the literature suggests that the structure of this type compound is the trans-symmetrical structure. In each structure the two phosphines are equivalent, so that the fact that two peaks occur in unequal intensities implies that there are two structures in equilibrium in solution, but the rate of interconversion must be slow on the nmr time scale, since the satellite peaks are observed. From our extrapolation of the data from the chloride and bromide dimers (assuming they have trans-symmetrical structure) it appears that the downfield peak (with larger J) most likely corresponds to this structure. The upfield peak could tentatively be assigned to the cis-symmetrical structure (for which there are no data to compare) or the unsymmetrical isomer. The latter possibility is not unreasonable since in that isomer one mercury has two phosphorus atoms and two iodine atoms attached, as is the case in the monomers $\mathrm{L_2HgI_2}$. The δ and J values for the upfield peak in $\mathrm{L_2Hg_2I_4}$ are somewhat similar to those in $\mathrm{L_2HgI_2}$. This phenomenon was not observed in a recent study[14] and we have done no further definitive work on it to date.

Acknowledgment. We are grateful for support from the National Science Foundation (Grants GP-30703 and 12539) and the U. S. Air Force Office of Scientific Research (Grant AFOSR-782-67). We also thank Patricia Q. Lee for furnishing several of the compounds.

Registry No. $(\mathrm{Bu_3P})_2\mathrm{HgCl_2}$, 41665-91-2; $(\mathrm{Bu_3P})_2\mathrm{HgBr_2}$, 20968-25-6; $(\mathrm{Bu_3P})_2\mathrm{HgI_2}$, 41665-93-4; $(\mathrm{Bu_2PhP})_2\mathrm{HgCl_2}$, 43112-06-7; $(\mathrm{Bu_2PhP})_2\mathrm{HgBr_2}$, 20968-26-7; $(\mathrm{Bu_2PhP})_2\mathrm{HgI_2}$, 43112-08-9; $(\mathrm{BuPh_2P})_2\mathrm{HgCl_2}$, 43112-09-0; $(\mathrm{BuPh_2P})_2\mathrm{HgBr_2}$, 20968-27-8; $(\mathrm{BuPh_2P})_2\mathrm{HgI_2}$, 43112-11-4; $(\mathrm{Bu_3P})_2\mathrm{Hg_2Cl_4}$, 41665-95-6; $(\mathrm{Bu_3P})_2\mathrm{Hg_2Br_4}$, 41665-96-7; $(\mathrm{Bu_3P})_2\mathrm{Hg_2I_4}$, 41665-97-8; $(\mathrm{Bu_2PhP})_2\mathrm{Hg_2Cl_4}$, 43112-15-8; $(\mathrm{Bu_2PhP})_2\mathrm{Hg_2Br_4}$, 43112-16-9; $(\mathrm{Bu_2PhP})_2\mathrm{Hg_2I_4}$, 43112-17-0; $(\mathrm{BuPh_2P})_2\mathrm{Hg_2Br_4}$, 43112-18-1; $(\mathrm{Et_2PhP})_2\mathrm{Hg_2Cl_4}$, 43111-80-4; $(\mathrm{Et_2PhP})_2\mathrm{Hg_2Br_4}$, 43111-81-5; $(\mathrm{Et_2PhP})_2\mathrm{Hg_2I_4}$, 43111-82-6; P, 7723-14-0.

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