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Contribution from the Guelph-Waterloo Centre for Graduate Work in Chemistry,
University of Guelph, Guelph, Ontario, Canada N1G 2W1

Reinvestigation of Tricyclohexylphosphine Complexes of Zinc(II) and Cadmium(II) Halides. Preparation, Characterization, and Phosphorus-31 Nuclear Magnetic Resonance and Vibrational Spectroscopic Studies

RAM G. GOEL,* WILLIAM P. HENRY, and NARENDRA K. JHA[1]

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Zinc(II) halides form isolable 1:1 complexes with tricyclohexylphosphine. Previously reported 1:2 complexes, $ZnX_2[P(cy)_3]_2$, are indicated to be $ZnX_2P(cy)_3[OP(cy)_3]$ by $^{31}P\{^1H\}$ NMR spectral measurements. Cadmium(II) halides form isolable 1:1 as well as 1:2 complexes with tricyclohexylphosphine. Molecular weight data show that the 1:1 complexes of both zinc(II) and cadmium(II) halides exist in solution as dimeric molecular species, $M_2X_4[P(cy)_3]_2$. The far-infrared and Raman spcectra for these complexes, in the solid state, are consistent with a dimeric structure of C_{2h} skeletal symmetry. Vibrational spectra of the $CdX_2[P(cy)_3]_2$ complexes, in the solid state, are consistent with a pseudotetrahedral structure of C_{2v} skeletal symmetry. Phosphorus-31 NMR spectral measurements at 306 ± 2 K show that the 1:2 complexes, $CdX_2[P(cy)_3]_2$, dissociate extensively in solution into the 1:1 complexes and $P(cy)_3$; no such dissociation is evident at 213 K. Phosphorus-31 NMR spectra of the $Zn_2X_4[P(cy)_3]_2$ and $Cd_2X_4[P(cy)_3]_2$ complexes have also been examined at 306 ± 2 K and at 183 or 213 K.

Introduction

Tertiary phosphine complexes of zinc(II),[2,3] cadmium(II),[3,4] and mercury(II)[3,4] halides have been known for many years. During the last decade several ^{31}P NMR as well as vibrational spectroscopic studies[5-14] have appeared on phosphine complexes of mercury(II) halides as well as other derivatives. Such studies have hitherto been lacking on complexes of zinc(II) and cadmium(II). In our continuing investigations on the steric and electronic effects in phosphine complexes of d^8 and d^{10} metals, complexes of zinc(II), cadmium(II), and mercury(II) with a variety of phosphines have been investigated by ^{31}P NMR and vibrational spectroscopy,[8-11,15-18] as well as by X-ray diffraction[19,20] studies. Phosphorus-31 NMR[8] and vibrational[17] spectroscopic investigations on tricyclohexylphosphine complexes of mercury(II) halides have been reported recently. Similar investigations on complexes of zinc(II) and cadmium(II) halides are reported herein. Our recent work on tri-*tert*-butylphosphine complexes of zinc(II) halides appears to be the only other ^{31}P NMR study[15] reported on phosphine complexes of zinc(II). A brief note[21] on the ^{31}P NMR spectra of the cadmium(II) iodide complexes CdI_2L_2, where L = PMe_2Ph, $PhMePh_2$, PEt_3, PEt_2Ph, or $PEtPh_2$, appeared 10 years ago. Phosphorus-31 NMR spectra of tri-*tert*-butylphosphine complexes of cadmium(II) halides and thiocyanate were examined recently along with those for the zinc(II) complexes. Phosphorus-31 NMR and vibrational spectra of complexes of cadmium(II) halides with several triarylphosphines have been reported[18] recently. A report[22] on ^{31}P, ^{111}Cd, and ^{113}Cd NMR spectral investigations on tributylphosphine complexes of cadmium(II) halides appeared after the completion of this work. Very recently, ^{31}P NMR spectra of triphenylphosphine complexes[23] of cadmium(II) perchlorate, nitrate, and trifluoroacetate have also been examined.

Table I. Analytical and Molecular Weight Data

complex	% C calcd	% C found	% H calcd	% H found	mol wt[a] calcd	mol wt[a] found
$Zn_2Cl_4[P(cy)_3]_2$	51.88	51.90	7.98	7.96	832	757
$Zn_2Br_4[P(cy)_3]_2$	42.76	42.87	6.58	6.69	1010	854
$Zn_2I_4[P(cy)_3]_2$	36.06	36.64	5.55	5.68	1199	1160[b]
$ZnCl_2P(cy)_3[OP(cy)_3]$	60.62	60.24	9.34	9.31		
$ZnBr_2P(cy)_3[OP(cy)_3]$	53.90	53.74	8.31	8.22		
$ZnI_2P(cy)_3[OP(cy)_3]$	48.24	48.19	7.43	7.47		
$Cd_2Cl_4[P(cy)_3]_2$	46.62	46.62	7.17	7.32	927	842
$Cd_2Br_4[P(cy)_3]_2$	39.12	39.66	6.02	6.34	1105	1150
$Cd_2I_4[P(cy)_3]_2$	33.43	32.98	5.14	5.11	1293	1292
$CdCl_2[P(cy)_3]_2$	58.10	58.10	8.94	8.77	744	716
$CdBr_2[P(cy)_3]_2$	51.90	52.00	7.98	8.20	833	806[b]
$CdI_2[P(cy)_3]_2$	46.63	46.97	7.17	6.92	927	925[b]

[a] In 1,2-dichloroethane for 10^{-2}–10^{-3} M solutions unless stated otherwise. [b] In benzene for 10^{-2}–10^{-3} M solutions.

Tricyclohexylphosphine complexes of zinc(II), cadmium(II), and mercury(II) halides were first reported[24] by Moers and Langhout, who found that the halides of all three metals form

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Table II. $^{31}P\{^1H\}$ NMR Spectral Data[a,b]

	$\delta[P(cy)_3]$		$\delta[OP(cy)_3]$		^3J(P-OP), Hz		$^1J(^{111}Cd-^{31}P)$, Hz		$^1J(^{113}Cd-^{31}P)$, Hz	
complex	ambient temp	low temp[c]	ambient temp	low temp[c]	ambient temp	low temp[c]	ambient temp	low temp[c]	ambient temp	low temp[c]
$Zn_2Cl_4[P(cy)_3]_2$	5.3	5.4								
$Zn_2Br_4[P(cy)_3]_2$	1.5	2.0								
$Zn_2I_4[P(cy)_3]_2$	−8.2	−6.2								
$ZnCl_2P(cy)_3[OP(cy)_3]$	3.4	3.8	62.9	63.7	14	14				
$ZnBr_2P(cy)_3[OP(cy)_3]$	0.5	0.1	63.7	64.3	14	14				
$ZnI_2P(cy)_3[OP(cy)_3]$	−7.7	−7.4	64.7	65.1	14	14				
$Cd_2Cl_4[P(cy)_3]_2$	27.6	26.5					2156	2232	2265	2341
$Cd_2Br_4[P(cy)_3]_2$	22.6	21.9					1977	2059	2070	2148
$Cd_2I_4[P(cy)_3]_2$	9.4	10.6					1689	1750	1766	1823
$CdCl_2[P(cy)_3][OP(cy)_3]$	22.5	28.7	59.0	64.3		10	...	2060	...	2158
$CdBr_2[P(cy)_3][OP(cy)_3]$	24.1	25.3	63.5	64.5		10	1836	1920	1920	2016
$CdI_2[P(cy)_3][OP(cy)_3]$	11.1	17.3	63.3	64.8		10	1590	1708	1670	1790
$CdCl_2[P(cy)_3]_2$		20.9						1572		1640
$CdBr_2[P(cy)_3]_2$		16.9						1497		1565
$CdI_2[P(cy)_3]_2$		7.3						1340		1401

[a] For solutions in dichloromethane containing 10% acetone-d_6. [b] δ[free $P(cy)_3$] = 9.0, 8.7, and 8.8, respectively, at ambient probe temperature, 213 K, and 183 K. [c] 213 K for the $Cd_2X_4[P(cy)_3]_2$ and the $CdX_2[P(cy)_3]_2$ complexes, 183 K for the other complexes.

stable 1:2 complexes, $MX_2[P(cy)_3]_2$, and that the cadmium(II) and mercury(II) halides also form isolable 1:1 complexes, $MX_2[P(cy)_3]$. The infrared and Raman spectra of these complexes were also reported[24] by these workers, but the infrared spectral measurements were limited to the region above 200 cm^{-1}. These complexes were reinvestigated in this laboratory due to our interest in their ^{31}P NMR spectral parameters as well as their skeletal stretching vibrations. In the course of the preparation of these compounds it was discovered that, contrary to the results of Moers and Langhout,[24] it is difficult to isolate the 1:2 complexes of zinc(II) halides. It was also found that at room temperature the 1:2 complexes of cadmium(II) halides dissociate extensively in solution to give the 1:1 complex and free phosphine, which is oxidized readily to the phosphine oxide; subsequent reaction of the phosphine oxide with the 1:1 complexes results in the formation of $CdX_2P(cy)_3[OP(cy)_3]$ complexes. Hitherto unknown 1:1 complexes, $Zn_2X_4[P(cy)_3]_2$, were also isolated in the present work. Zinc(II) halides, in marked contrast to cadmium(II) and mercury(II) halides, have been reported to form only the 1:2 complexes with tertiary phosphines.[25] Recently it was found that tri-*tert*-butylphosphine[15] forms only 1:1 complexes with zinc(II) halides (as well as with cadmium(II) and mercury(II) halides). Results of the present investigation indicate that tricyclohexylphosphine, like tri-*tert*-butylphosphine, also forms only 1:1 isolable complexes with zinc(II) halides.

Results and Discussion

Treatment of zinc(II) halides (chloride, bromide, and iodide) with tricyclohexylphosphine, in 1:1 mole ratio, under an atmosphere of nitrogen, afforded the previously unknown 1:1 complexes, $ZnX_2P(cy)_3$, in quantitative yields. The analytical data for the three complexes are given in Table I. All three complexes are air-stable white crystalline solids soluble in polar organic solvents such as dichloromethane and acetone; the iodo complex is also soluble in benzene. The molecular weight measurements of the three complexes in 1,2-dichloroethane or benzene (data given in Table I) showed them to be the dimeric molecular species $Zn_2X_4[P(cy)_3]_2$.

The $^{31}P\{^1H\}$ NMR spectrum for each complex at ambient probe temperature (306 ± 2 K) as well as at 183 K exhibited a single resonance. The observed ^{31}P NMR chemical shifts for the complexes as well as the free phosphine at both temperatures are listed in Table II. The data in Table II show that, instead of the expected downfield shift upon complexation, the chemical shift for each complex is rather upfield from that of free phosphine. This observation, though unexpected, is now not very surprising in view of our recent findings[18,23] that the ^{31}P NMR chemical shifts for the phosphine complexes of cadmium(II) do not appear to vary in any systematic manner. From the data in Table II it can be seen that the absolute value of $\Delta\delta$ [δ(complex) − δ(free phosphine)] decreases in the order Cl > Br >> I. The data also show that the chemical shifts are temperature dependent.

Table III. Infrared and Raman Spectral Data[a] for $Zn_2X_2(\mu\text{-}X)_2[P(cy)_3]_2$ Complexes in the 400–50 cm^{-1} Region

X = Cl		X = Br		X = I		
IR	R	IR	R	IR	R	assignt
385 m		385 m		382 m, b		*b*
		379 sh				*b*
		317 w				*b*
331 s	336 ms					ν_t(Zn–Cl)
		244 s	251 m			ν_t(Zn–Br)
	229 sh		228 sh			*b*
223 s						ν_b(Zn–Cl)
	220 ms		219 ms		219 m	*b*
				204 s	208 m	ν_t(Zn–I)
187 m	191 m					ν_b(Zn–Cl)
		183 s				ν_b(Zn–Br)
				180 s		ν_b(Zn–I)
			179 m			*b* or ν_b(Zn–Br)
157 m	167 m					ν(Zn–P)
		165 s				ν_b(Zn–Br)
				155 ms	158 w	ν_b(Zn–I)
		141 m	151 s			ν(Zn–P)
				144 m		ν_b(Zn–I)
126 ms		93 ms		71 mw		δ_t(Zn–X)
				118 ms	125 s	ν(Zn–P)
94 mw		52 m				

[a] For the solid state. Description of abbreviations: IR, infrared; R, Raman; ν or ν_t, stretching frequency involving terminal bonds; ν_b, stretching frequency involving bridging bonds; δ_t, bending frequency involving terminal bonds; b, broad; m, medium, s, strong; sh, shoulder; v, very; w, weak. [b] Bands due to $P(cy)_3$.

The infrared and Raman spectra for the three complexes were examined in the solid state in the 4000–50 cm^{-1} region. The skeletal vibrations for all three complexes seem to occur below 400 cm^{-1}; the observed infrared and Raman bands in this region, together with their assignments, are given in Table III. The data in Table III show that the infrared as well as the Raman spectra for all three complexes are consistent with a dimeric structure of C_{2h} skeletal symmetry. The assignments for the terminal Zn–X stretching and bending frequencies in

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Table III follow from those for the pseudotetrahedral $ZnX_2(py)_2$[26] and $ZnX_2(PPh_3)_2$[27] complexes. The proposed assignments for the bridging Zn–X stretching and the Zn–P stretching frequencies are based on those for the $Zn_2X_4[P(t\text{-}Bu)_3]_2$[15] complexes, which are also indicated to have a dimeric structure of C_{2h} skeletal symmetry in the solid state. The observed lack of coincidence of the infrared and Raman frequencies for the $Zn_2X_4[P(cy)_3]_2$ complexes is consistent with the proposed centrosymmetric skeletal symmetry.

Treatment of zinc(II) halides with 2 mol equiv of tricyclohexylphosphine, according to the procedure reported by Moers and Langhout,[24] gave products that showed infrared spectra similar to those attributed to the $ZnX_2[P(cy)_3]_2$ complexes by these workers. Phosphorus-31 NMR measurements (data given in Table II), however, showed the products to be $ZnX_2[P(cy)_3]$. As indicated by the data in Table II, the $^{31}P\{^1H\}$ NMR spectrum of each product, at 306 ± 2 K as well as at 183 K, was comprised of two doublets of equal intensity, one at δ 63–65 and the other at δ −2 to +4. The separation of the two peaks in each doublet was identical and was of the order of 14 Hz. As can be seen from the data in Table II, the high-field resonance is not markedly different from that observed for the $Zn_2X_4[P(cy)_3]_2$ complexes; the low-field doublet can be assigned to coordinate $OP(cy)_3$. Thus, the $^{31}P\{^1H\}$ NMR data are in complete accord with the proposed characterization of the species as $ZnX_2[P(cy)_3][OP(cy)_3]$, in which the two inequivalent phosphorus nuclei are coupled to each other [$^3J(P\text{–}P) = 14$ Hz]. As shown in Table I, the analytical data for the products were also in accord with the proposed formulation.

Attempts to prepare the 1:2 complexes, $ZnX_2[P(cy)_3]_2$, by treating zinc(II) halides with 2 mol equiv of tricyclohexylphosphine under an atmosphere of nitrogen gave products that were indicated by $^{31}P\{^1H\}$ NMR measurements to contain the species $Zn_2X_4[P(cy)_3]_2$ and $ZnX_2[P(cy)_3][OP(cy)_3]$ as well as small amounts of some uncharacterized phosphorus-containing species. We, therefore, conclude that the $ZnX_2[P(cy)_3]_2$ complexes, if formed at all, dissociate in solution into the 1:1 complex and free phosphine, which is rapidly oxidized to the phosphine oxide, which reacts with the 1:1 complex to give the species $ZnX_2P(cy)_3[OP(cy)_3]$. Oxidation of the dissociated phosphine appears to be catalyzed by the 1:1 complexes since the $^{31}P\{^1H\}$ NMR spectrum of free tricyclohexylphosphine, manipulated under similar conditions, showed only a single resonance attributable tó $P(cy)_3$.

Treatment of cadmium(II) halides with 1 mol equiv of the phosphine, in dichloromethane, under an atmosphere of nitrogen, afforded the 1:1 complexes in quantitative yields. Similar reaction with 2 mol equiv of the phosphine, in benzene, gave the 1:2 complexes. The procedure of Moers and Langout,[24] for the 1:2 complexes, afforded products that were shown to be $CdX_2P(cy)_3[OP(cy)_3]$ by $^{31}P\{^1H\}$ NMR measurements (vide infra). Both the 1:1 and the 1:2 complexes are air-stable white solids. The 1:1 complexes are soluble in polar solvents such as dichloromethane and acetone; the iodo complex is also soluble in benzene. All three 1:2 complexes are soluble in benzene. Analytical data for the complxes are given in Table I, which also includes molecular weight data. The molecular weight data show that the 1:1 complexes, like their zinc(II) analogues, exist as dimeric molecular species in solution. Moers and Langhout[24] arrived at a similar conclusion from the molecular weight measurement of the iodo complex. Molecular weights for the 1:2 complexes were also measured in this work, and the results were consistent with the existence of monomeric molecular species. As shown by the data in Table I, the molecular weights for the 1:2 complexes, in benzene or 1,2-dichloroethane, are also consistent with the existence of monomeric molecular species. However, $^{31}P\{^1H\}$ NMR measurements, at 306 ± 2 K, unequivocally showed that the solutions contained the species $CdX_2P(cy)_3[OP(cy)_3]$ instead of the expected $CdX_2[P(cy)_3]_2$[28] (vide infra).

Proton-decoupled ^{31}P NMR spectra for the 1:1 as well as 1:2 complexes were examined at 306 ± 2 K as well as at 213 K. The spectral parameters for the 1:1 complexes at both temperatures and for the 1:2 complexes at 213 K are listed in Table II.

The $^{31}P\{^1H\}$ spectra for the 1:1 complexes at 306 ± 2 K showed a main resonance and two satellite doublets due to coupling of the ^{31}P nucleus with the ^{111}Cd and ^{113}Cd nuclei, which are present in natural abundances of 12.75 and 12.26%, respectively. From the data in Table II it can be seen that the ratio $^1J(^{113}Cd\text{–}^{31}P){:}^1J(^{111}Cd\text{–}^{31}P)$ is in good agreement with the theoretical value of 1.046. The data also show that the $^1J(Cd\text{–}P)$ values decrease markedly with decreasing electronegativity of the halogen X. The $^1J(Cd\text{–}P)$ values for the analogous tri-*tert*-butylphosphine complexes, which also show Cd–P nuclear spin–spin couplings at 306 ± 2 K, vary in a similar manner. A similar trend is also reported for the 1:1 complexes of tri-*n*-butylphosphine, but the Cd–P couplings for these complexes[29] can only be observed at lower temperatures. The ^{31}P NMR chemical shifts for the $Cd_2X_4[P(cy)_3]_2$ complexes, unlike those for their zinc(II) analogues, are downfield from the free-phosphine resonance. The magnitude of $\Delta\delta$ for the cadmium(II) complexes, as for the zinc(II) complexes, decreases with decreasing electronegativity of X. The $\Delta\delta$ values for the tri-*tert*-butylphosphine analogues also vary in a similar manner, but the chemical shifts for the complex $Cd_2I_4P(t\text{-}Bu)_3$ are considerably upfield from the free-phosphine resonance; $\Delta\delta$ values for the tributylphosphine complexes have not been reported.

The $^{31}P\{^1H\}$ spectrum for $Cd_2Cl_4[P(cy)_3]_2$ at 213 K showed two main resonances of unequal intensity. Both the resonances were accompanied by satellites due to the $^{111}Cd\text{–}^{31}P$ and $^{113}Cd\text{–}^{31}P$ spin–spin couplings. The chemical shift and the $^1J(Cd\text{–}P)$ values for the more intense resonance were similar to those observed for $Cd_2Cl_4[P(cy)_3]_2$ at ambient temperatures. The less intense resonance was due to $CdCl_2[P(cy)_3]_2$ as shown by the spectral measurement of an authentic sample (vide infra). The integrated intensities for the signals due to the $Cd_2Cl_4[P(cy)_3]_2$ and $CdCl_2[P(cy)_3]_2$ species were in the 6:1 ratio. The resonance due to $CdCl_2[P(cy)_3]_2$ disappeared completely when the spectrum was recorded at ambient probe temperature. The observed solution behavior is, thus, indicative of a temperature-dependent redistribution reaction represented by eq 1. The equilibrium lies to the left at room temperature

$$Cd_2Cl_4[P(cy)_3]_2 \xrightleftharpoons{\text{solvent}} CdCl_2[P(cy)_3]_2 + CdCl_2(\text{solvent}) \tag{1}$$

$$\text{solvent} = CH_2Cl_2 + 10\%\ (CD_3)_2CO$$

and shifts to the right at lower temperatures. In their original work on phosphine complexes of cadmium(II) halides, Mann and co-workers[4] also noted a temperature-dependent equilibrium between $Cd_2I_4(PEt_3)_2$ and $CdI_2(PEt_3)_2$. However, in contrast to the present results, Mann and co-workers found

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(29) Unlike the tricyclohexyl- and tri-*tert*-butylphosphine complexes the 1:1 tri-*n*-butylphosphine complexes are not isolable, but their presence has been ascertained by low-temperature ^{113}Cd and ^{31}P NMR measurements.[22]

that the formation of $CdI_2(PEt_3)_2$ is favored at higher temperature. Recently reported low-temperature ^{31}P, ^{111}Cd, and ^{113}Cd NMR measurements show[22] that solutions of 1:1 mixtures of CdX_2 and PBu_3 contain the 1:2 and 1:1 complexes and cadmium(II) halide in a 1:2:1 ratio.

The $^{31}P\{^1H\}$ NMR spectra for $Cd_2Br_4[P(cy)_3]_2$ and $Cd_2I_4[P(cy)_3]_2$, at 213 K, were similar to those at 306 ± 2 K and did not show the presence of any other species.

As shown by the data in Table II, the chemical shifts and the $^1J(Cd-P)$ values for all three $Cd_2X_4[P(cy)_3]_2$ complexes show slight temperature dependence. The coordination chemical shifts do not show any systematic variation, but the $^1J(Cd-P)$ values increase by ca. 4% in going from ambient temperatures to 213 K. The increase in the magnitude of $^1J(Cd-P)$ appears to be similar to that noted for the mercury(II) complexes,[30,31] where it is attributed[31] to the slowing of halide exchange.

The $^{31}P\{^1H\}$ NMR spectra for the $CdX_2[P(cy)_3]_2$ complexes at 213 K showed a main resonance and the expected satellites due to the $^{111}Cd-^{31}P$ and $^{113}Cd-^{31}P$ spin–spin couplings. The $^1J(Cd-P)$ values for the 1:2 complexes are ca. 25–30% less than those for the 1:1 analogues. Like those for the 1:1 complexes, the $^1J(Cd-P)$ values for the 1:2 complexes also decrease with decreasing electronegativity of the halogen X. A comparison of the $^1J(Cd-P)$ values for the $CdX_2(PR_3)_2$ complexes, measured under similar conditions, shows that the $^1J(Cd-P)$ values for the tricyclohexylphosphine complexes are ca. 20–25% higher than those for the triphenylphosphine[18] complexes. The analogous $CdX_2[P(cy)_3]_2$ and $CdX_2[P(p\text{-}Me_2NC_6H_4)_3]_2$ complexes have similar $^1J(Cd-P)$ values. The pK_a values[32] for $P(cy)_3$, $P(p\text{-}Me_2NC_6H_4)_3$, and PPh_3 are 9.56, 8.65, and 2.73, respectively. The lower $^1J(Cd-P)$ values for the triphenylphosphine complexes are, thus, consistent with the lower basicity of the phosphine. However, as discussed elsewhere,[32] $^1J(Cd-P)$ is not simply related to the electron-donating abilities of phosphines.

Phosphorus-31 NMR spectral measurements showed that at 306 ± 2 K the 1:2 complexes dissociate in solution to give the 1:1 complexes and free phosphine, which undergoes rapid oxidation to give the phosphine oxide. Subsequent reaction of the phosphine oxide with the 1:1 complex results in the formation of $CdX_2P(cy)_3[OP(cy)_3]$. The $^{31}\{^1H\}$ NMR spectra of the $CdX_2[P(cy)_3]_2$ complexes at 306 ± 2 K showed two equally intense broad resonances at ca. δ 60–64 and 10–25, respectively. The upfield resonance was accompanied by satellites due to the $^{111}Cd-^{31}P$ and $^{113}Cd-^{31}P$ spin–spin couplings. The spectral parameters that are given in Table II show that the observed $^1J(Cd-P)$ values are considerably higher than those for the 1:2 complexes (observed at 213 K) and are only slightly lower than the values for the 1:1 complexes (observed at 306 ± 2 K). The observed spectral features can be attributed to the species $CdX_2P(cy)_3[OP(cy)_3]$. Further evidence for the presence of the $CdX_2[P(cy)_3][OP(cy)_3]$ species was provided by low-temperature NMR measurements. The $^{31}P\{^1H\}$ NMR data at 183 K are given in Table II; the spectrum of $CdCl_2P(cy)_3[OP(cy)_3]$ derived from $CdCl_2[P(cy)_3]_2$ is shown in Figure 1. As can be seen from the spectrum in Figure 1, the resonances due to $OP(cy)_3$ as well as $P(cy)_3$ (including the satellites) were observed as doublets when the probe temperature was lowered to 183 K. The doublet A (δ 28.7) in the spectrum shown in Figure 1 is due to $P(cy)_3$, and the doublet B (δ 64.3) is due to $OP(cy)_3$. The two satellite doublets of doublets A′ and A″ are due to the $^{111}Cd-^{31}P$ and $^{113}Cd-^{31}P$ spin–spin couplings [$^1J(^{111}Cd-^{31}P)$ = 2600 Hz, $^1J(^{113}Cd-^{31}P)$ = 2158 Hz]; the magnitude of $^3J(P-Cd-OP)$ is 10 Hz. Thus, the $^{31}P\{^1H\}$ data clearly show that the $CdX_2[P(cy)_3]_2$ complexes are stable in solution only at lower temperatures whereas the 1:1 complexes are quite stable at room temperature. The lability of the 1:2 complexes in solution cannot be attributed to the steric reasons alone because the analogous mercury(II) complexes[8] do not dissociate under similar conditions.

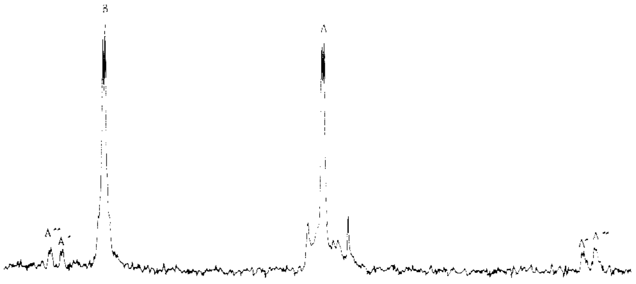

Figure 1. $^{31}P\{^1H\}$ NMR spectrum of a solution of $CdCl_2[P(cy)_3][OP(cy)_3]$ at 183 K. The solution was prepared at room temperature, and $^{31}P\{^1H\}$ NMR measurements were made at ambient probe temperature and then at 183 K.

Table IV. Infrared and Raman Spectral Data[a] for $Cd_2X_2(\mu\text{-}X)_2[P(cy)_3]_2$ Complexes in the 400–50 cm^{-1} Region

X = Cl		X = Br		X = I		
IR	R	IR	R	IR	R	assignt
				395 w		*b*
				386 sh		*b*
380 m, b		380 m, b		380 m		*b*
273 s	275 m					$\nu_t(Cd-Cl)$
249 s	251 m, b					$\nu_b(Cd-Cl)$
223 s						$\nu_b(Cd-Cl)$
	219 s		220 s		220 s	*b*
		208 vs	212 s			$\nu_t(Cd-Br)$
206 s	203 w					$\nu_b(Cd-Cl)$
	185 m		182 m		185 m	*b*
				172 vs	169 vs	$\nu_t(Cd-I)$
		169 w 152 vs 144 vs	165 m			$\nu_b(Cd-Br)$
134 sh	144 m		140 vs			$\nu(Cd-P)$
				132 m	140 s	$\nu_b(Cd-I)$
				122 m	120 s	$\nu(Cd-P)$
				110 vs		$\nu_b(Cd-I)$
104 s		75 ms		70 w		$\delta(Cd-X)$
72 m				61 m		$\delta(Cd-X)$

[a] For the solid state; for a description of abbreviations used, see footnote *a* of Table III. [b] Bands due to $P(cy)_3$.

The infrared and Raman spectral data for the $Cd_2X_4[P(cy)_3]_2$ complexes, in the solid state, in the 400–50 cm^{-1} region, together with their assignments, are listed in Table IV. The spectral data, like those for the analogous zinc(II) complexes, are indicative of the presence of both the terminal[18,27] and the bridging[15] Cd–X bonds and can be interpreted in terms of a dimeric structure of C_{2h} skeletal symmetry. A polymeric structure in which each cadmium is coordinated to a phosphorus and four bridging chlorines has been established recently for $CdCl_2PMe_2Ph$ by a crystal structure determination.[33] However, such a structure can be ruled out for the $Cd_2X_4[P(cy)_3]_2$ complexes in view of the observation of Cd–X stretching frequencies that are even higher than those observed for the $CdX_2(PR_3)_2$[18,27] complexes, which have a pseudotetrahedral structure. The assignments for the terminal Cd–X and Cd–P stretching frequencies in Table IV follow from those for the $CdX_2(PR_3)_2$ complexes.[18] The bridging Cd–X stretching frequencies have been assigned by comparison with

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Table V. Infrared and Raman Spectral Data[a] for $CdX_2[P(cy)_3]_2$ Complexes in the 400–50 cm^{-1} Region

X = Cl		X = Br		X = I		
IR	R	IR	R	IR	R	assignt
398 sh				395 w		*b*
380 m, b		380 m, vb		380 m		*b*
256 s	256 s					ν(Cd–Cl)
222 sh	220 s		220 s		218 s	*b*
208 sh						*b*
		180 s				ν_a(Cd–Br)
177 sh				177 sh		*b*
		166 ms	168 s			ν_s(Cd–Br)
				144 s	144 s	ν(Cd–I)
136 m	144 ms	134 m	144 ms			ν(Cd–P)
				124 s	124 s	ν(Cd–I) and/or ν(Cd–P)
90 ms		70 m		68 m		δ(X–Cd–X)
70 w		62 sh		52 w		

[a] For the solid state; for a description of abbreviations used, see footnote *a* of Table III. [b] Bands due to $P(cy)_3$.

those for the analogous tri-*tert*-butylphosphine complexes.[15]

Some of the infrared and Raman bands for $Cd_2Cl_4[P(cy)_3]_2$ are similar to those reported by Moers and Langhout[24] for the α form of $CdCl_2P(cy)_3$. However, these workers have reported many more Raman bands due to the metal–halogen vibrational frequencies than observed in the present work. A similar situation exists for $Cd_2Br_4[P(cy)_3]_2$ and $Cd_2I_4[P(cy)_3]_2$. Some of the Raman bands assigned to the metal–halogen vibrations by the previous wokers[24] are undoubtedly due to the internal vibrations of the phosphine. For example, a Raman band at ca. 180–186 cm^{-1} observed for all the three 1:1 cadmium(II) complexes as well as the mercury(II) complex $HgCl_2P(cy)_3$ has been attributed to a metal–halogen vibration. We find that this band is also present in the spectrum for the free phosphine. The Raman bands at 148 cm^{-1} for $CdCl_2P(cy)_3$ and at 143 cm^{-1} for $CdBr_2P(cy)_3$ assigned to the metal–halogen vibrations by previous workers are probably similar to those assigned to the Cd–P stretching vibrations in the present work.

The infrared and Raman bands for the 1:2 complexes, in the solid state, in the 400–50 cm^{-1} region, and their proposed assignments are given in Table V. The spectral features for all three 1:2 complexes are similar to those for the other $CdX_2(PR_3)_2$[18] complexes and can be interpreted in terms of a pseudotetrahedral structure of C_{2v} skeletal symmetry. Such a structure has been established for $CdCl_2(PPh_3)_2$ by a crystal structure determination.[34]

Moers and Langhout did not report any infrared spectral data for $CdBr_2[P(cy)_3]_2$ and $CdI_2[P(cy)_3]_2$. For $CdCl_2[P(cy)_3]_2$, these workers have reported two infrared (260 and 248 cm^{-1}) and two Raman (256 and 250 cm^{-1}) frequencies due to the Cd–Cl stretching modes. As shown by the data in Table V, we observed only one band (at 256 cm^{-1}) in the infrared as well as in the Raman attributable to the Cd–Cl stretching frequency. a sample of "$CdCl_2[P(cy)_3]_2$" obtained by the procedure of Moers and Langhout[24] showed infrared bands similar to those reported by these workers. However, $^{31}P\{^1H\}$ NMR spectral measurements at 183 K showed it to be $CdCl_2P(cy)_3[OP(cy)_3]$. Thus, it is evident that the vibrational spectral data reported by Moers and Langhout are in fact due to the $CdX_2P(cy)_3[OP(cy)_3]$ complexes. The Cd–P stretching frequencies assigned by Moers and Langhout for all three $CdX_2[P(cy)_3]_2$ complexes are too high and are certainly out of line with those observed for other $CdX_2(PR_3)_2$ complexes[18] as well as the analogous mercury(II) complexes.[17]

Experimental Section

General Considerations. Tricyclohexylphosphine (Pressure Chemical Co.) and reagent grade anhydrous zinc(II) and cadmium(II) halides were used as received. The purity of the phosphine was established by $^{31}P\{^1H\}$ NMR measurements. Solvents were dried according to standard procedures. Tricyclohexylphosphine and zinc(II) and cadmium(II) halides and their complexes were handled under an atmosphere of dry nitrogen with a Vacuum Atmospheres Corp. drybox. Standard vacuum-line techniques were used to remove solvents from solutions and reaction mixtures.

Physical Measurements. Elemental analyses were performed by M-H-W Laboratories, Phoenix, AZ, and by Guelph Chemical Laboratories Ltd., Guelph, Ontario, Canada. Molecular weights were determined in 1,2-dichloroethane or benzene with a Hitachi Perkin-Elmer 115 osmometer. Infrared spectra were measured with a Perkin-Elmer 180 spectrophotometer with use of samples prepared as mulls in Nujol. Raman spectra were measured with a Jarrell-Ash spectrometer with the 5145-Å exciting line of an argon ion laser. Proton-decoupled ^{31}P NMR spectra were measured on solutions in dichloromethane containing 10% acetone-d_6, the spectra were recorded in the Fourier transform mode with a Bruker WP60 FT spectrometer, and chemical shifts were measured relative to 85% H_3PO_4 as external reference. The positive shifts are downfield from 85% H_3PO_4.

Preparation of the $Zn_2X_4(P(cy)_3)_2$ Complexes. To a solution of zinc(II) halide, in diethyl ether, was added, dropwise, with constant stirring, an ethereal solution of 1 mol equiv of tricyclohexylphosphine. The resulting mixture was stirred for 30 min, and the precipitated white solid was filtered, washed with diethyl ether, and dried in vacuo.

Preparation of the $Cd_2X_4(P(cy)_3)_2$ Complexes. A 1-mol equiv quantity of cadmium(II) halide was added to a solution of tricyclohexylphosphine in dichloromethane, and the resulting mixture was stirred until a clear solution was obtained. The solvent was removed in vacuo, and the resulting solid was dissolved in dichloromethane. Hexane was added dropwise to this solution to give a white precipitate, which was filtered and dried in vacuo.

Attempted Preparation of the $ZnX_2(P(cy)_3)_2$ Complexes. The procedure of Moers and Langhout afforded products that were found to be $ZnX_2[P(cy)_3][OP(cy)_3]$ as shown by $^{31}P\{^1H\}$ NMR spectral measurements. Treatment of the zinc(II) halide with 2 mol equiv of tricyclohexylphosphine in benzene or dichloromethane gave products that contained the species $ZnX_2P(cy)_3[OP(cy)_3]$ as shown by $^{31}P\{^1H\}$ NMR spectral measurements.

Preparation of the $CdX_2(P(cy)_3)_2$ Complexes. Cadmium(II) halide was added to a benzene solution containing 2 mol equiv of tricyclohexylphosphine. The mixture was stirred until a clear solution was obtained. Removal of the solvent gave a white solid, which was washed with hexane and dried in vacuo. The procedure of Moers and Langhout gave products that contained $CdX_2P(cy)_3[OP(cy)_3]$ as shown by $^{31}P\{^1H\}$ NMR spectral measurements.

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Registry No. $Zn_2Cl_4[P(cy)_3]_2$, 81572-28-3; $Zn_2Br_4[P(cy)_3]_2$, 81572-29-4; $Zn_2I_4[P(cy)_3]_2$, 81572-30-7; $ZnCl_2P(cy)_3[OP(cy)_3]$, 81572-31-8; $ZnBr_2P(cy)_3[OP(cy)_3]$, 81572-32-9; $ZnI_2P(cy)_3[OP(cy)_3]$, 81572-33-0; $Cd_2Cl_4[P(cy)_3]_2$, 81601-71-0; $Cd_2Br_4[P(cy)_3]_2$, 81601-72-1; $Cd_2I_4[P(cy)_3]_2$, 81601-73-2; $CdCl_2[P(cy)_3]_2$, 50725-80-9; $CdBr_2[P(cy)_3]_2$, 50725-81-0; $CdI_2[P(cy)_3]_2$, 50725-82-1; $CdCl_2P(cy)_3[OP(cy)_3]$, 81572-34-1; $CdBr_2P(cy)_3[OP(cy)_3]$, 81572-35-2; $CdI_2P(cy)_3[OP(cy)_3]$, 81572-36-3.

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