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Registry No. Fe(salen)O$_2$NO, 97337-05-8; [Fe(salen)ONO$_2$]$_2$, 97337-06-9; [Fe(salpn)ONO$_2$]$_2$, 97337-07-0; [Fe(5-Clsalen)ONO$_2$]$_2$, 97337-08-1; [Fe(5-MeOsalen)ONO$_2$]$_2$, 97337-09-2; Fe(TPP)O$_2$NO, 76282-27-4; [Fe(salen)]$_2$O, 18601-34-8; [Fe(salpn)]$_2$O, 97337-10-5; [Fe(5-Clsalen)]$_2$O, 18601-71-3; [Fe(5-MeOsalen)]$_2$O, 97374-04-4; ^{15}N, 14390-96-6.

Supplementary Material Available: Figure S1, the Raman spectra of [Fe(salen)ONO$_2$]$_2$ and Fe(salen)O$_2$NO, and Table SI, magnetic data for Fe(salen)O$_2$NO and [Fe(salen)ONO$_2$]$_2$ at various temperatures (2 pages). Ordering information is given on any current masthead page.

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Polydentate Ligands Containing Phosphorus. 8. Coordination Complexes of a New Uninegative Tridentate Ligand, Tris(diphenylthiophosphinoyl)methanide, and Related Compounds and the Molecular Structure of (Bis(dimethylthiophosphinoyl)(diphenylthiophosphinoyl)methanido)chloromercury(II)[1]

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The reaction of mercury(II) chloride, bromide, or iodide in ethanol solution with tris(diphenylthiophosphinoyl)methane, $[(C_6H_5)_2P(S)]_3CH$, or bis(dimethylthiophosphinoyl)diphenylthiophosphinoylmethane, $[(CH_3)_2P(S)]_2[(C_6H_5)_2P(S)]CH$, yields coordination compounds of the type $\{[(C_6H_5)_2P(S)][R_2P(S)]_2C\}HgX$, where R is C_6H_5 or CH_3, and X is Cl, Br, or I. The X-ray crystallographic structural determination of (bis(dimethylthiophosphinoyl)(diphenylthiophosphinoyl)methanido)chloromercury(II), $\{[(CH_3)_2P(S)]_2[(C_6H_5)_2P(S)]C\}HgCl$ (monoclinic, $P2_1/a$, $Z = 4$, $a = 1.48$ (1) nm, $b = 1.394$ (9) nm, $c = 1.194$ (8) nm, and $\beta = 112.038$ (6)°), proves that the organophosphorus ligand coordinates to mercury in a tridentate fashion via the three sulfur atoms to form a cage compound of six-membered chelate rings. Chlorine occupies the fourth coordination position about the pseudotetrahedral mercury atom. Raman spectra of the solid coordination compounds $\{[R_2P(S)]_3C\}MX$, where M = Hg, Cd, indicate an unusually large decrease of the P–S stretching frequency compared to those of the neutral parent ligands. Phosphorus-31 NMR data are also reported for the complexes.

Introduction

The chemistry of phosphorus compounds that have three phosphorus atoms attached to the same carbon atom is relatively new. In 1966, Birum and Matthews[3] reported mesomeric ylide salts containing this atomic arrangement, and in 1970 Issleib and Abicht[4] reported the synthesis of the first analogue, tris(diphenylphosphino)methane, $(Ph_2P)_3CH$, and its trisulfide, $[Ph_2P(S)]_3CH$, of the compounds reported here. Additional analogues of these potential ligands have been synthesized and characterized recently.[5–11] However, very little coordination chemistry of these tris ligands[12] has been reported. Osborn[13,14] has reported on the behavior of $(Ph_2P)_3CH$, HTris,[12] as a tridentate ligand in nickel, iridium, and several other metal carbonyl clusters in which each phosphine is bonded to a different metal atom of a triangular face of the cluster. Likewise van Koten[15] has shown that one molecule of HTris can simultaneously bond to three silver atoms in a novel complex. Finally, we[9] have shown HTris can be bidentate in complexes of the group 6 metal carbonyls. In view of the large variety of potential ligands available in the new class of tris compounds, viz. $[R_2P(X)][R_2P(Y)][R_2P(Z)]CH$, where R = Ph, Me and X, Y, Z = electron pair, O, S, Se, and in view of the various polydentate and ambidentate bonding patterns possible, we have begun a systematic investigation of the coordination chemistry of these ligands. Further, removal of the methine proton of a tris(trichalcogenide) would generate an anion that is potentially tridentate, i.e., an anionic tripod ligand. The only precedent for a uninegative tridentate ligand is the well-known polypyrazolylborate[16,17] ligand system. It is therefore of great interest

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(12) Compounds with three phosphorus atoms attached to one carbon will be referred to as a class as "tris" ligands. In particular $(Ph_2P)_3CH$, $[Ph_2P(S)][Ph_2P]_2CH$, $[Ph_2P(S)]_2[Ph_2P]CH$, and $[Ph_2P(S)]_3CH$ will be abbreviated HTris, HTrisS, HTrisS$_2$, and HTrisS$_3$, respectively. $[Me_2P(S)]_2[Ph_2P(S)]CH$ is H4mTrisS$_3$, and the anionic tripods $\{[Ph_2P(S)]_3C\}^-$ and $\{[Me_2P(S)]_2[Ph_2P(S)]C\}^-$ are TrisS$_3^-$ and 4mTrisS$_3^-$, respectively.

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Table I. Analytical Data for $\{[Ph_2P(S)]_3C\}MX$ and $\{[Ph_2P(S)][Me_2P(S)]_2C\}MX$[a]

		% C	% H	% P	% X	M_r
calcd for $(HTrisS_3)HgCl_2$[b]	$C_{37}H_{31}Cl_2HgP_3S_3$	47.47	3.34	9.92	7.57	936
calcd for $(TrisS_3)HgCl$	$C_{37}H_{30}ClHgP_3S_3$	49.39	3.36	10.33	3.94	900
found		49.38	3.69		3.66	
		49.53	3.31	10.40	4.05	899
calcd for $(HTrisS_3)HgBr_2$	$C_{37}H_{31}Br_2HgP_3S_3$	43.35	3.05	9.06	15.59	
calcd for $(TrisS_3)HgBr$	$C_{37}H_{30}BrHgP_3S_3$	47.07	3.20	9.84	8.46	
found		47.03	3.06		8.31	
		47.01	3.12	9.80	7.78	
calcd for $(HTrisS_3)HgI_2$	$C_{37}H_{31}HgI_2P_3S_3$	39.71	2.79	8.30	22.68	
calcd for $(TrisS_3)HgI$	$C_{37}H_{30}HgIP_3S_3$	44.83	3.05	9.37	12.80	
found		45.01	3.28	9.04	11.81	
		44.60	2.99	9.14	12.63	
calcd for $(H4mTrisS_3)HgCl_2$[c]	$C_{17}H_{23}Cl_2HgP_3S_3$	29.68	3.37	13.51	10.31	
calcd for $(4mTrisS_3)HgCl$	$C_{17}H_{22}ClHgP_3S$	31.34	3.40	14.26	5.44	
found		31.56	3.32	14.30	5.54	
calcd for $(H4mTrisS_3)HgBr_2$	$C_{17}H_{23}Br_2HgP_3S_3$	26.28	2.98	11.96	20.57	777
calcd for $(4mTrisS_3)HgBr$	$C_{17}H_{22}BrHgP_3S_3$	29.34	3.19	13.35	11.48	696
found		29.44	3.11	13.45	11.27	691
calcd for $(H4mTrisS_3)HgI_2$	$C_{17}H_{23}HgI_2P_3S_3$	23.45	2.66	10.67	29.14	
calcd for $(4mTrisS_3)HgI$	$C_{17}H_{22}HgIP_3S_3$	27.48	2.98	12.51	17.08	
found		27.57	2.96	12.52	16.99	
calcd for $(HTrisS_3)CdCl_2$	$C_{37}H_{31}CdCl_2P_3S_3$	52.40	3.68	10.96	8.36	600
calcd for $(TrisS_3)CdCl$	$C_{37}H_{30}CdClP_3S_3$	54.76	3.72	11.45	4.37	563
found		55.06	3.77	11.36	4.58	554
calcd for $(HTrisS_3)CdBr_2$	$C_{37}H_{31}Br_2CdP_3S_3$	47.43	3.33	9.92	17.06	
calcd for $(TrisS_3)CdBr$	$C_{37}H_{30}BrCdP_3S_3$	51.91	3.53	10.85	9.33	
found		52.04	3.41	10.92	9.49	
calcd for $(HTrisS_3)CdI_2$	$C_{37}H_{31}CdI_2P_3S_3$	43.10	3.03	9.01	24.62	
calcd for $(TrisS_3)CdI$	$C_{37}H_{30}CdIP_3S_3$	49.21	3.35	10.29	14.05	
found		48.93	3.28	10.31	14.19	
calcd for $(H4mTrisS_3)CdCl_2$	$C_{17}H_{23}CdCl_2P_3S_3$	34.04	3.86	15.49	11.82	
calcd for $(4mTrisS_3)CdCl$	$C_{17}H_{22}CdClP_3S_3$	36.25	3.94	16.50	6.29	
found		36.23	3.92	16.56	6.29	
calcd for $(H4mTrisS_3)CdBr_2$	$C_{17}H_{23}Br_2CdP_3S_3$	29.65	3.37	13.49	23.20	
calcd for $(4mTrisS_3)CdBr$	$C_{17}H_{22}BrCdP_3S_3$	33.60	3.65	15.29	13.15	
found		33.38	3.58	15.07	13.25	
calcd for $(H4mTrisS_3)CdI_2$	$C_{17}H_{23}CdI_2P_3S_3$	26.09	2.96	11.87	32.43	
calcd for $(4mTrisS_3)CdI$	$C_{17}H_{22}CdIP_3S_3$	31.18	3.39	14.19	19.38	
found		31.26	3.38	14.09	19.50	

[a] Because it is necessary to establish the stoichiometry of these complexes, the calculated percentage compositions are also given for the neutral ligand compounds (which are not formed) in addition to the anionic ligand compounds (which are formed). [b] $HTrisS_3$ is $[Ph_2P(S)]_3CH$, and $TrisS_3$ is $[Ph_2P(S)]_3C^-$. [c] $H4mTrisS_3$ is $[Ph_2P(S)][Me_2P(S)]_2CH$, and $4mTrisS_3$ is $[Ph_2P(S)][Me_2P(S)]_2C^-$.

to investigate the ligand behavior of the anion $[Ph_2P(S)]_3C^-$, $TrisS_3^-$, and its analogues.

Results and Discussion

Our earliest attempts to prepare $TrisS_3^-$ from the neutral parent $HTrisS_3$ by reaction with a wide variety of bases were unsuccessful.[18] However, the direct reaction of $HTrisS_3$ with mercuric halides in ethanol solution produces compounds with the stoichiometry $[(C_6H_5)_2P(S)]_3CHgX$, where X is Cl, Br, or I. The compounds are air-stable, high-melting, diamagnetic, monomeric crystalline solids. A preliminary report of the first mercury complex, $(TrisS_3)HgCl$, has appeared.[19] It is likely that coordination of one or more of the tertiary phosphine sulfide groups of $HTrisS_3$ to mercury renders the methine proton more acidic and facilitates the proton transfer to ethanol, although we have no direct evidence as to whether proton dissociation occurs before, after, or simultaneously with coordination of the ligand.

The analogous cadmium halide complexes are prepared similarly except that addition of a base such as triethylamine is required for complex formation. In the absence of a metal salt the reaction of Et_3N and $HTrisS_3$ yielded no salt. This observation supports the suggestion that coordination occurs either before or simultaneously with proton dissociation.

Elemental analyses (see Table I) establish the stoichiometric ratio of 1:1:1 for ligand:mercury:halogen; however, they cannot distinguish the presence or absence of the methine hydrogen, i.e., the presence of the neutral or anionic ligand. If the neutral ligand is coordinated, mercury(I) is required by stoichiometry. Mercury(I) complexes are expected to be paramagnetic if monomeric and may be diamagnetic if dimeric. These complexes are in fact diamagnetic and monomeric (by molecular weight determinations), and thus the compounds must contain mercury(II) and the anionic tris ligand, $TrisS_3^-$. Additional evidence for the existence of the anionic form of the ligand is as follows: (a) the failure to observe a signal for the methine proton in the ^1H NMR spectra of the complexes, whereas the neutral parent ligand has an easily detectable methine proton signal at 6.04 ppm (quartet, $^2J(PCH) = 16.5$ Hz);[8] (b) the failure to observe the methine carbon in the ^{13}C NMR spectra of the complexes, due to the long relaxation time of the protonless carbon; (c) the subsequent discovery[20] that $TrisS_3^-$ can be synthesized independent of a transition-metal ion and that it is quite thermally and chemically stable;[21] (d) finally, conclusive proof by the X-ray crystallographic determination (vide infra) of $\{[Me_2P(S)]_2[Ph_2P(S)]C\}HgCl$, $(4mTrisS_3)HgCl$, that the ligand is bound to the mercury via the three sulfur atoms with the fourth coordination position about the pseudotetrahedral mercury(II) occupied by chlorine. A preliminary report of this structure has appeared.[1a]

The ^{31}P NMR data for $(TrisS_3)MX$ and $(4mTrisS_3)MX$, where M = Cd, Hg and X = Cl, Br, I, are given in Table II. Each room-temperature spectrum of the $(TrisS_3)HgX$ compounds

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Table II. Phosphorus-31 NMR Data for $\mathrm{TrisS_3^-}$ and $\mathrm{4mTrisS_3^-}$ Complexes

compd	solvent	T, K	$\delta_{\mathrm{P(S)Ph_2}}$	$\delta_{\mathrm{P(S)Me_2}}$	^2J(P–P), Hz	^2J(P–Hg), Hz
$\mathrm{(TrisS_3)CdCl}$	*b*	301	42.8 s	...	...	...
$\mathrm{(TrisS_3)CdBr}$	*b*	301	42.8 s	...	...	...
$\mathrm{(TrisS_3)CdI}$	*b*	301	42.8 s	...	...	...
$\mathrm{(TrisS_3)HgCl}$	*b*	295	43.9 s	...	...	92
$\mathrm{(TrisS_3)HgBr}$	*b*	295	44.3 s	...	...	88
$\mathrm{(TrisS_3)HgI}$	*b*	295	44.2 s	...	...	80
$\mathrm{(4mTrisS_3)CdCl}$	*b*	301	42.9 t	38.6 d	10	
$\mathrm{(4mTrisS_3)CdBr}$	*b*	301	42.9 t	38.6 d	10	
$\mathrm{(4mTrisS_3)CdI}$	*b*	301	43.0 t	38.6 d	10	
$\mathrm{(4mTrisS_3)HgCl}$	*c*	213	44.0 t	41.4 d	7	70 ($\mathrm{Ph_2P}$), 112 ($\mathrm{Me_2P}$)
$\mathrm{(4mTrisS_3)HgBr}$	*c*	213	44.1 t	41.3 d	7	69 ($\mathrm{Ph_2P}$), 104 ($\mathrm{Me_2P}$)
$\mathrm{(4mTrisS_3)HgI}$	*c*	213	44.2 t	41.1 d	7	66 ($\mathrm{Ph_2P}$), 91 ($\mathrm{Me_2P}$)
$\mathrm{(4mTrisS_3)HgI}$	*e*	169	44.2 dd	43.3 dd (A) 40.4 dd (B)	6.8 ($\mathrm{Ph_2P{-}Me_2P}$) 4.4 ($\mathrm{Me_2P_A{-}Me_2P_B}$)	96.6 ($\mathrm{Me_2P_A}$) 84.0 ($\mathrm{Me_2P_B}$) 68.4 ($\mathrm{Ph_2P}$)

[a] Abbreviations: s, singlet; d, doublet; t, triplet. [b] $\mathrm{CH_2Cl_2{-}CDCl_3}$ (2:1). [c] $\mathrm{CH_2Cl_2{-}C_6D_6}$ (19:1). [e] $\mathrm{CH_2Cl_2{-}CFCl_3}$ (4:1).

consists of a singlet flanked by mercury-199 ($I = {}^1/_2$, relative abundance 16.4%) satellites with $^2J(^{199}\mathrm{Hg}{-}^{31}\mathrm{P})$ = 92, 88, and 80 Hz, respectively, for the chloride, bromide, and iodide. These spectra are unchanged at reduced temperature; i.e., the peaks, including the mercury satellites, remain sharp. The coupling constants increase with the electronegativity of the halogen. The order of variation of ^2J(Hg–P) with halide in these compounds is the same as has been previously observed for ^1J(Hg–P) in tertiary phosphine mercury halide complexes.[22] This kinetic stability is somewhat surprising because monodentate tertiary phosphine sulfides,[23] bidentate tertiary phosphine sulfides of the type $\mathrm{Ph_2P(S)CH_2PR_2}$,[24] and the analogous anionic ligand $\mathrm{4mTrisS_3^-}$ are all labile at room temperature on the NMR time scale when complexed with mercury(II) halides. This behavior of the $\mathrm{TrisS_3^-}$ ligand toward mercury is an example of its especially favorable bonding characteristics. The ^{31}P NMR spectra of the $\mathrm{(TrisS_3)CdX}$ compounds are in each case singlets. No coupling with cadmium (^{111}Cd, $I = {}^1/_2$, abundance 12.75%; ^{113}Cd, $I = {}^1/_2$, abundance 12.26%) was observed at room temperature. The conclusions based on the ^{31}P results for $\mathrm{TrisS_3^-}$ complexes are as follows: (a) all three phosphorus atoms are equivalent; (b) the ligands are kinetically inert on the NMR time scale at room temperature; (c) the mercury–phosphorus coupling constant is of the correct magnitude for a two-bond coupling.[23,24] This information does not allow unequivocal assignment of the solution structure, however, since two possible structures could reasonably fit the data: (a) a four-coordinate mercury(II) complex, approximately tetrahedral, with the ligand bonded in a tridentate fashion through the three sulfur atoms; (b) a two-coordinate metal complex, approximately linear at mercury, with the ligand bonded via the central carbon to the metal. Attempts to solve an X-ray structure of $\mathrm{(TrisS_3)HgCl}$ and $\mathrm{(TrisS_3)HgI}$ failed because the crystals darkened and presumably decomposed when exposed to X-rays and consequently did not give good diffraction data. However, in a related compound, $\mathrm{(TrisS_3)AgP(\textit{n}\text{-}Bu)_3}$, the tripod ligand, as shown by an X-ray crystallographic determination,[25] is bonded to Ag via S. Finally, the molecular structure of the analogous complex $\mathrm{(4mTrisS_3)HgCl}$, discussed later, contains four-coordinate mercury.

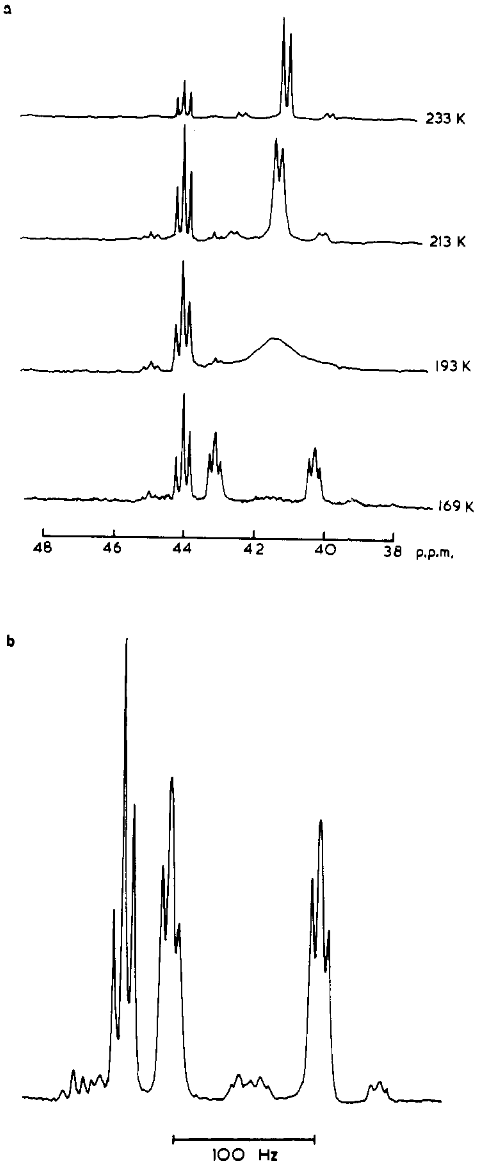

Figure 1. Proton-decoupled phosphorus-31 NMR spectra of $\{\mathrm{[Me_2P(S)]_2[Ph_2P(S)]C}\}\mathrm{HgI}$ in $\mathrm{CH_2Cl_2{-}CFCl_3}$: (a) spectra at various temperatures; (b) spectrum at 169 K with improved signal-to-noise ratio showing mercury-199 satellites of all three phosphorus atoms.

$\mathrm{[Me_2P(S)]_2[Ph_2P(S)]CH}$, $\mathrm{H4mTrisS_3}$, was originally synthesized[8] because the replacement of four phenyl groups by four methyl groups would alleviate, in part, the steric strain existent in $\mathrm{HTrisS_3}$ and probably in $\mathrm{TrisS_3^-}$ complexes also, while still retaining the essential tripod and electronic features of the tris ligand. $\mathrm{H4mTrisS_3}$ reacts with $\mathrm{HgX_2}$ and $\mathrm{CdX_2}$ in the same manner as $\mathrm{HTrisS_3}$ to yield the analogous products $\mathrm{(4mTrisS_3)MX}$, where M = Hg, Cd and X = Cl, Br, I. At room temperature the ^{31}P NMR spectra of the cadmium compounds consist of a triplet and a doublet of relative intensity 1:2, corresponding to the $\mathrm{Ph_2P(S)}$– and $\mathrm{Me_2P(S)}$– groups, respectively, with ^2J(PP) being about 10 Hz. The mercury compounds show the same pattern with the additional presence of the ^{199}Hg satellites

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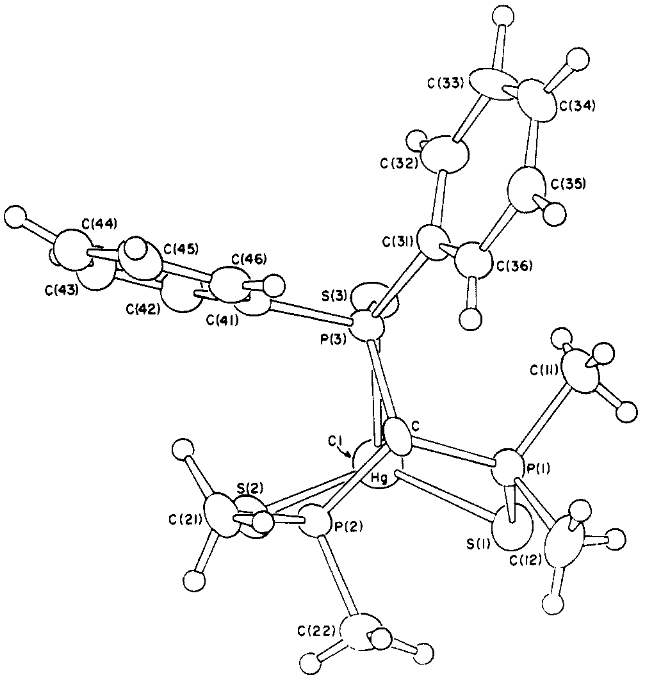
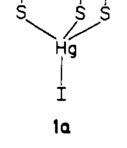


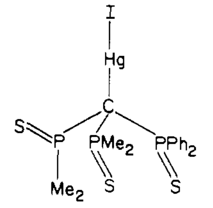
Figure 2. Molecular structure of $\{[(C_6H_5)_2P(S)][(CH_3)_2P(S)]_2C\}HgCl$ as viewed along the mercury–chlorine axis. The Cl lies beneath the Hg.

associated with each multiplet. As with the previous analogues $^2J(^{199}Hg-^{31}P)$ increases in the order I < Br < Cl. Also it is noted that $^2J(^{199}Hg-^{31}P)$ is larger for the $Me_2P(S)$– group than for the $Ph_2P(S)$– group.

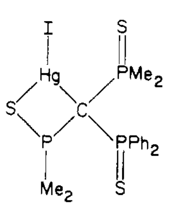
Interestingly, unlike those of the $(TrisS_3)HgX$ compounds, the ^{31}P NMR spectra of the mercury complexes of $4mTrisS_3^-$ are temperature dependent (Figure 1). In particular the room-temperature (295 K) spectrum of $\{[Me_2P(S)]_2[Ph_2P(S)]C\}HgI$ is broad, with P–P coupling barely observable and the mercury satellites beginning to collapse. At reduced temperature (233 K), the spectrum is a fairly sharp doublet ($Me_2P(S)$) and triplet ($Ph_2P(S)$) with the corresponding satellites, representing the expected A_2X spectrum. However, further cooling (193 K) causes the spectrum to broaden again (see Figure 1) and then resharpen at 169 K to an AMX pattern. The low-temperature ^{31}P spectra of $(4mTrisS_3)HgCl$ and $(4mTrisS_3)HgBr$ are both AMX spectra like the spectrum (Figure 1) for the iodide complex, $(4mTrisS_3)HgI$. However, because of lesser solubilities of the chloride and bromide complexes their spectra were not as well resolved as that (Figure 1b) for $(4mTrisS_3)HgI$, which reveals mercury satellites for each of the three thio–phosphoryl groups. This ^{31}P NMR spectral behavior upon cooling is in principle consistent with the solid-state structure (see Figure 2) determined by X-ray diffraction in which the ligand is bonded to the mercury through the three sulfur atoms. At temperatures close to and above room temperature there is intermolecular ligand exchange with concomitant line broadening and collapse of the ^{199}Hg satellites. At 233 K this exchange is slow on an NMR time scale and structure **1a** (an approximation to the solid-state structure) is adopted in which librational motions render the two Me_2P groups equivalent and an A_2X pattern is obtained with ^{199}Hg satellites for both signals. At 169 K this librational motion is also slow on an NMR time scale so that the two Me_2P groups are now inequivalent (as in the solid), and an AMX spectrum results, in which each signal has ^{199}Hg satellites with $^2J(^{199}Hg-S-^{31}P)$ of ca. 90 Hz. For this interpretation to be correct, there would have to be a barrier of some 44 kJ mol^{-1} to the interconversion of the enantiomers of Figure 2 (which renders the Me_2P groups equivalent), and it may be doubted whether this would be the case. There are other possible explanations. These include the following: (i) There exists a structure like **1b** with a mercury–carbon bond and with restricted rotation about the phosphorus–methine carbon bonds so that the two $Me_2P(S)$– groups are not equivalent. This type of restricted rotation has been noted for the free ligand $HTrisS_3$[11] but not for its mercury complexes, $(TrisS_3)HgX$. Restricted rotation in the free ligands $[Ph_2P(S)][Me_2P(S)]_2CH$ and $[Ph_2P(S)]_2[Me_2P(S)]CH$ has not been observed within our experimental low-temperature limit (168 K). Structure **1b** might be more likely to exist for $(4mTrisS_3)HgX$ than for $(TrisS_3)HgX$ because of the reduced steric hindrance toward a carbon-bound mercury atom in the case of four methyl groups for the former compared to four phenyl groups in the latter case. (ii) There exists a structure that has carbon bound to mercury in addition to one of the $Me_2P(S)$– groups, as in **1c**. This type of arrangement has been observed in a Pt complex of the anionic bidentate ligand $[Ph_2P(S)CHP(S)Ph_2]^-$, which in a stable isomer has Pt chelated in a four-membered ring to carbon and one sulfur.[26] At present we are unable to discriminate among these various possibilities for the low-temperature solution structure of $(4mTrisS_3)HgCl$, which cannot be said unequivocally to be the same as in the solid (i.e., a distorted form of **1a**).



1a



1b



1c

Table III. Raman and Infrared Spectra of $(TrisS_3)MX$ and $(4mTrisS_3)MX$ Compounds in the Region 400–700 cm^{-1}

compd	abs, cm^{-1} [a]
$HTrisS_3$ (Raman)	509 (0.1), 574 (1), 617 (0.3), 643 (0.1), 682 (0.5)
$HTrisS_3$ (IR)	485 (0.9), 506 (0.6), 528 (0.3), *572* (0.3), 615 (0.1), 631 (0.1), 642 (0.2), 682 (1), 692 (0.2)
$(TrisS_3)HgCl$ (Raman)	465 (1), 505 (0.2), 515 (0.2), 550 (0.8), 565 (0.4), 616 (0.6), 652 (0.2)
$(TrisS_3)HgCl$ (IR)	492 (0.8), 512 (0.3), 552 (1), 612 (0.5), 650 (0)
$(TrisS_3)HgBr$ (Raman)	465 (0.8), 515 (0.2), 550 (1), 617 (0.5), 650 (0.3)
$(TrisS_3)HgI$ (Raman)	467 (0.6), 551 (1), 577 (0.3), 615 (0.4), 652 (0.2)
$(TrisS_3)CdCl$ (Raman)	466 (1), 550 (0.8), 575 (0.6), 618 (0.5), 655 (0.2)
$(TrisS_3)CdCl$ (IR)	493 (1), 514 (0.5), 551 (1), 574 (0.3), 612 (0.4), 655 (0.8)
$H4mTrisS_3$ (Raman)	495 (0.1), 515 (0.1), 565 (1), 585 (0.2), 607 (0.1), 619 (0.1), 662 (0.3)
$H4mTrisS_3$ (IR)	489 (0.5), 514 (0.9), 563 (0.6), 585 (1), 602 (0.5), 660 (0.7)
$(4mTrisS_3)HgCl$ (Raman)	457 (0.3), 468 (1), 520 (0.5), 558 (0.3), 611 (0.1), 628 (0.2)
$(4mTrisS_3)HgCl$ (IR)	446 (0.3), 501 (0.2), 518 (0.8), 558 (0.2), 588 (0.2), 610 (1), 628 (1)
$(4mTris_3)CdCl$ (Raman)	466 (1), 520 (0.4), 531 (0.2), 560 (0.2), 612 (0.1), 627 (0.2)
$(4mTrisS_3)CdCl$ (IR)	456 (0.4), 502 (0.4), 520 (0.9), 560 (0.3), 613 (1), 628 (0.9)
$(4mTrisS_3)CdBr$ (Raman)	466 (1), 521 (0.4), 560 (0.2), 613 (0.2), 627 (0.2)

[a] The numbers in parentheses are the approximate intensities (peak heights) relative to the most intense peak in each spectrum.

Raman and infrared spectral data are presented in Table III. In the region from 400 to 800 cm^{-1} the parent neutral $HTrisS_3$ has three major peaks in the Raman spectrum: the most intense at 574 cm^{-1} is tentatively assigned to the P–S stretching mode; a peak half as intense appears at 682 cm^{-1}, and the remaining peak at 617 cm^{-1} has about one-third the intensity of the main peak. There are also several minor peaks that have about 10%

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(26) Browning, J.; Bushnell, G. W.; Dixon, K. R.; Pidcock, A. *Inorg. Chem.* **1983**, *22*, 2226.

or less of the intensity of the main peak. In the infrared spectrum the band at 682 cm^{-1} is most intense with the peak at 572 cm^{-1} (cf. 574) being about one-quarter intensity and the peak at 615 cm^{-1} (cf. 617) being only one-tenth the intensity of the main peak. The assignment of the 574-cm^{-1} peak as the P–S stretch is based on its intensity in the Raman and its relationship to assignments in other phosphine sulfides. It is somewhat lower than that in Ph_3PS (637,[27] 645,[28] 632,[29] cm^{-1})[30] and $Ph_2P(S)CH_2P(S)Ph_2$ (628,[31] 606[32] cm^{-1}),[30] and this perhaps reflects, in addition to electronic effects, greater steric efforts in $HTrisS_3$ which might lead to longer and weaker P–S bonds. To this point the mean P–S bond length in $HTrisS_3$ is 194.4 pm[11] compared to 192.8 pm in $(p\text{-}CH_3C_6H_4)_3PS$.[33] Me_3PS and Me_2PhPS have P–S stretching frequencies of 565[27,34–37a] and 585[35] cm^{-1}, respectively, and the methyl analogue of $HTrisS_3$, viz. $[Me_2P(S)]_3CH$, has $\nu_{P{=}S}$ assignments[37b] at 568, 578, and 589 cm^{-1}.

Upon complexation to form $(TrisS_3)MX$ compounds, where M = Cd, Hg and X = Cl, Br, I, several changes occur in the Raman and infrared spectra of the ligand. The band at 574 cm^{-1} disappears, and new bands appear at about 550 cm^{-1} (most intense in both the Raman and IR) and 466 cm^{-1} (with a relative intensity compared to the most intense peak of about 0.6 to 1 in the Raman). This latter peak is not seen in the infrared spectra, however. The 682-cm^{-1} band also disappears, and a new band appears at about 650 cm^{-1} with a relative intensity of 0.8 in the IR and 0.2–0.3 in the Raman. The band originally at 617 cm^{-1} in $HTrisS_3$ remains in the complexes. If 574 cm^{-1} is the P–S stretch in $HTrisS_3$, then it shifts to either 466 cm^{-1} with a $\Delta\nu_{P{=}S}$ of −108 cm^{-1} or to 550 cm^{-1} ($\Delta\nu_{P{=}S} = -24$ cm^{-1}) in the complexes. The decrease of about 108 cm^{-1} is very large compared to the change when neutral tertiary phosphines undergo coordination. Ordinarily, $\Delta\nu_{P{=}S}$ is in the range[27,28,31,32,34,35,37,38] of −25 to −48 cm^{-1}. However, in the present case, $\Delta\nu_{P{=}S}$ is associated with two changes from the neutral ligand: proton abstraction to form the anion $TrisS_3^-$ and complexation of the anion to form the complex, both of which should weaken the P–S bond. It is therefore difficult to compare the behavior of this anionic ligand with previous results for neutral ligands. Recent reports on the related anionic ligands $\{[Ph_2P(S)]_2CH\}^-$ and $[Ph_2P(S)CH_2]^-$ and their complexes did not give IR or Raman data.[39–41] However, we believe that the peak at 466 cm^{-1} rather than the peak at 550 cm^{-1} is probably due to the coordinated P–S stretch in the complexes because a peak (most intense band in the Raman spectrum) also appears at 548 cm^{-1} in the Raman spectrum of $[(n\text{-}Bu)_4N][TrisS_3]$.[42] It is also possible that the P–S bonds do not behave independently and thus two stretches (A and E modes) would be expected in the complexes. Because of the uncertainty of assignment of $\nu_{P{=}S}$ in the past[30] and the complexity of this system, these assignments must be taken as tentative. It should be clear however that the dramatic changes in the Raman spectra of $HTrisS_3$ upon coordination argue strongly for coordination via the sulfur.

Table IV. Crystallographic Data for $\{[Me_2P(S)]_2[P(S)Ph_2]C\}HgCl$

formula	$C_{17}H_{22}ClHgP_3S_3$
mol wt	651.52
cryst class	monoclinic
space group	$P2_1/a$
unit-cell params	$a = 1.48$ (1) nm $b = 1.394$ (9) nm $c = 1.194$ (8) nm $\beta = 112.038$ (6)°
vol	2.467 (1) nm^3
density, ρ_{calcd}	1.89 g cm^{-3}
Z	4
cryst size	0.08 × 0.11 × 0.23 mm
axis used for mounting	a
diffractometer	Picker FACS-I
radiation	graphite-monochromated Mo Kα ($X = 71.069$ pm)
abs coeff	74.1 cm^{-1}
A^*_{max}, A^*_{min}	1.89818, 1.41681
data collection technique	$2\theta-\theta$
scanning range	$2° < 2\theta < 50°$
2θ scan width	$1.2 + 0.69 \tan \theta$
scan speed	2° min^{-1}
bkdg time	10 s
intens control stds	3 measd every 100 reflcns
total reflcns measd	4558
unique reflcns measd	4018
reflcns with $I > 3\sigma(I)$	3063
final $R(F) = \sum(\lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert)/\sum\lvert F_o\rvert$	0.036
final $R_w(F) = [\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2/\sum(F_o)^2]^{1/2}$	0.037

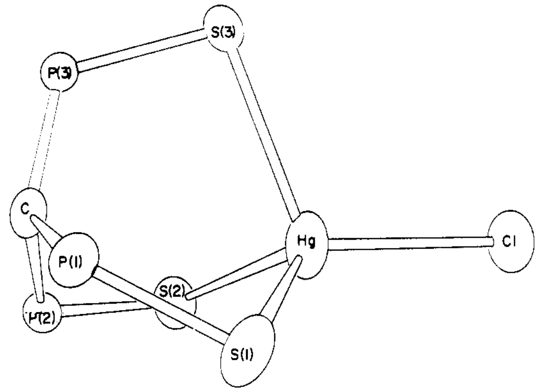

Figure 3. View of the cage structure of $\{[(C_6H_5)_2P(S)][(CH_3)_2P(S)]_2C\}HgCl$.

The assignment of the P–S stretching frequencies from the Raman and infrared spectra of $H4mTrisS_3$ and its complexes is more difficult than for $HTrisS_3$ because of the presence of two types of P–S groups, viz. $Ph_2P(S)$ and $Me_2P(S)$. For neutral $Ph_2P(S)CH_2P(S)Me_2$ these assignments[32] were 601 and 579 cm^{-1}, respectively, which is consistent with a weakening of the P–S bond upon replacement of phenyl by methyl groups.[27] $H4mTrisS_3$ has major Raman bands at 565 (relative intensity 1), 585 (0.2), and 662 (0.3) cm^{-1} with the corresponding infrared peaks at 563 (0.6), 585 (1), and 660 (0.7) cm^{-1}. The complexes have more complex spectra with Raman bands at about 466 (1), 520 (0.4), 559 (0.2), 612 (0.1), and 628 (0.2) cm^{-1}. The infrared bands are at 520 (0.9), 559 (0.2), 612 (1), and 628 (0.9) cm^{-1}. As with $TrisS_3^-$ complexes the new and most intense peak at 466 cm^{-1} in the Raman does not appear in the infrared. The assignments here are not conclusive except to note that major changes from the spectrum of $H4mTrisS_3$ indicates coordination via sulfur.

The molecular structure of $\{[Me_2P(S)]_2[Ph_2P(S)]C\}HgCl$, $(4mTrisS_3)HgCl$, has been solved by X-ray diffraction techniques. The crystallographic and data collection parameters are summarized in Table IV, the final atomic coordinates are given in

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Table V. Final Atomic Coordinates[a]

atom	*x*	*y*	*z*	*U*, Å^2 [b]
Hg	0.40764 (2)	0.07654 (3)	0.15273 (4)	0.04 (2)
Cl	0.2542 (1)	−0.0069 (2)	0.0864 (2)	0.04 (2)*
C	0.5987 (5)	0.2249 (5)	0.2348 (6)	0.03 (2)*
S(1)	0.5601 (1)	0.0131 (1)	0.3153 (2)	0.05 (2)*
P(1)	0.6503 (1)	0.1108 (1)	0.2831 (2)	0.03 (2)*
C(11)	0.7562 (5)	0.1152 (5)	0.4234 (7)	0.041 (5)*
C(12)	0.6965 (5)	0.0607 (5)	0.1762 (7)	0.04 (2)*
S(2)	0.4546 (2)	0.1378 (2)	−0.0192 (2)	0.028 (1)*
P(2)	0.5455 (1)	0.2440 (1)	0.0751 (2)	0.03 (2)*
C(21)	0.4765 (6)	0.3544 (5)	0.0383 (7)	0.05 (2)*
C(22)	0.6361 (6)	0.2598 (6)	0.0100 (7)	0.06 (2)*
S(3)	0.3979 (1)	0.2391 (1)	0.2730 (2)	0.04 (2)*
P(3)	0.5382 (1)	0.2792 (1)	0.3193 (2)	0.03 (2)*
C(31)	0.6058 (5)	0.2589 (5)	0.4799 (7)	0.04 (2)*
C(32)	0.5705 (6)	0.2000 (6)	0.5484 (8)	0.06 (2)*
C(33)	0.6203 (6)	0.1886 (6)	0.6700 (8)	0.07 (2)*
C(34)	0.7055 (6)	0.2380 (6)	0.7276 (7)	0.06 (2)*
C(35)	0.7424 (5)	0.2955 (5)	0.6630 (8)	0.04 (2)*
C(36)	0.6938 (5)	0.3065 (5)	0.5409 (7)	0.04 (1)*
C(41)	0.5462 (5)	0.4080 (5)	0.3098 (6)	0.03 (1)*
C(42)	0.4769 (5)	0.4656 (6)	0.3305 (7)	0.05 (1)*
C(43)	0.4808 (6)	0.5643 (5)	0.3281 (8)	0.05 (1)*
C(44)	0.5567 (6)	0.6067 (5)	0.3044 (7)	0.04 (1)*
C(45)	0.6259 (5)	0.5513 (5)	0.2844 (7)	0.036 (9)*
C(46)	0.6214 (5)	0.4521 (5)	0.2882 (7)	0.033 (7)*
H(111)	0.791 (4)	0.158 (4)	0.392 (6)	0.04 (2)
H(112)	0.708 (7)	0.123 (6)	0.489 (9)	0.12 (4)
H(113)	0.790 (6)	0.051 (6)	0.421 (8)	0.11 (3)
H(121)	0.648 (5)	0.053 (5)	0.075 (7)	0.07 (2)
H(122)	0.734 (4)	0.091 (4)	0.170 (5)	0.02 (2)
H(123)	0.715 (4)	0.002 (4)	0.214 (6)	0.04 (2)
H(211)	0.522 (5)	0.408 (5)	0.050 (7)	0.06 (2)
H(212)	0.437 (5)	0.354 (5)	0.063 (7)	0.07 (3)
H(213)	0.476 (6)	0.347 (6)	−0.040 (8)	0.12 (3)
H(221)	0.590 (5)	0.272 (5)	−0.062 (6)	0.05 (2)
H(222)	0.657 (5)	0.311 (5)	0.028 (7)	0.06 (2)
H(223)	0.660 (6)	0.204 (6)	−0.012 (8)	0.10 (3)
H(32)	0.521 (4)	0.175 (4)	0.519 (6)	0.05 (2)
H(33)	0.598 (4)	0.163 (4)	0.713 (5)	0.03 (2)
H(34)	0.714 (5)	0.235 (5)	0.811 (6)	0.06 (2)
H(35)	0.790 (3)	0.329 (4)	0.687 (5)	0.02 (2)
H(36)	0.710 (3)	0.343 (3)	0.503 (4)	0.00 (1)
H(42)	0.438 (4)	0.443 (4)	0.355 (5)	0.02 (2)
H(43)	0.431 (5)	0.612 (5)	0.346 (7)	0.07 (3)
H(44)	0.562 (4)	0.670 (4)	0.294 (5)	0.03 (2)
H(45)	0.677 (4)	0.569 (4)	0.263 (5)	0.03 (2)
H(46)	0.664 (4)	0.418 (4)	0.271 (5)	0.02 (1)

[a] Numbers in parentheses are estimated standard deviations in the least significant digit. [b] Atoms marked with an asterisk were refined isotropically, equivalent isotropic temperature factor = $^1/_3 \cdot \sum_i \sum_j \mu_{ij} a^*_i a_j (\mathbf{a}_i \cdot \mathbf{a}_j)$.

Table VI. Selected Interatomic Distances and Angles for $(4mTrisS_3)HgCl$

atoms	dist, pm	atoms	angle, deg
Hg–Cl	240.8 (3)	P(1)–C–P(2)	116.4 (4)
Hg–C	334.3 (7)	P(1)–C–P(3)	117.0 (4)
Hg–S(1)	252.2 (3)	P(2)–C–P(3)	115.7 (4)
Hg–S(2)	255.0 (3)	S(1)–P(1)–C	115.4 (3)
Hg–S(3)	271.6 (3)	S(2)–P(2)–C	114.7 (2)
P(1)–S(1)	204.2 (3)	S(3)–P(3)–C	114.8 (2)
P(2)–S(2)	203.4 (3)	Cl–Hg–C	170.7 (1)
P(3)–S(3)	201.9 (3)	S(1)–Hg–Cl	123.1 (1)
P(1)–C	176.5 (7)	S(2)–Hg–Cl	114.0 (1)
P(2)–C	179.0 (8)	S(3)–Hg–Cl	110.3 (1)
P(3)–C	175.3 (8)	S(1)–Hg–S(2)	107.5 (1)
P(1)–C(11)	181.7 (7)	S(1)–Hg–S(3)	95.5 (1)
P(1)–C(12)	180 (1)	S(2)–Hg–S(3)	103.4 (1)
P(2)–C(21)	180.8 (8)	Hg–S(1)–P(1)	94.7 (1)
P(2)–C(22)	180 (1)	Hg–S(2)–P(2)	97.0 (1)
P(3)–C(31)	182.3 (7)	Hg–S(3)–P(3)	97.0 (1)
P(3)–C(41)	180.5 (7)		

Table V, and selected bond distances and angles are given in Table VI.

The mercury atom is in a distorted-tetrahedral geometry with bonds to three sulfurs and the chlorine. The mean SHgS and SHgCl angles are 102.1 and 115.8°, respectively. Figure 2 shows the molecular conformation as viewed down the Hg–Cl bond axis, while Figure 3 shows a better view of the cage with the organic substituents on the phosphorus atoms omitted for clarity. The Hg–Cl bond length (240.8 (3) pm) is larger than in MeHgCl (228.5 (5) pm)[43] as might be expected for sp^3 hybridization of mercury compared to sp hybridization. The mean Hg–S bond length (260 pm) is greater than that of typical inorganic mercury sulfides (236 pm)[44] and greater than the sum of the covalent radii of the atoms (148 pm + 104 pm = 252 pm).[45] The deviation from the mean Hg–S bond length is considerable with Hg–S(3) of the diphenylthiophosphoryl group being 271.6 (3) pm compared to the significantly shorter lengths of 252.2 (3) and 255.0 (3) pm, respectively, for Hg–S(1) and Hg–S(2) of the dimethylthiophosphoryl groups. If this implies that the $Ph_2P(S)$–Hg bond is weaker than the $Me_2P(S)$–Hg bonds, it would also imply that the P(3)–S(3) bond of the $Ph_2P(S)$– group should be shorter (due to greater double-bond character) than the P(1)–S(1) and P(2)–S(2) bonds of the $Me_2P(S)$– groups. This is indeed the case with the Ph_2P–S bond length being 201.9 (3) pm compared to 204.2 (3) and 203.4 (3) pm for P(1)–S(1) and P(2)–S(2), respectively. The P–S bond lengths are longer than those found in simple uncoordinated tertiary phosphines such as $(p\text{-}CH_3C_6H_4)_3PS$ (192.8 pm)[33] and $(C_6H_{11})PS$ (196.6 pm).[46] This is reasonable since lengthening of the P–S bond is expected upon coordination. For example, in $(Ph_3P)Pd(Ph_2PS_2)_2$, one diphenyldithiophosphinate is monodentate with the bound P–S bond length 204.7 (10) pm compared to 196.6 (13) pm for the unbound P–S.[47]

The P–S bond lengths in complexes of the diphenylthiophosphoryl-containing anions $\{[Ph_2P(S)]_2CH\}^-$ and $[Ph_2P(S)CH_2]^-$ are 201.4 (5)[26] and 199.9 (3) pm,[39] respectively, which compares with the P(3)–S(3) length in our complex. However, both of the former complexes, $\{[Ph_2P(S)]_2CH\}Pt(PEt_3)Cl$ and $[Ph_2P(S)CH_2]Ni(PPh_3)Cl$, contain four-membered chelate rings –P–S–M–C–, whereas $(4mTrisS_3)HgCl$ contains six-membered chelate rings. The mean central carbon–phosphorus bond length of 176.9 pm is significantly less than the mean of 181 pm for the six exocyclic P–C bonds and demonstrates that the mesomeric nature (ylide-type) of the ligand is still retained in the complex. The corresponding P–C bond lengths in other mesomerically stabilized tris-phosphorus compounds are 176.2 pm[21] in $TrisS^-_3$ and 175 pm[48] in the dication $\{(Me_3P)_3C\}^{2+}$. The P–C bond lengths in the Pt and Ni complexes discussed above are 182.1 and 177.6 pm, respectively.[26,39] In simple ylides the P–C bond lengths are about 171 pm,[49] while in $(Ph_2P)_2C{=}PPh_3$[50] the ylidic P–C length is 172.0 pm compared to 179.4 and 179.5 pm for the other two central C–P bonds.

The bond angles within the cage at the mercury bridgehead and the adjacent sulfur atoms are smaller than tetrahedral with means of 102.1° for SHgS and 96.2° for PSHg. In a complex of a coordinated monodentate phosphine sulfide, $[(Me_3PS)_3Cu]ClO_4$, the PSCu angles[51] average 107.3°. However,

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in a complex of a bidentate bis(tertiary phosphine disulfide), [Ph$_2$P(S)CH$_2$P(S)Ph$_2$]CuCl,[52] which contains a six-membered chelate ring as in the present cage complex, the angles at sulfur, PSCu, average 93.6°. At the carbon bridgehead in (4mTrisS$_3$)HgCl the PCP angles average 116.4° and the CPS angles average 115.0° in the chelate rings. The six-membered chelate rings have distorted-boat conformations (the boat of course being required by the geometry of the cage) which are very similar to the distorted-boat conformation that is also adopted by the [Ph$_2$P(S)CH$_2$P(S)Ph$_2$]CuCl complex. The PCP angle (117.2°) in the latter is also unusually large, similar to the PCP angles at the bridgehead in the cage. It therefore appears that the cage has no unusual steric strain arising from the cage itself. The nonbonded C–Hg distance across the cage is 343.7 pm.

Experimental Section

Routine phosphorus-31 NMR spectra were recorded on a Varian XL-100 FT instrument equipped with a Nicolet Multi-Observe Nuclei Accessory (MONA) unit operating at 40.5 MHz. All spectra were broad-band proton decoupled. Additional ^{31}P{^{1}H} and ^{13}C{^{1}H} spectra and low-temperature spectra were obtained with a JEOL FX-60 spectrometer at observing frequencies of 24.2 and 15.0 MHz, respectively, and also a JEOL FX-90Q spectrometer at observing frequencies of 36.2 and 22.5 MHz, respectively. Unless otherwise noted, the solvent for the ^{31}P spectra was CH$_2$Cl$_2$. ^{31}P chemical shifts are positive if deshielded from the reference, 85% H$_3$PO$_4$.

Raman spectra of the pure solid samples in capillary tubes were obtained by excitation with 48.8 nm wavelength radiation from a Coherent 52 argon ion laser (ca. 200-mW power) using a Spex 1402 dual monochromator. The spectral slit width employed with ca. 3 cm^{-1}. The accuracy of band positions is ca. ±4 cm^{-1}. Infrared spectra were measured on KBr pellets and Nujol-mulled samples with a Perkin-Elmer 225 spectrophotometer. The spectral slit width employed was ca. 2 cm^{-1}, and the calibration checked against a polystyrene film is better than ±1 cm^{-1}.

Microanalyses were performed by Barry Saunderson, City of London Polytechnic, and Dr. Franz Kasler, University of Maryland. Molecular weight determinations (vapor pressure osmometry) were carried out by Galbraith Laboratories, Knoxville, TN. Magnetic susceptibilities were determined by Dr. Elizabeth M. Briggs, City of London Polytechnic. Melting points were determined with a Mel-Temp apparatus and are reported uncorrected.

Metal halides were obtained from J. T. Baker Chemical Co. HTrisS$_3$[4,8] and H4mTrisS$_3$[8] were prepared as previously described.

Synthesis of {[Ph$_2$P(S)]$_3$C}HgI, (TrisS$_3$)HgI. Mercuric iodide (0.34 g, 0.75 mmol) dissolved in 50 mL of warm absolute EtOH was added slowly under N$_2$ with rapid magnetic stirring to 0.50 g (0.75 mmol) of HTrisS$_3$ in 50 mL of tetrahydrofuran (THF). After complete addition, the solution was allowed to stand overnight, during which time a colorless precipitate slowly formed. Recrystallization from CH$_2$Cl$_2$/MeOH gave the desired product, mp 210–215 °C dec, in 51% yield.

(TrisS$_3$)HgBr, mp 210–215 °C dec (66% yield), and (TrisS$_3$)HgCl, mp 210–215 °C dec (92% yield), were prepared similarly.

Synthesis of (TrisS$_3$)CdI. HTrisS$_3$ (0.50 g, 0.75 mmol) was dissolved in 40 mL of THF and 5 mL of Et$_3$N under N$_2$. To this solution was added with stirring 0.75 mmol of CdI$_2$ in 50 mL of EtOH. The white precipitate that formed upon complete addition was collected, washed with EtOH, and dried in vacuo. The yield of product, mp 280–285 °C dec, was 75%.

(TrisS$_3$)CdBr, mp 280–285 °C dec (89% yield), and (TrisS$_3$)CdCl, mp 280–285 °C dec (94% yield), were prepared similarly. It should be noted that without the addition of Et$_3$N in the case of CdX$_2$, no apparent reaction occurs with HTrisS$_3$.

Synthesis of {[Ph$_2$P(S)][Me$_2$P(S)]$_2$C}HgI, (4mTrisS$_3$)HgI. The ligand, H4mTrisS$_3$ (0.50 g, 1.20 mmol), was dissolved in 50 mL of THF and 15 mL of Et$_3$N. Mercuric iodide (0.546 g, 1.20 mmol), dissolved in 50 mL of warm absolute EtOH, was added dropwise to the above solution under N$_2$ with rapid magnetic stirring. The solution was stirred overnight. Solvents were removed by rotary evaporation until a precipitate formed. The product, mp 175–180 °C dec (83% yield), was washed with EtOH and dried in vacuo.

(4mTrisS$_3$)HgBr, mp 175–180 °C dec (76% yield), (4mTrisS$_3$)HgCl, mp 175–180 °C dec (85% yield), (4mTrisS$_3$)CdI, mp 245–250 °C dec (93% yield), (4mTrisS$_3$)CdCl, mp 245–250 °C dec (56% yield), and (4mTrisS$_3$)CdCl, mp 245–250 °C dec (58% yield), were all prepared analogously. Analyses are given in Table I.

The ^{13}C NMR data for [Ph$_2$P(S)][Me$_2$P(S)]$_2$CH, which were not previously reported, follow. Phenyl region: C$_1$, 132.1 ppm, d, ^1J(PC) = 83.5 Hz; C$_{2,6}$, 132.1 ppm, d, ^2J(PC) = 10.3 Hz; C$_{3,5}$, 128.6 ppm, d, ^3J(PC) = 12.7 Hz; C$_4$, 132.2 ppm, d, ^4J(PC) = 3.2 Hz. Methine C: 46.5 ppm, dt, ^1J(Ph$_2$PC) = 22.5 Hz (d), ^1J(Me$_2$PC) = 20.2 Hz (t). Nonequivalent CH$_3$ groups: CH$_3$(A), 27.6 ppm, d, N(PC) = 54.6 Hz; CH$_3$(B), 24.4 ppm, d, N(PC) = 54.6 Hz (N(PC) = ^1J(PC) + ^3J(P′C).

Molecular Structure Determination of (4mTrisS$_3$)HgCl. Colorless prismatic crystals of (4mTrisS$_3$)HgCl were grown slowly from dichloromethane/methyl alcohol (3:2) in a test tube. A well-formed crystal of approximate dimensions 0.08 × 0.11 × 0.23 mm was chosen and mounted on a thin glass fiber parallel to its long axis (100) with quick-setting epoxy resin adhesive. The monoclinic space group $P2_1/a$ and approximate cell parameters were determined from oscillation and Weissenberg photographs with Cu radiation.

All subsequent X-ray measurements were carried out on a Picker FASC-I diffractometer with Mo radiation at 24 °C. The unit cell constants were determined by the least-squares refinement of data from 12 automatically centered reflections. The crystallographic and data collection parameters are summarized in Table IV. The intensities were measured with the θ–2θ scan technique with a scan rate of 2° min^{-1} and 10-s background; $2\theta_{\max} = 50°$, h = 0–16, k = 0–16, l = −13 to +13. The measured intensities were corrected for absorption (Gaussian quadrature, 8 × 8 × 8 point grid) and for Lorentz and polarization factors.

The structure was solved by using the heavy-atom technique. The E's were converted to normalized structure factors (E's), and the Hg vectors were readily located in an $E^2 - 1$ Patterson function. The C, P, S, and Cl atoms were located from several cycles of structure factor, electron density, and difference map calculations. The aromatic ring hydrogen atoms were placed at idealized positions (based upon d(C–H) = 107 pm and a regular trigonal geometry about the C atoms), and the methyl H's were located in a difference map. The full-matrix refinement with least-squares technique was carried out with anisotropic temperature factors for the non-hydrogen atoms (Hg, Cl, P, S, C) and isotropic terms for hydrogen. The function minimized during refinement was $\sum w(|F_o| - |F_c|)^2$, where $w = (1/\sigma(F))^2$. The final residuals are given in Table IV. The scattering factors for C, P, S, Cl, and Hg were generated from the analytical expressions of Cromer and Mann;[53] the scattering factors for H were those of Stewart et al.[54] All calculations were carried out on a UNIVAC 1100/82 computer with the XRAY-76[55] system of programs.

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Registry No. (TrisS$_3$)HgCl, 82288-24-2; (TrisS$_3$)HgBr, 82288-25-3; (TrisS$_3$)HgI, 82288-26-4; (4mTrisS$_3$)HgCl, 97391-00-9; (4mTrisS$_3$)HgBr, 97391-01-0; (4mTrisS$_3$)HgI, 97391-02-1; (TrisS$_3$)CdCl, 97391-03-2; (TrisS$_3$)CdBr, 97391-04-3; (TrisS$_3$)CdI, 97391-05-4; (4mTrisS$_3$)CdCl, 97391-06-5; (4mTrisS$_3$)CdBr, 97391-07-6; (4mTrisS$_3$)CdI, 97391-08-7.

Supplementary Material Available: Thermal parameters (Table VII), a complete list of interatomic distances and angles (Table VIII), and observed and final calculated structure factors (Table IX) (17 pages). Ordering information is given on any current masthead page.

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