Studies of some Mercury(II) and Cadmium(II) Complexes with Dicyclohexylphosphine and (1-(Dicyclohexylphosphino))-N-phenylthioformamide

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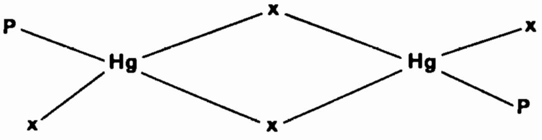
Dicyclohexylphosphine, HPcycl$_2$, reacts with mercury(II) and cadmium(II) halides to give isolable 1:1 adducts HgX$_2$(HPcycl$_2$) (X = Cl, Br, I), CdX$_2$(HPcycl$_2$) (X = Br, I) and 1:2 adducts HgX$_2$(HPcycl$_2$)$_2$, CdX$_2$(HPcycl)$_2$ (X = Cl, Br, I). The 1:2 adducts HgX$_2$(HPcycl$_2$)$_2$ react in solution with additional HPcycl$_2$ to give 1:3 adducts HgX$_2$(HPcycl$_2$)$_3$ whereas the corresponding CdX$_2$(HPcycl$_2$)$_2$ do not react further with HPcycl$_2$. Both mercury(II) and cadmium(II) 1:1 adducts react with halide ion to give anionic [MX$_3$HPcycl$_2$]$^-$ (M = Hg, Cd) species in solution.

The ligand (1-(dicyclohexylphosphino))-N-phenylthioformamide, LH, (LH = (C$_6$H$_{11}$)$_2$PC(S)N(H)C$_6$H$_5$) reacts with mercury(II) halides to give isolable 1:1 and 1:2 adducts, [HgX$_2$(LH)]$_2$ and HgX$_2$(LH)$_2$, in which coordination of the ligand occurs only through the phosphorus atom. There is no evidence for the addition of a third LH to mercury but the 1:1 adducts react with halide ion to give anionic [HgX$_3$LH]$^-$ species. The 1:2 adducts HgX$_2$(HPcycl$_2$)$_2$ and CdX$_2$(HPcycl$_2$)$_2$ react in solution with C$_6$H$_5$NCS to form the corresponding MX$_2$(LH)$_2$ complexes. NMR data imply formation in solution of dimeric [CdX$_2$(LH)]$_2$ compounds in which LH acts as a bridging ligand bonding through sulphur and phosphorus. Mixed ligand species HgX$_2$(HPcycl$_2$)(LH) and CdX$_2$(HPcycl$_2$)(LH) are also identified in solution.

Phosphorus-31, cadmium-113 and mercury-199 NMR spectra were used to characterise new species in solution. There is no evidence for phosphido formation in any of the systems investigated in this study.

Introduction

Tertiary phosphine adducts of mercury(II) salts have been extensively studied since Evans and coworkers [1] first characterised phosphine complexes of formulations HgX$_2$(phos)$_n$ (n = 1, 2; X = Cl, Br, I and phos = tertiary phosphine). The solid state structures of the 1:2 adducts are generally monomeric pseudotetrahedral [2, 3] whereas a common structure for 1:1 adducts is a centrosymmetric halogen-bridged dimer [4] (Scheme 1). A variety of solid state structural types has been found for other anion-phosphine combinations [5–7].



Scheme 1.

Phosphine adducts of cadmium(II) salts, on the other hand, have received comparatively little attention. A crystal structure determination [8] of CdCl$_2$(PPh$_3$)$_2$ shows tetrahedral cadmium atoms whereas the 1:1 adduct CdI$_2$[P(C$_6$H$_{11}$)$_3$] appears dimeric in solution [9].

Recently phosphorus-31, cadmium-113 and mercury-199 NMR techniques were used to investigate the formation, in dichloromethane solution, of tertiary phosphine adducts with a large range of cadmium(II) [10] and mercury(II) salts [11, 12]. These solution studies show that the number of tertiary phosphine molecules coordinated to cadmium or mercury depends upon both the steric requirements of the phosphine and the coordination ability of the anion.

More recently, reactions of the secondary phosphine HP(C$_6$H$_{11}$)$_2$ with some mercury(II) salts have been reported [13]. Dicyclohexylphosphine reacts with Hg(O$_3$SCF$_3$)$_2$ and Hg(OAc)$_2$ to form phosphido-bridged ring systems, Hg$_5$(μ_2-(C$_6$H$_{11}$)$_2$P)$_5$(O$_3$SCF$_3$)$_5$ and Hg$_4$(μ_2-(C$_6$H$_{11}$)$_2$P)$_4$(OAc)$_4$ involving respectively, ten-membered (Hg–P)$_5$ and eight membered (Hg–P)$_4$ heterocycles. The difference in ring size is attributed to varying degrees of coordination of the anion to the mercury atom [13]. Interestingly, these heterocyclic ring structures do not react with further dicyclohexylphosphine.

As part of our continuing studies of coordination behaviour of cadmium(II) and mercury(II) complexes in solution we now report results for reactions of

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dicyclohexylphosphine, $HPcycl_2$, and (1-(dicyclohexylphosphino))-N-phenylthioformamide, LH, with a range of cadmium(II) and mercury(II) halides. We also report results for the reactions of some of these adducts with phenylisothiocyanate.

Experimental

All NMR spectra were recorded on a JEOL FX100 spectrometer, phosphorus-31 at 40.26 MHz, mercury-199 at 17.76 MHz, and cadmium-113 at 22.04 MHz using an external ^7Li lock. Phosphorus-31 spectra were referenced against external 85% H_3PO_4, mercury-199 spectra against external 1 *M* phenylmercuric acetate in DMSO, and cadmium-113 against 4.5 *M* $Cd(NO_3)_2$ in water. Temperatures were maintained using a JEOL NM 5471 controller. Molecular weights were measured at 37 °C using a Mechrolab 301A osmometer. Elemental analyses were performed by AMDEL, Port Melbourne, Australia.

All reactions were carried out in dry nitrogen atmosphere. Dicyclohexylphosphine, $HPcycl_2$, was purchased from Strem Chemicals Inc. and used without further purification. The ligand (1-(dicyclohexylphosphino))-N-phenylthioformamide was prepared [14] by reaction between $HPcycl_2$ and phenylisothiocyanate according to the equation

$$(C_6H_{11})_2PH + C_6H_5NCS \rightarrow (C_6H_{11})_2PC(S)N(H)C_6H_5.$$

The compounds $HgX_2(HPcycl_2)_{1,2}$ (X = Cl, Br, I) were isolated by stirring the appropriate amounts of $HPcycl_2$ and mercury(II) halide in dichloromethane for 15 minutes, followed by precipitation using ethanol. The 1:3 adducts $HgX_2(HPcycl_2)_3$ could not be isolated but were made *in situ* from $HgX_2(HPcycl_2)_2$ and $HPcycl_2$. Similarly the adducts $[HgX_3(HPcycl_2)]^-$ were made *in situ* by reacting the appropriate amounts of Bu_4NI, Bu_4NBr or $[(C_6H_5)_3P(CH_2C_6H_5)]Cl$ with the 1:1 adducts $HgX_2(HPcycl_2)$ in dichloromethane. Adducts involving the ligand LH were prepared similarly.

Cadmium(II) complexes were made in the same manner as the mercury(II) complexes described above with the difference that isolation of adducts involving LH was only possible from solutions containing about 10% excess C_6H_5NCS. $[CdCl_2(LH)]_2$ mp 160 °C d. *Anal.* % Found: C, 44.08; H, 5.67; N, 2.81. % Calcd.: C, 44.16; H, 5.46; N, 2.71. $[CdBr_2(LH)]_2$ mp 147 °C d. % Found: C, 37.97; H, 4.65; N, 2.39. % Calcd.: C, 37.67; H, 4.67; N, 2.31. $[CdI_2(LH)]_2$ mp 144 °C d. % Found: C, 32.24; H, 3.94; N, 1.94. % Calcd.: C, 32.61; H, 4.04; N, 2.00. $CdBr_2(LH)_2$ mp 97–98 °C d. % Found: C, 47.97; H, 5.86; N, 3.41. % Calcd.: C, 48.60; H, 6.01; N, 2.99. $CdI_2(LH)_2$ mp 108–109 °C d. % Found: C, 44.31; H, 5.0; N, 2.74. % Calcd.: C, 44.18; H, 5.46; N, 2.71.

Results and Discussion

Dicyclohexylphosphine Complexes of Mercury(II) Halides

Mercury(II) halides readily react with $HPcycl_2$ to form isolable 1:1 and 1:2 adducts $HgX_2(HPcycl_2)$ and $HgX_2(HPcycl_2)_2$ which are respectively dimeric and monomeric in solution (Table I). Neither 1:1 nor 1:2 adducts show any appreciable conductance in dichloromethane solution.

Phosphorus-31 NMR spectra of the 1:1 adducts $[HgX_2(HPcycl_2)]_2$ (X = Cl, Br, I) in dichloromethane comprise single broad resonances at room temperature. Cooling these solutions causes the phosphorus-31 resonances to sharpen and eventually show mercury-199 satellites. The mercury-199 spectrum of each of these solutions at low temperatures consists of a doublet with coupling constant J(Hg–P) the same as that derived from the corresponding phosphorus-31 spectrum.

The phosphorus-31 NMR spectra of the 1:2 adducts $HgX_2(HPcycl_2)_2$ also show coupling to mercury-199 at low temperature and the corresponding mercury-199 spectra each comprise a triplet with J(Hg–P) again the same as derived from the phosphorus-31 spectra. Furthermore the proton-coupled phosphorus-31 spectra of both the 1:1 and 1:2 adducts clearly show J(P–H) coupling consistent with a proton directly bound to the phosphorus. NMR data for 1:1 and 1:2 adducts are presented in Table II.

An equimolar mixture of $HgI_2(HPcycl_2)_2$ and $HgBr_2(HPcycl_2)_2$ in dichloromethane at −70 °C gives a single phosphorus-31 resonance the chemical shift and coupling to mercury-199 being the average of those of the initial components. Only one triplet is observed in the mercury-199 spectrum of this solution which indicates that the halogens are exchanging rapidly and that the phosphines are static about the mercury atom on the NMR time scale. On cooling to −110 °C the phosphorus-31 resonance splits into three new resonances, of approximate relative intensities 1:2:1, each accompanied by mercury-199 satellites. The two outermost resonances are identified by their chemical shift and J(Hg–P) values as due to the initial components and the central resonance is assigned to the mixed halogen species $HgIBr(HPcycl_2)_2$. The mercury-199 spectrum consists of three triplets of total relative intensities 1:2:1 and confirms the assignment made from the phosphorus-31 spectrum. Similarly other mixtures result in the formation of $HgClBr(HPcycl_2)_2$ and $HgClI(HPcycl_2)_2$ and indicate that these mercury complexes must also be considered essentially four coordinate in solution, at least at low temperatures. NMR data for these mixed halo-complexes are given in Table II.

Addition of $HPcycl_2$ to solutions of $HgX_2(HPcycl_2)_2$ causes a shift to lower frequency of the

TABLE I. Molecular Weight[a] and Melting Point Data for 1:1 and 1:2 Adducts $[MX_2(HPcycl_2)]_2$ and $MX_2(HPcycl_2)_2$ (M = Hg, Cd).

Compound	Concentration g.l^{-1}	Molecular weight	Compound	Concentration g.l^{-1}	Molecular weight
$[HgCl_2(HPcycl_2)]_2$	93.96	917			
(Calc. 939.6)	46.98	946			
mp 217–219 °C d	9.39	933			
$[HgBr_2(HPcycl_2)]_2$	111.72	1096	$[CdBr_2(HPcycl_2)]_2$	80.00	963
(calc. 1117.4)	78.22	1106	(calc. 941)	40.00	952
mp 150–151 °C	11.17	1083	mp 181–182 °C	20.00	952
$[HgI_2(HPcycl_2)]_2$	130.50	1252	$[CdI_2(HPcycl_2)]_2$	100.00	1136
(calc. 1305)	65.25	1256	(calc. 1129)	50.00	1136
mp 141–143 °C	13.05	1300	mp 179–181 °C	25.00	1120
$HgCl_2(HPcycl_2)_2$	66.80	663	$CdCl_2(HPcycl_2)_2$	120.00	572
(calc. 652.5)	33.40	648	(calc. 579.9)	60.00	572
mp 182–183 °C d	6.68	647	mp 117–119 °C	30.00	592
$HgBr_2(HPcycl_2)_2$	75.69	749	$CdBr_2(HPcycl_2)_2$	14.00	666
(calc. 757)	52.98	740	(calc. 668.8)	7.00	636
mp 133–134 °C	7.57	741	mp 97–98 °C		
$HgI_2(HPcycl_2)_2$	85.09	848	$CdI_2(HPcycl_2)_2$	70.00	769
(calc. 850.9)	59.56	860	(calc. 762.8)	25.00	757
mp 149–150 °C	8.51	866	mp 144–145 °C	10.00	757

[a] 1:1 Adducts measured in chloroform solution; 1:2 adducts measured in dichloromethane solution.

TABLE II. Phosphorus-31 and Mercury-199 NMR Data for $HPcycl_2$ Adducts with Mercury(II) Halides in Dichloromethane Solution.

Species	$\delta(^{31}P)$ (ppm)	$\delta(^{199}Hg)$ (ppm)	J(Hg–P) (Hz)	J(P–H) (Hz)	Temperature (°C)
1:1 Adducts					
$[HgCl_2(HPcycl_2)]_2$	20.7	749(d)	7070	400	–70
$[HgBr_2(HPcycl_2)]_2$	14.6	406(d)	6110	390	–50
$[HgI_2(HPcycl_2)]_2$	–5.1	–490(d)	4465	366	–20
1:2 Adducts					
$HgCl_2(HPcycl_2)_2$	15.1	1071(t)	4865	366	–20
$HgBr_2(HPcycl_2)_2$	10.1	898(t)	4240	356	–50
$HgI_2(HPcycl_2)_2$	–5.7	416(t)	3315	337	–50
1:3 Adducts[a]					
$HgCl_2(HPcycl_2)_3$	8.7	b	b		–110
$HgBr_2(HPcycl_2)_5$	4.8	1103(q)	2935		–110
$HgI_2(HPcycl_2)_3$	–6.1	896(q)	2550		–110
Mixed Halide Species[b]					
$HgClBr(HPcycl_2)_2$	13.2	1014(t)	4660		–110
$HgClI(HPcycl_2)_2$	4.8	745(t)	4075		–110
$HgBrI(HPcycl_2)_2$	2.9	725(t)	3915		–110

[a] Uncomplexed $HPcycl_2$, $\delta(^{31}P)$ –28.9 J(P–H) 200 Hz, is also observed in each of these solutions. [b] Phosphine exchange too rapid for observation of either J(Hg–P) or sharp $\delta(^{199}Hg)$ resonances. [c] Oberved in 1:1 mixtures of appropriate $HgX_2(HPcycl_2)_2$ and $HgX_2'(HPcycl_2)_2$. In each case initial components are also observed.

phosphorus-31 resonance and a decrease in coupling constant J(P–H) (Table II). The mercury-199 spectrum of each of these solutions comprises a quartet, indicating that each mercury is directly bonded to three phosphine molecules and that the mercury is probably five-coordinate in each case. The formation of the 1:3 adducts appears almost quantitative. Addition of a large excess of $HPcycl_2$ to solutions of

$HgX_2(HPcycl_2)_3$ causes no change other than the appearance of an additional phosphorus-31 resonance at the position for uncomplexed $HPcycl_2$.

The phosphorus-31 and mercury-199 NMR spectra of a dichloromethane solution containing equimolar quantities of $HgBr_2(HPcycl_2)_3$ and $HgI_2(HPcycl_2)_3$ were recorded at low temperature in an attempt to observe the mixed compound $HgBrI(HPcycl_2)_3$ and thereby prove five coordination for the mercury atoms in the 1:3 adducts. Unfortunately at −110 °C the resonances are still broad and poorly resolved so that the presence of the mixed species $HgBrI(HPcycl_2)_3$ could not be verified.

The changes in NMR parameters in going from 1:1 to 1:2 to 1:3 adducts are similar to those previously observed for analogous adducts with tributylphosphine [11, 12]. There are linear correlations between $\delta(^{199}Hg)$ and the electronegativity of the halogen attached to mercury and between $\delta(^{31}P)$ and J(Hg–P). All of these correlations suggest that the chemical shifts and coupling constants are largely determined by σ-bond effects.

Dicyclohexylphosphine Complexes of Cadmium(II) Halides

Dicyclohexylphosphine reacts with cadmium(II) halides to give isolable 1:1 and 1:2 adducts $CdX_2(HPcycl_2)$ (X = Br, I) and $CdX_2(HPcycl_2)_2$ (X = Cl, Br, I). These adducts are respectively dimeric and monomeric in solution (Table I) and show no appreciable conductance in dichloromethane. All attempts at isolation of the 1:1 adduct $CdCl_2(HPcycl_2)$ were unsuccessful and the product obtained is always the 1:2 adduct $CdCl_2(HPcycl_2)_2$.

The phosphorus-31 NMR spectra of the 1:1 adducts in dichloromethane solution are broad singlets at room temperature indicating rapid exchange of the phosphines about the cadmium atom. Cooling these solutions causes the phosphorus resonances to sharpen and cadmium-111 and cadmium-113 satellites are then observed. At low temperature the cadmium-113 NMR spectra are doublets with coupling constant values J(Cd–P) the same as those derived from the phosphorus-31 spectra (Table III).

Dichloromethane solutions of the 1:2 adducts also require cooling before sharp phosphorus-31 resonances, accompanied by cadmium satellites, are observed. The cadmium-113 NMR spectra of these solutions at low temperature comprise triplets with coupling constants J(Cd–P) the same as those derived from the corresponding phosphorus-31 spectra. The cadmium-113 and phosphorus-31 spectra of dichloromethane solutions containing equimolar amounts of dicyclohexylphosphine and $[CdX_2(HPcycl_2)]_2$ are the same as for solutions containing the 1:2 adducts $CdX_2(HPcycl_2)_2$.

The phosphorus-31 spectrum at −110 °C of a dichloromethane solution containing equimolar quantities of $CdI_2(HPcycl_2)_2$ and $CdBr_2(HPcycl_2)_2$ shows a fairly broad resonance, with shoulders on either side, accompanied by broad cadmium satellites. The cadmium-113 spectrum of this solution comprises three triplets of total relative intensities 1:2:1. The chemical shift and coupling constant values of the two outer triplets identifies them as due to $CdI_2(HPcycl_2)_2$ and $CdBr_2(HPcycl_2)_2$ whilst the central triplet is assigned to the mixed halogen species $CdIBr(HPcycl_2)_2$. Similarly, other mixtures lead to the formation of $CdClBr(HPcycl_2)_2$ and $CdClI(HPcycl_2)_2$ by what appear to be Calingaert redistribution reactions [15]. These results (Table III) show that these cadmium(II) complexes must remain essentially four coordinate, at least at low temperature. Similar results were observed for reactions involving the more

TABLE III. Phosphorus-31 and Cadmium-113 NMR Data for $HPcycl_2$ Adducts with Cadmium(II) Halides in Dichloromethane Solution.

Species	$\delta(^{31}P)$ (ppm)	$\delta(^{113}Cd)$ (pmm)	$J(^{113}Cd-P)$ (Hz)	J(P–H) (Hz)	Temperature (°C)
1:1 Adducts					
$[CdBr_2(HPcycl_2)]_2$	−14.7	446(d)	2005	330	−70
$[CdI_2(HPcycl_2)]_2$	−26.1	293(d)	1605	335	−50
1:2 Adducts					
$CdCl_2(HPcycl_2)_2$	−17.2	672(t)	1440	315	−90
$CdBr_2(HPcycl_2)_2$	−18.9	623(t)	1320	315	−70
$CdI_2(HPcycl_2)_2$	−26.3	539(t)	1210	315	−100
Mixed Halide Species[a]					
$CdClBr(HPcycl_2)_2$	−18.1	659(t)	1400		−120
$CdClI(HPcycl_2)_2$	−19.4	620(t)	1295		−120
$CdBrI(HPcycl_2)_2$	−21.0	581(t)	1265		−120

[a] Observed in 1:1 mixtures of appropriate $CdX_2(HPcycl_2)_2$ and $CdX_2'(HPcycl_2)_2$. In each case initial components are also observed.

bulky tricyclohexylphosphine [10]. Obervation of J(P–H) in various proton coupled phosphorus-31 spectra (Table III) confirms that the dicyclohexylphosphine molecules have acted as simple σ-donors and that no phosphido complexes have been formed. Unlike their mercury(II) analogues, the 1:2 adducts $CdX_2(HPcycl_2)_2$ do not react with further $HPcycl_2$, presumably because there is insufficient space about cadmium. The NMR spectra of solutions of $CdX_2(HPcycl_2)_2$ containing a large excess of $HPcycl_2$ show the presence of only these two species.

Reaction with Halide

Addition of Bu_4NI to $HgI_2(HPcycl_2)_2$ in dichloromethane solution at −50 °C causes the phosphorus-31 resonance to broaden significantly and coupling to mercury is no longer observable. Cooling to −70 °C is required to reestablish phosphorus–mercury coupling and at that temperature both the mercury-199 and phosphorus-31 spectra indicate $HgI_2(HPcycl_2)_2$ as the only mercury containing species. Apparently the presence of additional halide ion to $HgI_2(HPcycl_2)_2$ labilises exchange of the phosphine molecules, possibly *via* a five coordinate intermediate $[HgI_3(HPcycl_2)_2]^-$. Cooling decreases the rate of phosphine exchange with the concomitant result that the original four coordinate species dominates in solution.

The dimeric 1:1 adducts $[HgX_2HPcycl_2]_2$ react with an extra mol of halide ion in dichloromethane solution to give the new species $[HgX_3HPcycl_2]^-$ (X = Cl, Br, I). NMR data for these new species are given in Table IV. Attempts at isolation of these new species were unsuccessful. Addition of further halide ion to dichloromethane solutions of $[HgX_3HPcycl_2]^-$ causes no change in the phosphorus-31 spectra. Similar reactions were observed between halide ion and the 1:1 and 1:2 cadmium adducts. NMR data for these new species are also given in Table IV.

(1-(Dicyclohexylphosphino))-N-phenylthioformamide Adducts

The ligand (1-(dicyclohexylphosphino))-N-phenylthioformamide, LH, ($LH = (C_6H_{11})_2PC(S)N(H)C_6H_5$) reacts with mercury(II) halides to form isolable 1:1 and 1:2 adducts $HgX_2(LH)$ and $HgX_2(LH)_2$ (X = Cl, Br, I). These adducts are respectively dimeric and monomeric in solution (Table V) and show no appreciable conductance in dichloromethane.

TABLE V. Molecular Weight[a] and Melting Point Data for $HgX_2(LH)_{1,2}$ and $[HgX_3(LH)]^-$.

Compound	Concentration g.l^{-1}	Molecular weight
$[HgCl_2(LH)]_2$	120.91	1190
(calc. 1210)	60.55	1201
mp 151–152 °C	30.32	1195
$[HgBr_2(LH)]_2$	130.52	1370
(calc. 1388)	100.00	1373
mp 157–158 °C d	50.00	1373
$HgCl_2(LH)_2$	100.00	940
(calc. 938)	50.00	945
mp 158–159 °C	25.00	947
$HgBr_2(LH)_2$	105.81	1040
(calc. 1027)	52.54	1043
mp 149–150 °C	33.33	1040
$HgI_2(LH)_2$	112.10	1129
(calc. 1121)	56.05	1131
mp 124–125 °C	28.03	1131
	14.02	1128
$[HgCl_3(LH)][(C_6H_5)_3PCH_2C_6H_5]$	99.39	1026
(calc. 994)	39.76	1026
mp 147–148 °C	19.88	970
$[HgBr_3(LH)][Bu_4N]$	101.63	880
(calc. 1016)	40.65	846
mp 139–140 °C	16.26	856

[a] 1:1 adducts measured in chloroform; 1:2 adducts measured in dichloromethane.

TABLE IV. NMR Data for $[MX_3HPcycl_2]^-$ Species in Dichloromethane Solution.

Species	δ(^{31}P) (ppm)	δ(^{199}Hg) (ppm)	J(Hg–P) (Hz)	Temperature (°C)
M = Hg				
$[HgCl_3HPcycl_2]^-$	18.4	787(d)	6550	−20
$[HgBr_3HPcycl_2]^-$	8.2	368(d)	5175	−30
$[HgI_3HPcycl_2]^-$	−11.6	−602(d)	3500	−80
	δ(^{31}P)	δ(^{113}Cd)	J(^{113}Cd–P)	Temperature
M = Cd				
$[CdBr_3HPcycl_2]^-$	−19.0	534(d)	1400	−60
$[CdI_3HPcycl_2]^-$	−27.7	356(d)	1115	−65

Phosphorus-31 and mercury-199 NMR data for the 1:1 and 1:2 adducts in dichloromethane solution are consistent with the phosphorus atom directly bonded to mercury (Table VI). The mercury chemical shifts and couplings J(Hg–P) are similar to those observed for analogous 1:1 and 1:2 adducts involving $HPcycl_2$. Furthermore the infrared spectra of $[HgX_2(LH)]_2$ and $HgX_2(LH)_2$ in the regions associated with γ_{NH} (3200 cm^{-1}) and γ_{SCN} (1490, 1324 cm^{-1}) are very similar to those regions in the spectrum of uncoordinated LH. All these data imply that the potentially multidentate ligand LH coordinates to mercury only via the phosphorus atom and that these complexes have structures very similar to those of the 1:1 and 1:2 adducts of dicyclohexylphosphine.

Phosphorus-31 spectra of $[HgX_2(LH)]_2$ to which varying quantities of LH have been added show that formation of the 1:2 adducts $HgX_2(LH)_2$ is almost quantitativie. There is no evidence for coordination of a third LH molecule.

Mixed halogen species $HgXX'(LH)_2$ are formed in solution from 1:1 mixtures of $HgX_2(LH)_2$ and $HgX'_2(LH)_2$. The simultaneous observation of $HgX_2(LH)_2$, $HgX'_2(LH)_2$ and $HgXX'(LH)_2$ imply that these compounds are very similar to the dicyclohexylphosphine adducts and must also be considered essentially four coordinate in solution. The reactions of halide ion with $[HgX_2(LH)]_2$ and $HgX_2(LH)_2$ are also very similar to those observed with the corresponding dicyclohexylphosphine adducts. The formation of $[HgX_3(LH)]^-$ species by addition of halide ion to the 1:1 adducts is deduced from the phosphorus-31 and mercury-199 NMR spectra (Table VI).

The complexes $HgX_2(HPcycl_2)_2$ (X = Cl, Br, I) react with phenylisothiocyanate in dichloromethane solution to produce $HgX_2(LH)_2$. The insertion of phenylisothiocyanate is not quantitative and for solutions containing equimolar quantities of $HgX_2(HPcycl_2)_2$ and C_6H_5NCS mixed ligand species $HgX_2(HPcycl_2)(LH)$ are also observed in the phosphorus-31 and mercury-199 NMR spectra (Fig. 1). The mixed ligand species $HgX_2(HPcycl_2)(LH)$ are also formed in 1:2 mixtures of $[HgX_2(HPcycl_2)]_2$ and LH (Table VII). Phenylisothiocyanate does not react with the 1:1 adducts $[HgX_2(HPcycl_2)]_2$ presumably because the stronger coordination of phosphorus to mercury is accompanied by an inductive effect which also strengthens the phosphorus–proton bond.

The compounds $CdX_2(HPcycl_2)_2$ also react with C_6H_5NCS in dichloromethane solution but insertion of C_6H_5NCS is less facile than for the analogous mercury(II) compounds. For X = Cl, Br a substantial excess of C_6H_5NCS leads to the formation of $CdX_2(LH)_2$ with trace amounts of the 1:1 adduct $[CdX_2(LH)]_2$ also being observed in the cadmium-113 spectra of these solutions. Insertion of C_6H_5NCS into $CdI_2(HPcycl_2)_2$ is even more difficult and the cadmium-113 spectrum of a solution containing the above reactants in a 6:1 molar ratio shows a broad triplet assigned to $CdI_2(LH)_2$, a doublet of doublets due to the mixed ligand species $CdI_2(HPcycl_2)(LH)$ and a second doublet of doublets assigned to $[CdI_2(LH)]_2$. The chemical shift and coupling constant values for this last doublet of doublets is consistent with a dimeric $CdI_2(LH)$ unit containing phosphorus–sulphur bridging LH ligands rather than bridging halogens (Scheme 2). The total relative

TABLE VI. Phosphorus-31 and Mercury-199 NMR Data for (1-(Dicyclohexylphosphino))-N-phenylthioformamide Adducts with Mercury(II) Halides in Dichloromethane Solution.

Species	$\delta(^{31}P)$ (ppm)	$\delta(^{199}Hg)$ (ppm)	J(Hg–P) (Hz)	Temperature (°C)
1:1 Adducts				
$[HgCl_2(LH)]_2$	65.5	718(d)	5940	20
$[HgBr_2(LH)]_2$	57.6	396(d)	5215	–30
$[HgI_2(LH)]_2$	50.3	[a]	3575	
1:2 Adducts				
$HgCl_2(LH)_2$	58.5	1000(t)	4180	20
$HgBr_2(LH)_2$	51.9	876(t)	3830	20
$HgI_2(LH)_2$	33.8	404(t)	3025	20
Mixed Halide Species[b]				
$HgClBr(LH)_2$	54.5	942(t)	4075	–60
$HgClI(LH)_2$	48.8	772(t)	3635	–70
$HgBrI(LH)_2$	45.0	674(t)	3470	–60
$[HgCl_3(LH)]^-$	60.7	824(d)	5780	–30
$[HgBr_3(LH)]^-$	51.1	352(d)	4505	20
$[HgI_3(LH)]^-$	23.2	–591(d)	2980	–70

[a] Insufficiently soluble to allow measurement of $\delta(^{199}Hg)$. [b] Observed in 1:1 mixtures of appropriate $HgX_2(LH)_2$ and $HgX'_2(LH)_2$. In each case initial components are also observed.

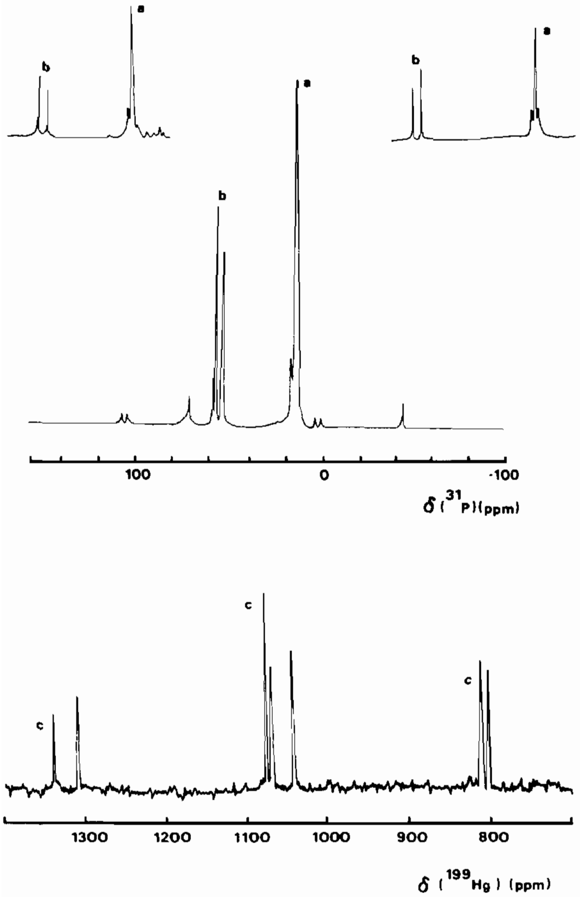
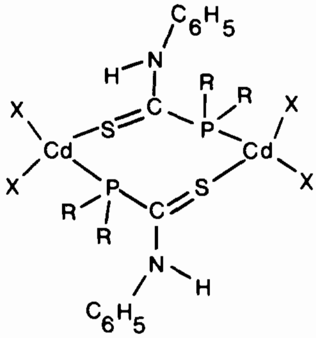


Fig. 1. Phosphorus-31 and mercury-199 spectra at −50 °C of a 1:1 solution of $HgCl_2(HPcycl_2)_2$ and C_6H_5NCS. Regions a and b are associated with the phosphorus resonances of coordinated $HPcycl_2$ and LH respectively. c is the triplet due to $HgCl_2(HPcycl_2)_2$ and the doublet of doublets is assigned as due to the mixed ligand species $HgCl_2(HPcycl_2)(LH)$.

intensities of these multiplets is approximately in the ratio 3:3:1. Addition of further C_6H_5NCS to the above solution causes no significant change to either the phosphorus-31 or cadmium-113 spectrum.



Scheme 2.

The phosphorus-31 and cadmium-113 spectra of a solution containing an isolated sample of $CdI_2(LH)_2$ slowly changes with time so that after three hours the cadmium-113 spectrum shows a mixture of $CdI_2(LH)_2$, $CdI_2(HPcycl_2)(LH)$ and $[CdI_2(LH)]_2$ in a ratio similar to that observed for the solution of $CdI_2(HPcycl_2)_2$ and excess C_6H_5NCS. Apparently $CdI_2(LH)_2$ is stable in the solid state but is thermodynamically unstable in solution by elimination of a C_6H_5NCS to give an equilibrium mixture of $CdI_2(LH)_2$, $CdI_2(HPcycl_2)(LH)$ and $[CdI_2(LH)]_2$. Interestingly both $CdX_2(HPcycl_2)$ (X = Br, I) also react in solution with LH to give predominantly the mixed ligand species $CdI_2(HPcycl_2)(LH)$. The cadmium-113 and phosphorus-31 spectra of a solution containing equimolar quantities of $CdCl_2(HPcycl_2)$ and C_6H_5NCS show $CdCl_2(HPcycl_2)(LH)$ as the main species in solution, accompanied by a trace of $[CdCl_2(LH)]_2$. NMR data for these cadmium systems are presented in Tables VIII and IX.

Unlike their mercury(II) analogues, the cadmium(II) complexes $[CdX_2(HPcycl_2)]_2$ (X = Br, I) react with C_6H_5NCS in dichloromethane solution. The products are only very sparingly soluble and analyse for $[CdX_2(LH)]_2$. We are presently attempting to prepare crystals of these compounds which are suitable for X-ray structure determinations. Presumably both compounds contain the ligand LH in an unusual bridging role.

TABLE VII. NMR Data for Mixed Ligand[a] Species $HgX_2(HPcycl_2)(LH)$ in Dichloromethane Solution.

Species	$\delta(^{31}Pa)^b$ (ppm)	$\delta(^{31}Pb)^b$ (ppm)	J(Pa–Pb) (Hz)	J(Hg–Pa) (Hz)	J(Hg–Pb) (Hz)	$\delta(^{199}Hg)$ (ppm)
$HgCl_2(HPcycl_2)(LH)$ (−50 °C)	16.4	55.6	122	4745	4230	1058 (d) of (d)
$HgBr_2(HPcycl_2)(LH)$ (−100 °C)	10.1	47.5	112	4475	3870	932 (d) of (d)
$HgI_2(HPcycl_2)(LH)$ (−65 °C)	−3.6	31.2	95	3440	2800	457 (d) of (d)

[a] Observed in solutions of $HgX_2(HPcycl_2)_2$ containing various quantities of C_6H_5NCS. [b] Pa represents phosphorus atom in $HPcycl_2$: Pb represents phosphorus atom in LH (LH = $(C_6H_{11}PC(S)N(H)C_6H_5)$.

TABLE VIII. Phosphorus-31 and Cadmium-113 NMR Data for (1-(Dicyclohexylphosphino))-N-phenylthioformamide Adducts with Cadmium(II) Halides in Dichloromethane Solution at −100 °C.

Species	$\delta(^{31}P)$ (ppm)	$J(^{113}Cd-P)$ (Hz)	$\delta(^{113}Cd)$ (ppm)
$CdCl_2(LH)_2$	32.3	1410	652(t)
$CdBr_2(LH)_2$	28.2	1280	613(t)
$CdI_2(LH)_2$	18.6	1090	515(t)
$[CdCl_2(LH)]_2$	33.6	1535	605(d)
$[CdBr_2(LH)]_2$	29.2	1430	548(d)
$[CdI_2(LH)]_2$	27.3	1360, 40	429 (d) of (d)

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TABLE IX. Phosphorus-31 and Cadmium-113 NMR Data for Mixed Ligand[a] Species $CdX_2(HPcycl_2)(LH)$ in Dichloromethane Solution at −100 °C.

	$\delta(^{31}Pa)$ (ppm)	$\delta(^{31}Pb)$ (ppm)	$J(Pa-Pb)$ (Hz)	$J(^{113}Cd-Pa)$ (Hz)	$J(^{113}Cd-Pb)$ (Hz)	$\delta(^{113}Cd)$ (ppm)
$CdCl_2(HPcycl_2)(LH)$	−15.4	31.4	74	1555	1285	669
$CdBr_2(HPcycl_2)(LH)$	−18.0	26.1	70	1465	1170	635
$CdI_2(HPcycl_2)(LH)$	−23.5	16.6	60	1260	1000	544

[a] *Pa* represents phosphorus atom in $HPcycl_2$; *Pb* represents phosphorus atom in LH ($LH = (C_6H_{11})_2PC(S)N(H)C_6H_5$).