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Far-Infrared, Raman, and ^{31}P Nuclear Magnetic Resonance Spectral Investigation of the Electronic Effects in Triarylphosphine Complexes of Cadmium(II) Halides

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The complexes $CdX_2[P(p\text{-}YC_6H_4)_3]_2$ and $CdX_2[P(m\text{-}CH_3C_6H_4)_3]_2$, where X = Cl, Br, or I and Y = H, CH_3, CH_3O, or $(CH_3)_2N$, have been synthesized, and their far-infrared, Raman, and ^{31}P NMR spectra have been examined. The vibrational spectral data are in accord with a pseudotetrahedral structure of C_{2v} skeletal symmetry in the solid state. The molecular nature of the complexes, in solution, is established by molecular weight measurements in 1,2-dichloroethane. The ^{31}P NMR spectra of the complexes in dichloromethane at ambient temperatures consist of a single broad resonance, indicating fast phosphine exchange on the NMR time scale. The satellites due to the $^{113}Cd–^{31}P$ and $^{111}Cd–^{31}P$ spin–spin couplings are observed for all the complexes except $CdCl_2(PPh_3)_2$ at lower temperatures. For the complexes of a given phosphine, the magnitude of cadmium–phosphorus nuclear spin–spin coupling increases linearly with the Pauling's electronegativity of X. For the given halide, the coupling constants increase linearly with the pK_a value of the phosphine. No simple relationship between the ^{31}P chemical shifts and other parameters is observed.

Introduction

Although metal–phosphorus nuclear spin–spin couplings, ^1J(M–P), have been reported[1] for complexes of many metals, investigations on the dependence of ^1J(M–P) on the nature of phosphorus ligand have been limited to the complexes of the transition metals tungsten,[2] platinum,[3,4] and rhodium,[5,6] and the complexes of mercury(II).[7-9] On the basis of earlier studies,[2,3,5,7] it has been concluded that the magnitude of ^1J(M–P) in complexes of tungsten(0), platinum(II), and rhodium decreases with increasing basicity of the phosphine and that the opposite is true for the complexes of mercury(II). Contrary to these conclusions, recent work in this laboratory has shown that the $^1J(^{195}Pt–P)$ values[4] for the complexes *cis*-$PtCl_2[P(p\text{-}XC_6H_5)_3]_2$ increase with increasing basicity of the phosphine, and the $^1J(^{199}Hg–P)$ values[9c] for the complexes, $Hg[P(p\text{-}XC_6H_4)_3]_2(ClO_4)_2$, vary in the opposite manner. It is, therefore, evident that the factors affecting the magnitude of ^1J(M–P) in coordination compounds of phosphorus donor ligands are not well understood. As part of a continuing spectroscopic investigation on the electronic and steric effect in phosphine complexes of d^8 [4-10] and d^{10} [9,11-14] metals, the phosphine complexes of cadmium(II) halides have been examined in the present work. Our objectives were to evaluate ^{31}P NMR parameters and the cadmium–ligand stretching frequencies for isostructural complexes of different phosphines varying only in the electronic or steric environment at phosphorus. Complexes of para substituted triarylphosphines were selected for a study of the electronic effects since the electronic effects of the parasubstituent can be transmitted across a phenyl group to the phosphorus without substantially changing its steric requirement. Complexes of tri-*m*-tolylphosphine and tri-*o*-tolylphosphine were investigated to seek information on the steric effects.

Earlier work[15] on cadmium(II) complexes of triarylphosphines has been limited to the complexes of triphenylphosphine which is reported to form stable 1:2 complexes. Far-infrared spectra[16] of these complexes have been found to be consistent with a pseudotetrahedral structure of C_{2v} skeletal symmetry which has been confirmed for $CdCl_2(PPh_3)_2$ by a crystal structure determination.[17]

Cadmium contains isotopes ^{111}Cd and ^{113}Cd (in 12.75% and 12.26% abundance, respectively) both of which have $I = 1/2$. ^{31}P NMR spectra[18] of the 1:2 cadmium(II) iodide complexes of triethylphosphine and few mixed alkylphenylphosphines have been reported briefly. ^{31}P NMR spectra of the 1:1 dimeric complexes $Cd_2X_4[P(t\text{-}Bu)_3]_2$ were examined very recently in this laboratory.[13] After the submission of this work for publication, Colton and co-workers[19] have also reported NMR studies on some phosphine complexes of mercury(II) and cadmium(II).

Results and Discussion

The new complexes $CdX_2[P(p\text{-}YC_6H_4)_3]_2$ and $CdX_2[P(m\text{-}CH_3C_6H_4)_3]_2$ [X = Cl, Br, I; Y = CH_3, OCH_3, $(CH_3)_2N$], like the previously known $CdX_2(PPh_3)_2$ complexes,[15,16] are readily obtained from the reaction of the cadmium(II) halide with the phosphine in refluxing ethanol. However, no complex could be isolated from reactions of cadmium(II) halides with $P(p\text{-}FC_6H_4)_3$, $P(p\text{-}ClC_6H_4)_3$, or $P(o\text{-}CH_3C_6H_4)_3$ even when a large excess of the phosphine was used. Both $P(p\text{-}FC_6H_4)_3$ and $P(p\text{-}ClC_6H_4)_3$ are less basic[20] than PPh_3, but P(*o*-

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Table I. Analytical and Molecular Weight Data for the Complexes

complex	mp, °C	% C found	% C calcd	% H found	% H calcd	mol wt[d] found	mol wt[d] calcd
$CdCl_2[P(C_6H_5)_3]_2$	233-234	61.15	61.03	4.23	4.24	*e*	
$CdBr_2[P(C_6H_5)_3]_2$	226-228	54.13	54.29	3.67	3.76	*e*	
$CdI_2[P(C_6H_5)_3]_2$	236-238	48.35	48.53	3.15	3.37	*e*	
$CdCl_2[P(m\text{-}CH_3C_6H_4)_3]_2$	168-169	64.00	63.68	5.23	5.31	*e*	
$CdBr_2[P(m\text{-}CH_3C_6H_4)_3]_2$	165-167	57.50	57.25	4.74	4.77	*e*	
$CdI_2[P(m\text{-}CH_3C_6H_4)_3]_2$	149-152	51.86	51.72	4.15	4.31	935	974
$CdCl_2[P(p\text{-}CH_3C_6H_4)_3]_2$	210 dec	63.88	63.68	5.29	5.31	*e*	
$CdBr_2[P(p\text{-}CH_3C_6H_4)_3]_2$	239-243	57.22	57.25	4.95	4.77	870	880
$CdI_2[P(p\text{-}CH_3C_6H_4)_3]_2$	261-264	51.64	51.72	4.23	4.31	998	974
$CdCl_2[P(p\text{-}CH_3OC_6H_4)_3]_2$	208	56.70	56.80	4.76	4.78	*e*	
$CdBr_2[P(p\text{-}CH_3OC_6H_4)_3]_2$	211	51.73	51.63	4.38	4.34	990	976
$CdI_2[P(p\text{-}CH_3OC_6H_4)_3]_2$	184	47.10	47.10	3.98	3.96	1030	1070
$CdCl_2\{P[p\text{-}(CH_3)_2NC_6H_4]_3\}_2$[a]	295-300 dec	60.09	59.65	6.52	6.27	*e*	
$CdBr_2\{P[p\text{-}(CH_3)_2NC_6H_4]_3\}_2$[b]	305-309 dec	54.48	54.63	5.77	5.74	1025	1055
$CdI_2\{P[p\text{-}(CH_3)_2NC_6H_4]_3\}_2$[c]	310-314 dec	50.48	50.16	5.36	5.27	1167	1140

[a] % N: found, 8.63; calcd, 8.7. [b] % N: found, 7.92; calcd, 7.97. [c] % N: found, 7.04; calcd, 7.31. [d] In 1,2-dichloroethane. [e] Not soluble enough.

Table II. Cd-X and Cd-P Stretching and Cd-X Bending Frequencies[a] for the Complexes

complex	ν(Cd-X) IR	ν(Cd-X) Raman	ν(Cd-P) IR	ν(Cd-P) Raman	δ(Cd-X) IR
$CdCl_2(PPh_3)_2$	268 vs	261 s	136 ms	136 m	105 s 87 vs
$CdCl_2[P(m\text{-}CH_3C_6H_4)_3]_2$	270 s, br	263 vs	138 s 130 s sh	132 s	94 vs, br
$CdCl_2[P(p\text{-}CH_3C_6H_4)_3]_2$	270 s, br	262 s, br			102 m
$CdCl_2[P(p\text{-}CH_3OC_6H_4)_3]_2$	270 vs, br	262 s, br	138 m		100 s
$CdCl_2\{P[p\text{-}(CH_3)_2NC_6H_4]_3\}_2$	266 s sh 250 s	250 vs, br			104 s, vbr 86 sh
$CdBr_2(PPh_3)_2$	198 vs 176 vs	198 vs 176 s	134 ms	132 ms	70 s, br
$CdBr_2[P(m\text{-}CH_3C_6H_4)_3]_2$	196 vs 181 vs	196 s 182 vs	136 s	130 s	70 vs
$CdBr_2[P(p\text{-}CH_3C_6H_4)_3]_2$	198 s 177 s	199 m 175 vs			65 s, br
$CdBr_2[P(p\text{-}CH_3OC_6H_4)_3]_2$	200 vs 180 vs	200 m 181 vs	136 m		66 s, br
$CdBr_2\{P[p\text{-}(CH_3)_2NC_6H_4]_3\}_2$	187 vs 175 s	190 w 174 s			62 m
$CdI_2(PPh_3)_2$	166 s 143 s	166 s 142 s	132 m	124 vs	50 m
$CdI_2[P(m\text{-}CH_3C_6H_4)_3]_2$	165 vs 133 vs	164 m 133 s	127 s	100 vs	51 ms
$CdI_2[P(p\text{-}CH_3C_6H_4)_3]_2$	165 vs 140 s	165 m 140 vs			54 m
$CdI_2[P(p\text{-}CH_3OC_6H_4)_3]_2$	159 vs 138 s				54 m, br
$CdI_2\{P[p\text{-}(CH_3)_2NC_6H_4]_3\}_2$	154 vs 139 vs	155 w 137 s			56 m, br

[a] In cm^{-1} for the solid state. Description of abbreviations: br, broad; m, medium; s, strong; sh, shoulder; v, very, w, weak.

$CH_3C_6H_4)_3$ is more basic. Thus, the instability of the complexes of $P(p\text{-}FC_6H_4)_3$ and $P(p\text{-}ClC_6H_4)_3$ with cadmium(II) halides is due to the electronic effects and that of $P(o\text{-}CH_3C_6H_4)_3$ due to the steric reasons. Both $P(p\text{-}FC_6H_4)_3$ and $P(p\text{-}ClC_6H_4)_3$, however, form 1:1 as well as 2:1 complexes[7c,19] with mercury(II) halides which also form stable 1:1 complexes[11] with $P(o\text{-}CH_3C_6H_4)_3$. The failure to isolate complexes of these phosphines with cadmium(II) halides is, thus, also due to a weaker affinity of cadmium(II) for tertiary phosphines. All the complexes prepared in this study are air-stable white crystalline solids which are sparingly or moderately soluble in polar organic solvents such as acetone and dichloromethane. Their melting points and analytical and molecular weight data are given in Table I. Molecular weights of only those complexes could be determined which were sufficiently soluble in 1,2-dichloroethane.

Vibrational Spectra and Structure. The Cd-X and Cd-P stretching as well as the Cd-X bending frequencies for the complexes $CdX_2(PPh_3)_2$ have been assigned[16] in terms of molecular structures of C_{2v} symmetry. These assignments were confirmed in the present work by Raman measurements. Spectral data obtained in the present work also show that the complexes of substituted triarylphosphines reported herein are isostructural with the triphenylphosphine complexes.

For the isostructural complexes of a given phosphine, the Cd-X stretching and bending frequencies are expected to decrease with increasing mass of X. Thus, these frequencies can be assigned with reasonable certainty by comparing the spectra of the complexes and the free phosphine. The assigned frequencies are listed in Table II. For a pseudotetrahedral complex of C_{2v} skeleton, X_2CdP_2, both the symmetric and antisymmetric Cd-X stretching vibrations are active in the infrared as well as in the Raman. As shown by the data in Table II, the infrared spectra for the bromo and the iodo complexes showed two well-resolved bands attributable to the symmetric and antisymmetric Cd–X stretching frequencies.[21] These frequencies were also observed in the Raman spectra except in the case of $CdI_2[P(p\text{-}CH_3OC_6H_4)_3]_2$ for which Raman spectrum could not be observed due to fluoroescence. In each case, the relative intensity of the lower frequency was markedly higher in the Raman whereas the opposite was true for the relative intensities of the infrared bands. Therefore, the lower frequency is assigned to the symmetric Cd–X stretching mode and the higher to the antisymmetric stretching mode. The symmetric and the antisymmetric Cd–Cl stretching frequencies were, however, not well resolved in the infrared except in the case of $CdCl_2\{P[p\text{-}(CH_3)_2NC_6H_4]_3\}_2$ for which strong infrared bands at 266 and 250 cm^{-1} were observed in the Cd–Cl stretching region.[21] The infrared spectra of the other complexes, in this region, exhibited a strong broad band showing maxima at ca. 270 cm^{-1}. The Raman spectra of all the chloro complexes except $CdCl_2\{P[p\text{-}(CH_3)_2NC_6H_4]_3\}_2$ showed a strong band at ca. 262 cm^{-1}; in the case of $CdCl_2\{P[p\text{-}(CH_3)_2NC_6H_4]_3\}_2$ this frequency is lowered to 250 cm^{-1}. Since the symmetric Cd–Cl stretching mode is expected to have a higher Raman intensity than the antisymmetric stretching mode, the Raman frequency is assigned to the symmetric Cd–Cl stretching mode and the infrared frequency to the antisymmetric mode. The failure to observe the antisymmetric Cd–Cl stretching mode in the Raman spectra is explicable in terms of a decrease in the polarizability of the Cd–X bond with decreasing mass of the halogen.

The X–Cd–X deformation frequencies for the substituted triarylphosphine complexes are similar to those observed for the triphenylphosphine complexes, and their assignments follow from the earlier work.[16] These frequencies were not observed in the Raman spectra. This may well be due to the fact that the major contribution to these frequencies comes from the two CdX_2 rocking modes belonging to the b_1 and b_2 representations which are expected to be weak in the Raman.

In agreement with the previous infrared study, a medium to a strong infrared band in the 138–127-cm^{-1} region assignable to the antisymmetric Cd–P stretching frequency is observed for the complexes of triphenylphosphine, tri-*m*-tolylphosphine, and tris(*p*-methoxyphenyl)phosphine. A medium to strong band in the 136–124-cm^{-1} region is also observed in the Raman spectra of the triphenylphosphine and the tri-*m*-tolylphosphine complexes which is assigned to the symmetric Cd–P stretching mode. The proposed assignments for the Cd–P stretching frequencies compare well with the metal–phosphorus stretching modes for the isostructural complexes of mercury(II) halides.[12] The symmetric Cd–P stretching frequency for $CdI_2[P(m\text{-}CH_3C_6H_4)_3]_2$ appears to be coupled with the symmetric Cd–I stretching frequency, giving rise to strong Raman bands at 133 and 100 cm^{-1}. Support for this suggestion is provided by the fact that, although the antisymmetric Cd–I stretching frequency for this complex is similar to that for $CdI_2(PPh_3)_2$ and $CdI_2[P(p\text{-}CH_3C_6H_4)_3]_2$, the symmetric frequency is 7–9 cm^{-1} lower. The infrared spectrum of tri-*p*-tolylphosphine contains a strong band at ca. 150 cm^{-1} which shifts to lower frequencies upon coordination making the assignment of the Cd–P stretching frequencies very difficult. The infrared spectra for the complexes of tri-*p*-[(dimethylamino)phenyl]phosphine also contain a strong and very broad band at ca. 120 cm^{-1} due to the phosphine.

From the data in Table II it is quite clear that the Cd–X stretching frequencies for all the complexes are in the regions expected[21] for the terminal Cd–X bonds similar to those in CdX_4^{2-}. The Cd–X stretching frequencies due to the bridging Cd–X bonds in the dimeric complexes,[13] $Cd_2X_4[P(t\text{-}Bu)_3]_2$, as well as in the polymeric complex,[22,23] $CdCl_2PMe_2Ph$, are markedly lower. Although the Cd–X stretching frequencies for the chloro and the iodo complexes of tris[*p*-(dimethylamino)phenyl]phosphine are slightly lower than those for the triphenylphosphine complexes, the Cd–X stretching frequencies for the remaining complexes do not change with phosphine. Thus, there can be little doubt that all the complexes included in this study have a structure similar to that established for $CdCl_2(PPh_3)_2$. Significant variations are not observed in the Cd–P stretching frequencies, showing that the effects of the subtle changes in the electronic environment of the phosphine are not amenable for study by vibrational spectroscopy.

^{31}P NMR Spectra. The ^{31}P NMR spectra of the complexes, in dichloromethane, at ambient temperatures, showed a broad single resonance, indicating fast phosphine exchange on the NMR time scale. A sharp central peak and sharp satellites due to ^{113}Cd–^{31}P and ^{111}Cd–^{31}P couplings were observed for all the complexes except $CdCl_2(PPh_3)_2$, $CdCl_2[P(p\text{-}CH_3C_6H_4)_3]_2$, and $CdBr_2(PPh_3)_2$ at 213 K. Attempts to slow down the ligand exchange to observe the $^{113}Cd/^{111}Cd$–^{31}P couplings did not succeed in the case of $CdCl_2(PPh_3)_2$ even up to 163 K. Sharp satellites due to $^{113}Cd/^{111}Cd$–^{31}P couplings were observed for $CdCl_2[P(p\text{-}CH_3C_6H_4)_3]_2$ at 183 K and for $CdBr_2(PPh_3)_2$ at 163 K. Thus, the ligand-exchange rate for the $CdX_2(PPh_3)_2$ complexes at a given temperature appear to decrease in the order Cl > Br > I which is opposite to that reported[7c] for the isostructural complexes of mercury(II) halides. For $CdCl_2[P(p\text{-}CH_3C_6H_4)_3]_2$ satellites were also observed at 213 K. The peaks were broad, but the values for $^1J(^{113}Cd$–$^{31}P)$ and $^1J(^{111}Cd$–$^{31}P)$ were similar to those observed at 183 K. Variable-temperature measurements showed that the $^1J(^{113}Cd/^{111}Cd$–$^{31}P)$ values for the $CdX_2[P(p\text{-}CH_3C_6H_4)_3]_2$ complexes remained unchanged as the temperature was decreased from 213 to 183 K; the chemical shifts moved slightly upfield at lower temperature. Thus, unlike the ^{199}Hg–^{31}P coupling which increases markedly with a decrease in temperature,[24–26] the $^{113}Cd/^{111}Cd$–^{31}P couplings are not markedly affected by temperature.

The ^{31}P NMR parameters for the complexes are listed in Table III. The data in Table III show that the ratio $^1J(^{113}Cd$–$^{31}P)$:$^1J(^{111}Cd$–$^{31}P)$, for all the complexes, is in excellent agreement with the expected ratio of 1.046. The qualitative trends noted[7–9a] for $^1J(^{199}Hg$–$^{31}P)$ are also evident for $^1J(^{113}Cd/^{111}Cd$–$^{31}P)$. For the complexes of a given phosphine, $^{113}Cd/^{111}Cd$–^{31}P spin–spin couplings increase in magnitude with increasing electronegativity of the halogen X. In fact, as shown in Figure 1, the plots of $^1J(^{113}Cd$–$^{31}P)$ against the Pauling's electronegativity of the halogen give straight lines of similar slopes. The relationship is explicable in terms of an increase in the metal "s" orbital contribution to the metal–phosphorus bonds with an increase in the electron-withdrawing power of the anionic ligands. Recently reported[27] structural and ^{31}P NMR data for the complexes $HgX_2(PPh_3)_2$ (X = NO_3, SCN, I, CN) are in agreement with this proposal; the expected increase in $^1J(^{199}Hg$–$^{31}P)$ is accompanied by decrease in the Hg–P distance, increase in the P–Hg–P angle, and a decrease in the X–Hg–X angle.

For complexes of mercury(II)[7a,b] with phosphines PR_nPh_{3-n}, the magnitude of $^1J(^{199}Hg$–$^{31}P)$ increases with *n*, but for

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Table III. ^{31}P NMR Data[a] for the $CdX_2(PR_3)_2$ Complexes

complex	δ[b]	$\Delta\delta$[c]	$^1J(^{111}Cd-^{31}P)$, Hz	$^1J(^{113}Cd-^{31}P)$, Hz	$^1J(^{111}Cd-^{31}P)$: $^1J(^{113}Cd-^{31}P)$
$CdCl_2[P(C_6H_5)_3]_2$	−7.1	0.60	*d*	*d*	
$CdBr_2[P(C_6H_5)_3]_2$[e]	4.22	11.92	1265	1323	1.048
$CdI_2[P(C_6H_5)_3]_2$	−8.84	−1.14	1091	1142	1.047
$CdCl_2[P(m\text{-}CH_3C_6H_4)_3]_2$	0.76	8.26	1439	1508	1.048
$CdBr_2[P(m\text{-}CH_3C_6H_4)_3]_2$	−2.49	5.01	1333	1393	1.045
$CdI_2[P(m\text{-}CH_3C_6H_4)_3]_2$	−4.53	2.97	1119	1168	1.044
$CdCl_2[P(p\text{-}CH_3C_6H_4)_3]_2$[f]	−1.20	9.10	1455	1523	1.046
$CdBr_2[P(p\text{-}CH_3C_6H_4)_3]_2$	−3.61	6.69	1337	1396	1.044
$CdI_2[P(p\text{-}CH_3C_6H_4)_3]_2$	−10.05	0.25	1147	1198	1.044
$CdCl_2[P(p\text{-}CH_3OC_6H_4)_3]_2$	−3.22	9.88	1475	1543	1.046
$CdBr_2[P(p\text{-}CH_3OC_6H_4)_3]_2$	−5.80	7.30	1369	1433	1.047
$CdI_2[P(p\text{-}CH_3OC_6H_4)_3]_2$	−12.26	0.84	1184	1237	1.045
$CdCl_2\{P[p\text{-}(CH_3)_2NC_6H_4]_3\}_2$	−3.52	10.58	1580	1650	1.044
$CdBr_2\{P[p\text{-}(CH_3)_2NC_6H_4]_3\}_2$	−5.93	8.17	1489	1560	1.048
$CdI_2\{P[p\text{-}(CH_3)_2NC_6H_4]_3\}_2$	−11.46	2.64	1333	1396	1.047

[a] At 213 K in CH_2Cl_2 containing 10% CD_2Cl_2 or $CDCl_3$ unless stated otherwise. Positive chemical shifts are downfield from 85% H_3PO_4. [b] Chemical shifts for the complex. [c] $\Delta\delta$ = chemical shift for the complex − chemical shift for the phosphine. [d] Cd–P satellites were not observed even at 173 K in $(CH_3)_2CO$. [e] In acetone containing 10% $(CD_3)_2CO$ at 163 K; δ (at 213 K) −2.61. [f] At 183 K; δ (at 213 K) 0.80.

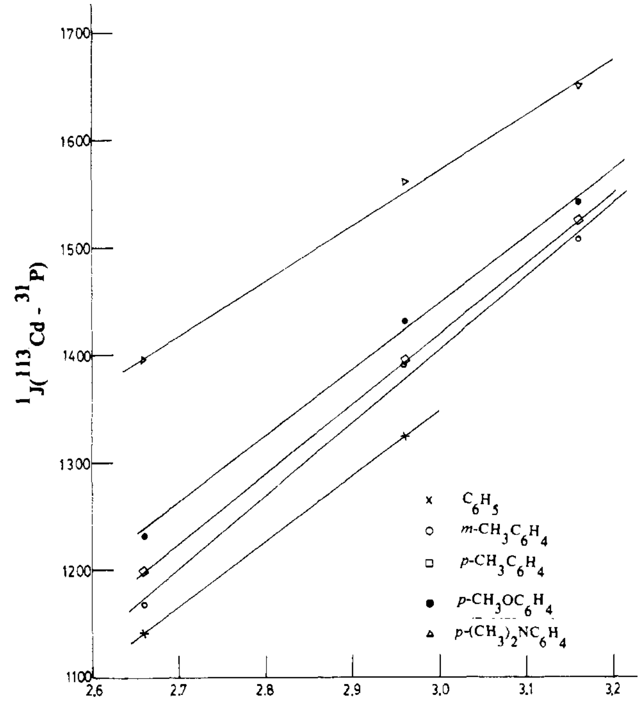

Figure 1. Plots of $^1J(^{113}Cd-^{31}P)$ vs. Pauling's electronegativity.

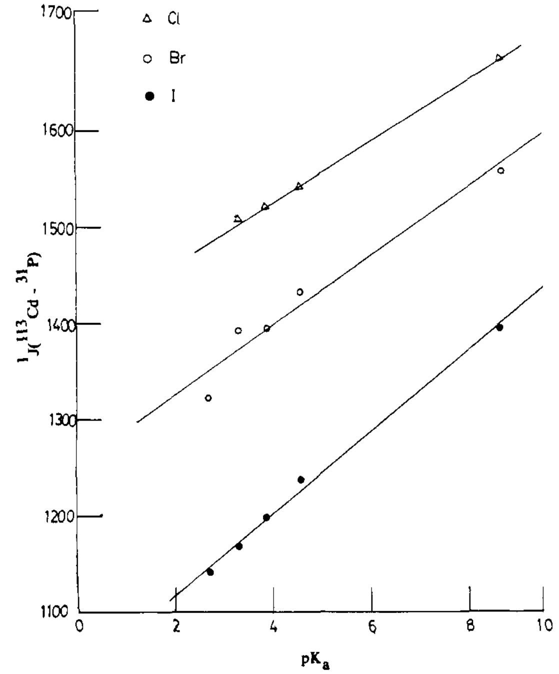

Figure 2. Plots of $^1J(^{113}Cd-^{31}P)$ vs. pK_a values of the phosphines.

tungsten(0)[2a] or platinum(II),[3] $^1J(M-P)$ decreases as n increases. $^1J(^{113}Cd/^{111}Cd-^{31}P)$ values[18] for the cadmium(II) iodide complexes $CdI_2(PEt_nPh_{3-n})_2$ also increase with increasing n. As mentioned earlier, from these results it has been concluded that the magnitude of $^1J(M-P)$ for complexes of metals such as Hg(II) or Cd(II), for which d orbital participation is not important, increases with increasing basicity of the phosphine whereas the opposite is ture for complexes of tungsten(0) or platinum(II) for which d orbital participation can be important. However, no attempts have been made in these studies to quantitatively determine the basicity of the phosphines. The studies also suffer from the disadvantage that the changes in the basicity of the phosphine upon substitution of an alkyl group by a phenyl group are accompanied by changes in the steric effects. The steric requirements of the phosphines used in the present work are expected to be similar, and their basicities[20] have been determined from nonaqueous potentiometric titrations with perchloric acid following a modified procedure of Streuli.[28] Thus, the dependence of the cadmium-phosphorus coupling on the electronic properties of the phosphines can be examined quantitatively. As shown in Figure 2, the plots of $^1J(^{113}Cd-^{31}P)$ against the pK_a of the phosphines for the complexes of each cadmium(II) halide give straight lines, showing a linear dependence of the coupling constant on the phosphine basicity. A slight deviation of the point for $CdBr_2(PPh_3)_2$ from the straight line is probably due to the fact that its ^{31}P NMR spectrum was measured in acetone which is a donor solvent. If we include the reported $^1J(^{113}Cd-^{31}P)$ and pK_a values for $CdI_2(PEt_3)_2$ in the plot of the cadmium(II) iodide complexes, the point falls way out from the straight line. This is not surprising in view of the differences in the steric effects of PEt_3 and the phosphines used in this work.

It has been mentioned earlier that the $^1J(^{195}Pt-^{31}P)$ values for the complexes *cis*-$PtCl_2[P(p\text{-}YC_6H_4)_3]_2$ also increase with increasing basicity of the phosphine. Thus, the electronic effects of phosphine on $^1J(M-P)$ in the complexes of plati-

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(28) C. A. Streuli, *Anal. Chem.*, **32**, 985 (1960).

num(II) chloride and cadmium(II) halides are indicated to be similar for phosphines with similar steric effects, and the opposite trend noted for $^1J(^{195}\text{Pt}-^{31}\text{P})$ in previous studies is most likely due to the interplay between the electronic and steric effects.

Empirical correlations between the ^{31}P chemical shifts and other parameters for phosphine complexes of mercury(II)[7] as well as some transition metals[29] have been proposed. A linear correlation between the coordination chemical shift (δ(complex) − δ(phosphine)) and $^1J(^{199}\text{Hg}-^{31}\text{P})$ has been noted[7,9a] for the complexes of mercury(II) halides as well as several other mercury(II) salts. On this basis, the absolute values of the coordination chemical shifts have been interpreted in terms of the strength of the metal–phosphorus bond[7] and the basicity[26] of the phosphine. Results of a recent ^{31}P NMR study[25] on the complexes of mercury(II) carboxylates have, however, shown that the proposed interpretations are very misleading. The chemical shifts and the coordination chemical shifts for the complexes of cadmium(II) halides given in Table III further show that there are no simple relationships of the coordination chemical shift with any other parameter. For a given phosphine, although the coordination chemical shift increases in the order Cl > Br ≫ I, the shift for $CdI_2(PPh_3)_2$ is, in fact, upfield instead of downfield. Unlike mercury complexes, the plots of metal–phosphorus coupling constants against coordination chemical shifts do not give straight lines except in the case of the $CdX_2\{P[p\text{-}(CH_3)_2NC_6H_4]_3\}_2$ complexes for which a straight line is obtained. For a given halide, the coordination chemical shifts for the chloro and the bromo complexes (excluding the triphenylphosphine complexes) decrease in the order of decreasing basicity of the phosphine, but for the iodo complexes the order is $P(m\text{-}CH_3C_6H_4)_3 > P[p\text{-}(CH_3)_2NC_6H_4]_3 > P(p\text{-}CH_3OC_6H_4)_3 > P(p\text{-}CH_3C_6H_4)_3 > PPh_3$.

A linear relationship[29] between the coordination chemical shift and the chemical shift of the phosphine has been found for a variety of transition-metal complexes. Such a correlation does not exist for the cadmium(II) halide complexes as shown by plots of $\Delta\delta$ against δ. Thus, despite extensive ^{31}P chemical shift data on metal–phosphine complexes, it is still very difficult to ascertain the effects of various factors on the chemical shifts.

Experimental Section

Materials. Triarylphosphines (from Strem Chemicals) were recrystallized and their purity was checked by ^{31}P NMR. Anhydrous cadmium(II) halides were reagent grade. Ethanol was refluxed over magnesium and distilled. Other solvents were reagent grade and were stored over molecular sieves.

Physical Measurements. Melting points were determined with a Gallenkamp melting point apparatus and are uncorrected. Elemental analyses were performed by M-H-W Laboratories, Phoenix, AZ, or by Guelph Chemical Laboratories Ltd., Guelph, Ontario. Molecular weights were determined in 1,2-dichloroethane with a Hitachi Perkin-Elmer 115 vapor-phase osmometer. Infrared spectra were recorded with a Perkin-Elmer 180 spectrophotometer. Samples were prepared as mulls in Nujol and were placed between polyethylene disks. Raman spectra were measured in the solid state with a Jarrel-Ash spectrophotometer using the 5145-Å exciting line of an argon-ion laser. $^{31}P\{^1H\}$ spectra of the solutions of the complexes in dichloromethane [containing 10% $CDCl_3$ or $(CD_3)_2CO$] were recorded at ambient temperatures as well as low temperatures in the Fourier transform mode with a Bruker WP60 FT spectrometer. The chemical shifts were measured relative to 85% H_3PO_4 as external reference and are reported positive when downfield from H_3PO_4.

Preparation of the Complexes. All operations involved in the preparation and purification were carried out under an atmosphere of oxygen-free dry nitrogen. In a typical preparation, cadmium(II) halide (2 mmol) and triarylphosphine (4.2 mmol) were stirred together in refluxing ethanol (~15 mL) for ~5 h. The complex precipitated upon cooling to room temperature (concentration of the solution was sometimes necessary). After filtration it was washed with ethanol (2 × 3 mL) and benzene (2 × 5 mL) and recrystallized from a mixture of dichloromethane and hexane. Except for the losses during filtration and crystallization, yields were quantitative.

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Registry No. $CdCl_2(PPh_3)_2$, 14494-80-5; $CdBr_2(PPh_3)_2$, 14586-73-3; $CdI_2(PPh_3)_2$, 14126-39-7; $CdCl_2[P(m\text{-}CH_3C_6H_4)_3]_2$, 77061-37-1; $CdBr_2[P(m\text{-}CH_3C_6H_4)_3]_2$, 77061-38-2; $CdI_2[P(m\text{-}CH_3C_6H_4)_3]_2$, 77061-39-3; $CdCl_2[P(p\text{-}CH_3C_6H_4)_3]_2$, 77061-40-6; $CdBr_2[P(p\text{-}CH_3C_6H_4)_3]_2$, 77061-41-7; $CdI_2[P(p\text{-}CH_3C_6H_4)_3]_2$, 77061-42-8; $CdCl_2[P(p\text{-}CH_3OC_6H_4)_3]_2$, 77061-43-9; $CdBr_2[P(p\text{-}CH_3OC_6H_4)_3]_2$, 77061-44-0; $CdI_2[P(p\text{-}CH_3OC_6H_4)_3]_2$, 77061-45-1; $CdCl_2\{P[p\text{-}(CH_3)_2NC_6H_4]_3\}_2$, 77061-46-2; $CdBr_2\{P[p\text{-}(CH_3)_2NC_6H_4]_3\}_2$, 77061-47-3; $CdI_2\{P[p\text{-}(CH_3)_2NC_6H_4]_3\}_2$, 77061-48-4.

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Temperature-Dependent Phosphite Complex Equilibria Observable with NMR and IR Techniques

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The complexes $[(OR)_3P]_2CuH_3BR'$ (R = Me, Et; R′ = H, $COOC_2H_5$) experience changes in equilibria of the type

$$L_2CuH_3BR' \underset{}{\overset{+L}{\rightleftharpoons}} L_3CuH_3BR' \overset{+L}{\rightleftharpoons} L_4Cu^+H_3BR'$$

which are observed by NMR and IR techniques. Temperatures at which these equilibria occur and chemical shift trends are dependent on whether L is phosphine or phosphite.

Introduction

A variety of studies have been made regarding phosphine dissociation with transition-metal phosphine and phosphite complexes.[3-9] Ligand dissociation equilibria of phosphine complexes containing tetrahydroborate or its derivatives have

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