equivalent hydrogen atoms, H(11), of neighboring molecules at a distance of 2.91 Å. The two hydrogen atoms are related by the molecular mirror plane and form a trans angle at the nickel atom of 155°. The C(11)—H(11)···Ni angle is 136°.

Acknowledgment. L.F.L. and W.E.M. thank the Australian Research Grants Committee for support and the Australian Institute of Nuclear Science and Engineering for the use of facilities.

Registry No. Ni(Etaen), 55519-92-1; Cu(Etaen), 62816-09-5; Ni(*i*-Praen), 62816-08-4; Cu(*i*-Praen), 62816-07-3; Ni(*i*-Buaen), 55519-93-2; Cu(*i*-Buaen), 62816-06-2; Ni(*t*-Buaen), 55524-07-7; Cu(*t*-Buaen), 62816-05-1; EtaenH_2, 62816-28-8; *i*-PraenH_2, 62816-27-7; *i*-BuaenH_2, 62796-06-9; *t*-BuaenH_2, 62796-05-8; Ni(Meaen), 36802-27-4; Ni(Meapn), 40792-91-4; ^{13}C, 14762-74-4.

Supplementary Material Available: A listing of structure factor amplitudes (5 pages). Ordering information is given on any current masthead page.

References and Notes

(1) (a) James Cook University. (b) Australian National University.
(2) L. F. Lindoy and W. E. Moody, *J. Am. Chem. Soc.*, 97, 2275 (1975).
(3) P. J. McCarthy, R. J. Hovey, K. Ueno, and A. E. Martell, *J. Am. Chem. Soc.*, 77, 5820 (1955).
(4) The ligands are abbreviated RaenH_2 where R represents the alkyl group which replaces one methyl group of each acetylacetone-derived ring in **1**.
(5) M. J. Carter, D. P. Pillema, and F. Basolo, *J. Am. Chem. Soc.*, **96**, 392 (1974), and references therein.
(6) M. Calligaris, G. Nardin, and L. Randaccio, *Coord. Chem. Rev.*, 7, 385 (1972).
(7) R. H. Holm, G. W. Everett, and A. Chakravorty, *Prog. Inorg. Chem.*, 7, 83 (1966), and references therein.
(8) R. J. Hovey, J. J. O'Connell, and A. E. Martell, *J. Am. Chem. Soc.*, **81**, 3189 (1959).
(9) R. H. Holm, *J. Am. Chem. Soc.*, **82**, 5632 (1960).
(10) A. E. Martell, R. L. Belford, and M. Calvin, *J. Inorg. Nucl. Chem.*, **5**, 170 (1958).
(11) S. H. Chaston, S. E. Livingstone, T. N. Lockyer, and J. S. Shannon, *Aust. J. Chem.*, **18**, 1539 (1965); S. E. Livingstone and J. H. Mayfield, *ibid.*, **28**, 1517 (1975).
(12) R. P. Scaringe and D. J. Hodgson, *Inorg. Chem.*, **15**, 1193 (1976).
(13) Complexes of two of these ligands have been used for gas chromatography studies but details of their isolation and characterization have not appeared, see S. Dilli and E. Patsalides, *J. Chromatogr.*, **130**, 251 (1977).
(14) Ni(Meapn) represents the 1,2-diaminopropane analogue of Ni(Meaen).
(15) L. F. Lindoy, H. C. Lip, and W. E. Moody, *J. Chem. Soc., Dalton Trans.*, 44 (1974).
(16) J. T. Adams and C. R. Hauser, *J. Am. Chem. Soc.*, **66**, 1220 (1944); R. Levine, J. A. Conroy, J. T. Adams, and C. R. Hauser, *ibid.*, **67**, 1510 (1945).
(17) "International Tables for X-Ray Crystallography", Vol. I, Kynoch Press, Birmingham, 1965, (a) p 151; (b) p 119.
(18) A. R. Hendrickson, R. L. Martin, and D. Taylor, *J. Chem. Soc., Dalton Trans.*, 2182 (1975).
(19) "International Tables for X-Ray Crystallography", Vol. IV, Kynoch Press, Birmingham, 1974, (a) p 99; (b) p 148.
(20) D. Taylor and P. O. Whimp, unpublished data.
(21) P. J. McCarthy and A. E. Martell, *Inorg. Chem.*, **6**, 781 (1967).
(22) G. O. Dudek and R. H. Holm, *J. Am. Chem. Soc.*, **83**, 2099 (1961).
(23) G. Maki, *J. Chem. Phys.*, **29**, 162, 1129 (1958); R. D. Archer, *Inorg. Chem.*, **2**, 292 (1963).
(24) K. Ueno and A. E. Martell, *J. Phys. Chem.*, **61**, 257 (1957).
(25) P. H. Howells, J. L. Kenney, J. H. Nelson, and R. A. Henry, *Inorg. Chem.*, **15**, 124 (1976).
(26) B. N. Figgis, "Introduction to Ligand Fields", Interscience, New York, N.Y., 1966.
(27) E. M. Bulewiez and T. M. Sugden, *Trans. Faraday Soc.*, **52**, 1475 (1956).
(28) L. F. Lindoy, W. E. Moody, J. Lewis, and T. W. Matheson, *J. Chem. Soc., Dalton Trans.*, 1965 (1976).
(29) S. Bruckner, M. Calligaris, G. Nardin, and L. Randaccio, *Inorg. Chim. Acta*, **2**, 386 (1968).
(30) F. Cariati, F. Morazzoni, C. Busetto, G. Del Piero, and A. Zazzetta, *J. Chem. Soc., Dalton Trans.*, 342 (1976).

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Preparation, Characterization, and Spectral Studies of Neutral Tri-*tert*-butylphosphine Complexes of Zinc(II) and Cadmium(II)

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Received January 29, 1977 AIC700796

Complexes having the empirical formula $(t\text{-Bu})_3PMX_2$ are formed from the reaction of tri-*tert*-butylphosphine with anhydrous zinc(II) or cadmium(II) salts, in an aprotic solvent. The complexes $(t\text{-Bu})_3PZnX_2$ (X = Cl, Br, and I) and $(t\text{-Bu})_3PCdX_2$ (X = Cl, Br, I, and SCN) have been isolated and characterized by elemental analyses, conductance, and molecular weight measurements and by infrared, Raman, and ^1H and ^{31}P NMR spectral studies. The complexes $(t\text{-Bu})_3PZnBr_2$ and $(t\text{-Bu})_3PZnI_2$ are about 10% ionized in acetonitrile or nitromethane; other complexes are not appreciably ionized in these solvents. All the complexes behave as dimeric species in 1,2-dichloroethane. The far-infrared and Raman data for all the complexes indicate a dimeric tetrahedral structure (C_{2h} skeletal symmetry) in the solid state. The terminal as well as the bridging M–X stretching frequencies and the M–P stretching frequencies for all the complexes have been assigned. The M–P stretching frequencies for these complexes decrease in the order Cl ~ SCN > Br > I. ^1H NMR spectral measurements show that the complexes do not undergo a rapid phosphine exchange at room temperature. The ^{31}P NMR spectra of cadmium(II) complexes, at ambient temperatures, show sharp satellites due to the coupling of the ^{31}P nucleus with the ^{111}Cd and ^{113}Cd nuclei. The $^1J(P\text{–}Cd)$ values for the complexes vary in the order Cl ~ SCN > Br > I.

Introduction

Recent studies[1] demonstrate that the chemical reactivity and the stereochemistry of metal complexes of phosphorus ligands are markedly affected by the steric interactions involving the substituents on phosphorus. For example, platinum(II) and palladium(II) complexes of tertiary phosphines containing bulky substituents on phosphorus undergo intramolecular metalation.[2-4] Bulky phosphines also stabilize unusual coordination geometries of metals as exemplified by the formation of two-coordinate 14-electron complexes[5-7] of the type ML_2 where M = Pt or Pd and L = tricylcohexylphosphine. In this laboratory we initiated a systematic study of metal complexes of the little studied but very bulky and basic ligand tri-*tert*-butylphosphine.[8,9] In a previous study[9] it was found that the reaction of tri-*tert*-butylphosphine with cobalt(II), nickel(II), or zinc(II) halides in 1-butanol results in the formation of the anionic complexes $((t\text{-Bu})_3PH)[(t\text{-Bu})_3PMX_3]$, instead of the expected neutral complexes of the

Table I. Analytical, Molecular, Weight, and Conductance Data for $(t\text{-}Bu_3PMX_2)$ Complexes

		Analytical data				Molecular weight data[a]		Conductance data		
		Calcd		Found						
Complex	Mp, °C	% C	% H	% C	% H	Found	Calcd for $(t\text{-}Bu_3PMX_2)_2$	Solvent	Concn × 10^3, M	Λ_M[d]
$(t\text{-}Bu)_3PZnCl_2$[b]	250	42.60	7.99	42.88	7.78	686	676	CH_2Cl_2	1.24	0.02
								CH_3CN	1.01	8.00
$(t\text{-}Bu)_3PZnBr_2$	225	33.72	6.32	33.84	6.82	861	854	CH_2Cl_2	1.19	5.30
								CH_3CN	1.054	21.12
$(t\text{-}Bu)_3PZnI_2$	230	27.64	5.18	27.32	5.32	1039	1042	CH_3CN	1.094	27.72
$(t\text{-}Bu)_3PCdCl_2$[c]	300	37.40	7.03	37.64	7.00	772	770	CH_3NO_2	1.04	6.56
$(t\text{-}Bu)_3PCdBr_2$	244	30.38	5.70	30.02	5.87	952	948	CH_2Cl_2	1.05	1.31
									1.25	8.39
$(t\text{-}Bu)_3PCdI_2$	252	35.35	4.75	35.38	4.66	1139	1136	CH_3CN	1.00	8.96
$(t\text{-}Bu)_3PCd(SCN)_2$	205	39.07	6.28	38.93	6.51	859	860	CH_3NO_2	1.09	3.55

[a] In 1,2-dichloroethane; concentration range 10^{-4} to 10^{-3} M. [b] % Cl: calcd, 21.01; found, 20.99. [c] % Cl: calcd, 18.44; found, 18.19. [d] In Ω^{-1} cm^2 mol^{-1}.

type $((t\text{-}Bu)_3P)_2MX_2$. Further investigations on the reactions of tri-*tert*-butylphosphine with zinc(II) halides showed that the formation of the anionic complexes in the previous work was due to the protonation of the phosphine by the solvent. Neutral tri-*tert*-butylphosphine complexes of zinc(II) and cadmium(II) have been isolated in the present work by using aprotic solvents. The preparation, structural characterization, and spectral studies on these complexes are reported herein.

Results and Discussion

Reaction of tri-*tert*-butylphosphine with anhydrous zinc(II) or cadmium(II) halides, in an aprotic solvent such as anhydrous ether or dichloromethane, afforded moisture-sensitive complexes of the empirical formula $(t\text{-}Bu)_3PMX_2$. Attempts to isolate complexes containing more than 1 mol of phosphine/mol of metal were not successful, and the unreacted phosphine was recovered unchanged. The reaction of the phosphine and zinc(II) iodide initially yielded a mixture of $(t\text{-}Bu)_3PZnI_2$ and $((t\text{-}Bu)_3PH)[(t\text{-}Bu)_3PZnI_3]$ from which pure $(t\text{-}Bu)_3PZnI_2$ was obtained by treatment with benzene. The reaction of the phosphine and cadmium(II) thiocyanate gave the complex $(t\text{-}Bu)_3PCd(SCN)_2$. However, the analogous zinc(II) complex could not be isolated; an impure anionic complex $((t\text{-}Bu)_3PH)[(t\text{-}Bu)_3PZn(SCN)_3]$ was obtained instead. The reaction of the phosphine and hydrated zinc(II) nitrate gave $((t\text{-}Bu)_3PH)_2[Zn(NO_3)_3OH]$. An impure 1:1 complex was obtained from the reaction of the phosphine with $Cd(OAc)_2(H_2O)_2$, but no reaction was observed when tri-*tert*-butylphosphine was allowed to react with $Zn(OAc)_2(H_2O)_2$.

The formation of only 1:1 complexes in the present work is in marked contrast with the behavior of less bulky phosphines such as triphenylphosphine[10] and tricyclohexylphosphine,[11] both of which form stable 2:1 complexes with both zinc(II) and cadmium(II). Although neutral 1:1 complexes of cadmium halides and tertiary phosphines are known,[12,13] analogous zinc(II) complexes have hitherto not been isolated. In the present work, the failure to isolate complexes containing more than 1 mol of tri-*tert*-butylphosphine/mol of metal is undoubtedly due to very large steric requirements of tri-*tert*-butylphosphine. Crystallographic data show that the Ni–P bond in the anion $(t\text{-}Bu)_3PNiBr_3^-$[8] is considerably longer than that in $Ph_3PNiI_3^-$.[14] The elongation of the Ni–P bond in $(t\text{-}Bu)_3PNiBr_3^-$ is clearly due to the inability of the bulky phosphine to approach within a normal bonding distance because of steric repulsion between the bromines and the *tert*-butyl groups. Tolman[1,15] has proposed the use of metal–ligand cone angles to measure the steric requirements of phosphorus ligands. The Ni–P(*t*-Bu)$_3$ cone angle in the anion $(t\text{-}Bu)_3PNiBr_3^-$ is found to be 180 ± 2°. The cone angles for triphenylphosphine and tricyclohexylphosphine have been reported[1,15] to be 145 and 170°, respectively.

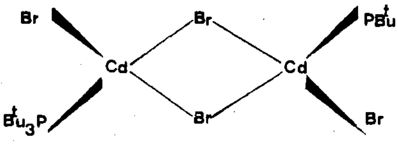

Figure 1. Structure of $[((t\text{-}Bu)_3P)CdBr_2]_2$.

Table II. Infrared and Raman Spectral Data[a] for $(t\text{-}Bu)_3PZnX_2$ Complexes

$(t\text{-}Bu)_3PZnCl_2$		$(t\text{-}Bu)_3PZnBr_2$		$(t\text{-}Bu)_3PZnI_2$		
IR	R	IR	R	IR	R	Assignment
	380 vw				386 vw	*b*
			374 w	376 vw	375 w	*b*
318 s	320 m					ν_t(Zn–Cl)
	294 s		295 vs	292 vw	294 vs	*b*
	272 sh		266 w		268 mw	*b*
	250 w					*b*
230 s						ν_b(Zn–Cl)
		225 s, b	232 m			ν_t(Zn–Br)
	206 m		203 m		204 m	*b*
				188 s	188 s	ν_t(Zn–I)
		179 s 167 s	185 s			}ν_b(Zn–Br)
				152 s	160 s	ν_b(Zn–I)
	152 w		137 s		116 vs	ν(Zn–P)
	114 vs		116 m			
	105 m		96 s		91 s	
	82 s		78 s			
	74 s		63 vs		60 vs	

[a] In cm^{-1} in the solid state. Description of abbreviations: IR, infrared; R, Raman; ν_t, terminal metal–halogen stretching frequency; ν_b, bridged metal–halogen stretching frequency; b, broad; m, medium; s, strong; sh, shoulder; v, very; w, weak. [b] Bands due to $(t\text{-}Bu)_3P$.

Structural Characterization and Spectral Studies. The melting points and analytical, conductance, and molecular weight data for the $(t\text{-}Bu)_3PMX_2$ complexes prepared in this work are recorded in Table I. The conductance data show that all the cadmium complexes as well as the zinc(II) chloride complex are nonelectrolytes in acetonitrile or nitromethane. The molar conductances for the complexes $(t\text{-}Bu)_3PZnBr_2$ and $(t\text{-}Bu)_3PZnI_2$ in acetonitrile are 21.12 and 28.82 Ω^{-1} cm^2 mol^{-1}, respectively. Since the molar conductances for the 1:2 electrolytes in acetonitrile occur in the range of 200–300 Ω^{-1} cm^2 mol^{-1}, the degree of ionization for the zinc(II) bromide and the zinc(II) iodide complexes is about 10%. The molecular weight data listed in Table I clearly show that all the $(t\text{-}Bu)_3PMX_2$ complexes exist as dimeric species in 1,2-dichloroethane. Previously reported 1:1 cadmium(II) complexes of tertiary phosphines have also been shown to be dimeric in solution.[12,13] A dimeric tetrahedral structure as shown in Figure 1 has been established for the complex Et_3PCdBr_2 by a preliminary crystallographic study.[12] A similar structure

Table III. Infrared and Raman Spectral Data[a] for $(t\text{-Bu})_3PCdX_2$ Complexes

$(t\text{-Bu})_3PCdCl_2$		$(t\text{-Bu})_3PCdBr_2$		$(t\text{-Bu})_3PCdI_2$		$(t\text{-Bu})_3PCd(SCN)_2$		
IR	R	IR	R	IR	R	IR	R	Assignment
388 vw		390 vw			383 sh	380 vw		*b*
374 vw			374 w		372 w			*b*
	296 s	298 vw	299 s	290 vw	296 vs		306 s	*b*
285 s	285 s							ν_t(Cd-Cl)
			270 w		270 w			*b*
	236 mw		248 vw		242 sh			}*b*
			228 vw		234 vw			
						210 m, b	198 s	ν_t(Cd-SCN)
208 s								ν_b(Cd-Cl)
	206 vw				202 vw			*b*
		198 s	200 vs					ν_t(Cd-Br)
				159 s	160 vs			ν_t(Cd-I)
		146 s	158 ms				158 s	ν_b(Cd-X)
					136 s			ν_b(Cd-I)
	128 ms		118 ms		104 s		131 s	ν(Cd-P)
	90 vs		84 s		82 s		100 m	
	66 m						80 m	

[a] In cm^{-1} in the solid state. Description of abbreviations: IR, infrared; R, Raman; ν_t, terminal Cd-X stretching frequency; ν_b, bridged Cd-X stretching frequency; m, medium; s, strong; sh, shoulder; v, very; w, weak. [b] Bands due to $(t\text{-Bu})_3P$.

Table IV. Metal-Halogen Stretching Frequency Ratios[a] for the Halide Complexes

Ratios	M = Zn	M = Cd
ν_t(M-Br)/ν_t(M-Cl)	0.71	0.70
ν_t(M-I)/ν_t(M-Cl)	0.59	0.56
ν_b(M-Cl)/ν_t(M-Cl)	0.72	0.73
ν_b(M-Br)/ν_t(M-Br)	0.76	0.76
ν_b(M-I)/ν_t(M-I)	0.83	0.85

[a] Description of abbreviations: ν_t(M-X), terminal metal-halogen stretching frequency; ν_b(M-X), bridged metal-halogen stretching frequency.

is indicated for the tri-*tert*-butylphosphine complexes of both zinc(II) and cadmium(II) on the basis of their infrared and Raman spectral studies, in the solid state.

The observed infrared and Raman spectral frequencies for the complexes, in the solid state, in the region below 400 cm^{-1}, together with their proposed assignments are given in Tables II and III. The basic features of the infrared and Raman spectra for the $(t\text{-Bu})_3PCdBr_2$ complex are shown in Figure 2. As shown by the data in Tables II and III, the infrared spectra for the complexes of zinc(II) and cadmium(II) halides show two strong bands below the 400-cm^{-1} region. Both of these bands progressively shift to lower frequencies as X is changed from Cl to Br to I. Thus, there can be little doubt that these bands are associated with the vibrations of the metal-halogen bonds. For each complex, the higher frequency is comparable to the metal-halogen antisymmetric stretching frequency reported[10] for the tetrahedral complexes $(Ph_3P)_2ZnX_2$ or $(Ph_3P)_2CdX_2$. The lower frequency in each case is markedly lower than the corresponding symmetric metal-halogen stretching frequency, but it is much higher than the metal-halogen bending frequency.[10,16] Therefore, the higher frequency band can be assigned to a stretching mode of the terminal metal-halogen bonds and the lower frequency band can be assigned to a stretching mode of the metal-halogen bridge bonds. As shown in Table IV, frequency ratios ν_t(M-Br)/ν_t(M-Cl) and ν_t(M-I)/ν_t(M-Cl) for the terminal metal-halogen frequencies for the zinc as well as for the cadmium complexes are in excellent agreement with the reported frequency ratios for the $(Ph_3P)_2ZnX_2$ and $(Ph_3P)CdX_2$ complexes. Little information is available in the literature on the bridged metal-halogen stretching frequencies for zinc or cadmium complexes. For the binuclear anion $Zn_2Cl_6^{2-}$, the infrared bands at 238 and 225 cm^{-1} have been assigned[13] to the bridged Zn-Cl stretching frequencies. The ratio[13,17] ν_b(M-X)/ν_t(M-X) for $Zn_2Cl_6^{2-}$, Al_2X_6, and the

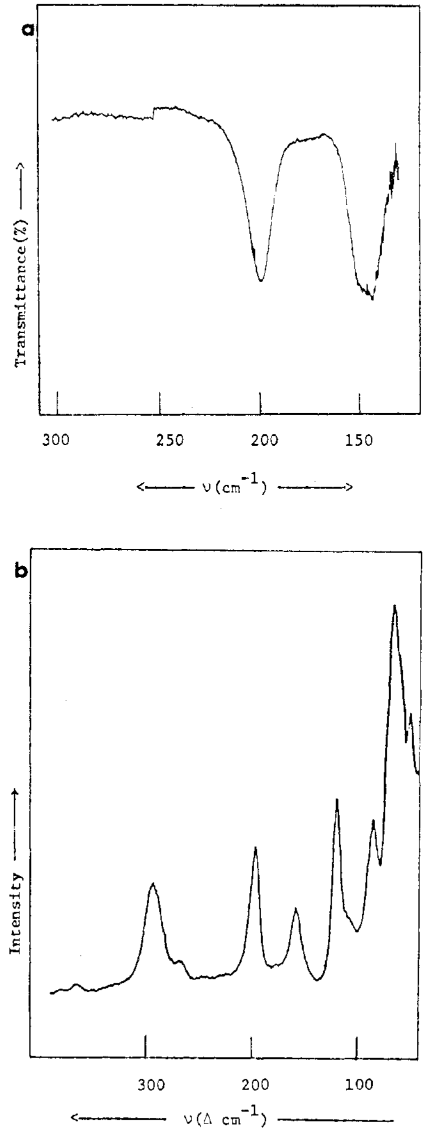

Figure 2. (a) Infrared spectrum of $((t\text{-Bu})_3P)CdBr_2$ in the solid state in the 300–130-cm^{-1} region. (b) Raman spectrum of $((t\text{-Bu})_3P)CdBr_2$ in the solid state in the region below 400 cm^{-1}.

dimeric square-planar complexes $M_2X_4L_2$ (where X = Cl, Br, or I; M = Pt or Pd; L = a tertiary phosphine) varies from 0.63

Table V. ^{1}H and ^{31}P NMR Data[a] for $(t\text{-Bu})_3PMX_2$ Complexes

	^{1}H NMR data[b]		^{31}P NMR data[c]			
Complex	δ, ppm	^3J(P-H), Hz	δ, ppm	$^1J(^{113}Cd-^{31}P)$, Hz	$^1J(^{111}Cd-^{31}P)$, Hz	$^1J(^{113}Cd-^{31}P)/{}^1J(^{111}Cd-^{31}P)$
$(t\text{-Bu})_3PZnCl_2$	1.61	13.5				
$(t\text{-Bu})_3PZnBr_2$	1.61	13.5				
$(t\text{-Bu})_3PZnI_2$	1.61	13.5				
$(t\text{-Bu})_3PCdCl_2$	1.58	14.0	66.343	2270	2168	1.0470
$(t\text{-Bu})_3PCdBr_2$	1.61	14.0	60.311	2095	2001	1.0469
$(t\text{-Bu})_3PCdI_2$	1.65	14.0	49.052	1840	1738	1.0561
$(t\text{-Bu})_3PCd(SCN)_2$	1.53	14.0	65.739	2226	2143	1.0387

[a] In CH_2Cl_2 at ambient temperature. [b] Downfield from Me_4Si internal standard; δ for free phosphine in CH_2Cl_2 is 1.30 ppm; ^3J(P-H) = 10.0 Hz. [c] Positive shifts are downfield from a H_3PO_4 external standard; δ for free phosphine in CH_2Cl_2 is 61.015 ppm.

to 0.83. As shown in Table IV, the $\nu_b(M-X)/\nu_t(M-X)$ ratios for the Bu_3PZnX_2 and the Bu_3PCdX_2 complexes are in the range of 0.72–0.85. Thus, the infrared data for the tri-*tert*-butylphosphine complexes of both zinc(II) and cadmium(II) halides clearly show that these complexes contain terminal as well as bridging metal–halogen bonds.

The structure shown in Figure 1 has a C_{2h} skeletal symmetry and according to group theory it should have only one infrared-active terminal M–X stretching mode and only one Raman-active terminal M–X stretching mode. As shown in Tables II and III, the Raman spectra for all the complexes show only one terminal metal–halogen stretching frequency. Thus, there can be little doubt that the halide complexes prepared in this work have a dimeric trans symmetric tetrahedral structure as shown in Figure 1. The Raman spectra for the bromide and the iodide complexes also show a medium to strong band which can be assigned to bridged metal–halogen stretching frequency. The failure to observe the bridged metal–chlorine stretching frequencies in the Raman spectra of $(t\text{-Bu})_3PZnCl_2$ and $(t\text{-Bu})_3PCdCl_2$ can be attributed to their low intensities.

The Raman spectra of all the complexes showed a medium to intense band which is not observed for the free ligand. For the zinc complexes the frequency of this band decreases from 152 to 137 to 116 cm^{-1} as X changes from chloride to bromide to iodide. A similar shift in the position of this band is observed for the cadmium(II) complexes. Since the Lewis acidity for the metal halides should decrease in the order Cl > Br > I, it is reasonable to assign this band to the zinc–phosphorus or cadmium–phosphorus stretching frequency. There are no reports on metal–phosphorus stretching frequencies for zinc(II) or cadmium(II) complexes except for the complexes $(R_3P)_2MX_2$[10,11] (R = phenyl or cyclohexyl), $Ph_3PZnX_3^-$,[18] and $(t\text{-Bu})_3PZnCl_3^-$.[9] Zinc–phosphorus stretching frequencies have been reported to occur in the range of 166–153 cm^{-1} for the triphenylphosphine[10] complexes and in the range of 208–168 cm^{-1} for the tricyclohexylphosphine[10] complexes. Cadmium–phosphorus stretching frequencies have been reported to be at ca. 135 cm^{-1} for the triphenylphosphine[10] complexes and in the 176–162-cm^{-1} region for the tricyclohexylphosphine[11] complexes. For the octahedral complexes[19] $(Me_3P)_2MCl_4$, where M = Si, Ge, or Sn, the symmetric M–P stretching frequency is reported to occur in the range of 158–145 cm^{-1} and for the trigonal-bipyramidal complex[20] $(Me_3P)_2InCl_3$ the symmetric In–P stretching mode has been reported to be at 135 cm^{-1}. Therefore we believe that the reported assignments[11] for the metal–phosphorus stretching frequencies for the tricyclohexylphosphine complexes of zinc and cadmium are erroneous and that the proposed assignments for the metal–phosphorus stretching frequencies for the $(t\text{-Bu})_3PMX_2$ complexes are in line with the reported metal–phosphorus frequencies for other non-transition-metal complexes.

The vibrational frequencies due to the internal vibrations of the SCN groups in $(t\text{-Bu})_3Pd(SCN)_2$ were observed at 2150 (sh), 2130 (s), 2060 (s), 750 (sh), and 450 (w) cm^{-1} in the infrared and at 2140 (s), 748 (m), 460 (m) and 452 (m) cm^{-1} in the Raman spectra. A comparison of these frequencies with the reported frequencies[21] for the internal vibration of the N-bonded, S-bonded, and the bridging SCN groups suggests the presence of both the terminal and bridging SCN groups in $(t\text{-Bu})_3PCd(SCN)_2$. For the N-bonded SCN, the CS stretching and the SCN bending frequencies usually occur in the 870–820- and 485–475-cm^{-1} regions, respectively. Thus, it is very unlikely that the terminal SCN groups in $(t\text{-Bu})_3PCd(SCN)_2$ are N bonded. The infrared and Raman frequencies for $(t\text{-Bu})_3PCd(SCN)_2$, in the region below 400 cm^{-1}, together with their assignments are listed in Table III. As shown in Table III, the very weak infrared band at 380 cm^{-1} is undoubtedly due to an internal vibration of the coordinated phosphine and the strong infrared band at 219 cm^{-1} can be assigned to the Cd–S stretching frequency of the terminal Cd–SCN bonds. Confirmation of this assignment is provided by the observation of a strong Raman band at 198 cm^{-1}. Another strong Raman band at 138 cm^{-1} can be assigned to a stretching mode due to the bridging Cd–SCN–Cd bonds. The very strong Raman band at 131 cm^{-1} is assigned to the Cd–P stretching frequency. Thus, the vibrational data for the $(t\text{-Bu})_3PCd(SCN)_2$ are also in accord with a dimeric structure.

The Raman spectra of all the $(t\text{-Bu})_3PMX_2$ complexes show one or more bands at ca. 100 cm^{-1} or below. Since Raman spectral data could not be obtained in solution, it is not possible to make clear-cut assignments for these bands.

The ^{1}H NMR spectra of all the complexes consisted of a single 1:1 doublet downfield from the doublet observed for free phosphine. The observed chemical shifts and ^3J(P–H) values are listed in Table V. ^{1}H NMR spectra of solutions of complexes to which some free phosphine had been added showed one doublet due to the coordinated phosphine and another doublet due to the free phosphine. From these results it is evident that the complexes do not undergo a fast phosphine exchange. Although NMR studies on phosphine complexes of zinc(II) are lacking, a ^{31}P NMR study on cadmium(II) iodide complexes of the type L_2CdI_2, where L = Me_2PhP, $MePh_2P$, Et_3P, Et_2PhP, and $EtPh_2P$, has been reported which shows that the phosphorus–cadmium coupling in these complexes occurs only at low temperatures (−40 °C and below). In contrast to these results, the ^{31}P NMR spectra of the $(t\text{-Bu})_3PCdX_2$ complexes, at ambient temperatures, showed satellite peaks due to the coupling of the phosphorus nucleus with the ^{111}Cd and ^{113}Cd nuclei. The ^{31}P chemical shifts and the phosphorus–cadmium coupling constants are included in Table V. As shown in Table V, the ratio $^1J(^{31}P-^{113}Cd)/{}^1J(^{31}P-^{111}Cd)$ is in good agreement with the theoretical value of 1.046. Thus the ^{31}P NMR data also show that the complexes prepared in the present work are not labile.

Another interesting feature of the ^{31}P NMR data in Table V is the marked dependence of ^1J(P–Cd) on X. The data in

Table V show clearly that the ^1J(P–Cd) values decrease in the order Cl $\sim$ SCN > Br > I. It may be recalled that the Cd–P stretching frequencies also vary in this order. The observed dependence of phosphorus–cadmium coupling constants on X thus provides further support for the proposed assignments for the metal–phosphorus stretching frequencies. Similar variations in phosphorus–mercury coupling constants[23,24] have been observed for phosphine and phosphite complexes of mercury(II) halides and pseudohalides, and these variations have been explained in terms of decreasing electronegativity of the halide or pseudohalide ligands. In the present work, the variation in the strength of the metal–phosphorus bond with X as indicated by NMR and vibrational spectral data can be due to electronic as well as steric effects. The acceptor properties of zinc(II) and cadmium(II) halides are expected to decrease in the order Cl > Br > I, but the steric interactions between the *tert*-butyl groups and the halogen would decrease in the order I > Br > Cl.

^{31}P NMR data for mercury(II) complexes[23,24] also show that phosphorus–mercury coupling constants for the dimeric 1:1 complexes $(R_3P)HgX_2$ are significantly larger than those for the monomeric 1:2 complexes $(R_3P)_2HgX_2$. Significantly larger phosphorus–cadmim coupling constants for the tri-*tert*-butylphosphine cadmium(II) complexes ($\sim$1800 Hz) as compared with those for the $(R_3P)_2CdI_2$ complexes ($\sim$1300 Hz) are thus consistent with the proposed dimeric structure for the tri-*tert*-butylphosphine complexes.

Experimental Section

Materials and Solvents. Tri-*tert*-butylphosphine was prepared as described previously.[9] Anhydrous zinc(II) thiocyanate, cadmium(II) thiocyanate, and cadmium(II) iodide were prepared by literature methods and were dried, under vacuum, before use. Other zinc or cadmium salts were reagent grade and were used without further purification. Diethyl ether, benzene, and petroleum ether were refluxed over sodium wire and subsequently distilled. Acetone, dichloromethane, and 1,2-dichloromethane were dried by refluxing over calcium hydride and subsequent distillation. Acetonitrile was treated with phosphorus pentoxide and distilled over potassium carbonate. Nitromethane was stored over molecular sieves and was distilled before use.

General Procedures. All operations involved in the preparation, purification, and subsequent handling of the tri-*tert*-butylphosphine complexes were carried out either in a drybox under an atmosphere of oxygen-free dry nitrogen or under vacuum. Elemental analyses were performed by M-H-W Laboratories, Garden City, Mich., and by Galbraith Laboratories, Knoxville, Tenn. Melting points, conductance, and infrared, Raman, and ^{1}H NMR spectra were measured as reported previously.[9] Molecular weights were determined with a Hitachi Perkin-Elmer 115 osmometer. ^{31}P NMR spectra were obtained at ambient temperatures on a Bruker HFX-60 Fourier transform spectrometer.

Preparation of Tri-*tert*-butylphosphine Complexes of Zinc(II) and Cadmium(II) Halides. A white precipitate was formed when an ethereal solution of tri-*tert*-butylphosphine (2.40 mmol in 10 mL of diethyl ether) was added with constant stirring to a solution of the metal halide (1.2 mmol) in 20 mL of diethyl ether. The mixture was stirred for 2 h after which the precipitated complex $(t\text{-Bu})_3PMX_2$ was filtered off, washed with ether, and recrystallized from dichloromethane. The filtrate was concentrated under vacuum to give a viscous liquid which was found to be unreacted tri-*tert*-butylphosphine as shown by its NMR spectrum (δ = 1.30 ppm, ^3J(P–H) = 10.0 Hz). The product obtained from the reaction of tri-*tert*-butylphosphine and zinc(II) iodide was a mixture as indicated by its ^{1}H NMR spectrum. It was treated with benzene which dissolved 75% of the product. The insoluble fraction was filtered off, washed with benzene, and dried under vacuum. It was shown to be pure $(t\text{-Bu})_3PZnI_2$ by the analytical and spectral data. Upon adding petroleum ether to the benzene solution a white precipitate was obtained which was characterized to be $((t\text{-Bu})_3H)[(t\text{-Bu})_3PZnI_3]$ by elemental analysis and by spectral and conductance data. Its ^{1}H NMR spectrum in dichloromethane showed two doublets (δ = 1.67 ppm, ^3J(P–H) = 13.0 Hz; δ = 1.75 ppm, ^3J(P–H) = 15.5 Hz) and its infrared spectrum showed characteristic bands due to the P–H stretching and bending frequencies at 2378 and 875 cm^{-1}, respectively. The molar conductance of a 10^{-3} M solution of $((t\text{-Bu})_3PH)[(t\text{-Bu})_3PZnI_3]$ in acetonitrile was 127 Ω^{-1} cm^2 mol^{-1}.

Preparation of Tri-*tert*-butylphosphine Complexes of Zinc(II) and Cadmium(II) Thiocyanates. A solution of tri-*tert*-butylphosphine (1.20 mmol) in 10 mL of dichloromethane was added with stirring to a slurry of zinc(II) or cadmium(II) thiocyanate (1.01 mmol) in 20 mL of dichloromethane. After 2 h of stirring, a clear solution was obtained. Upon addition of petroleum ether to the solution a white precipitate was formed which was filtered off and recrystallized from dichloromethane. The product of the reaction of $(t\text{-Bu})_3P$ and $Zn(SCN)_2$ was indicated to be a mixture of $((t\text{-Bu})_3PH)[(t\text{-Bu})_3PZn(SCN)_3]$ and $(t\text{-Bu})_3PZn(SCN)_2$. Its infrared spectrum contained bands at 2400 and 890 cm^{-1} similar to those observed for $((t\text{-Bu})_3PH)[(t\text{-Bu})_3PZnI_3]$. The ^{1}H NMR spectrum showed doublets at 1.70 ppm (^3J(P–H) = 15.5 Hz) and at 1.55 ppm (^3J(P–H) = 13.0 Hz). Attempts to isolate pure $(t\text{-Bu})_3PZn(SCN)_2$ were not successful. The product from the reaction of $(t\text{-Bu})_3P$ and $Cd(SCN)_2$ was characterized to be pure $(t\text{-Bu})_3PCd(SCN)_2$.

Attempted Preparations of Complexes of Other Zinc(II) and Cadmium(II) Salts. No reaction occurred when $Zn(OAc)_2(H_2O)_2$ (1 mol) and $(t\text{-Bu})_3P$ (2 mmol) were stirred in 25 mL of acetonitrile or benzene for 8 h. Under similar conditions, $Zn(NO_3)_2(H_2O)_6$ and $(t\text{-Bu})_3P$ reacted to give $((t\text{-Bu})_3PH)_2[Zn(NO_3)_3OH]$ as shown by the analytical and spectral data. When a mixture of $Cd(OAc)_2(H_2O)_2$ (1 mol) and $(t\text{-Bu})_3$ (2 mmol) in 25 mL of benzene was stirred for 2 h, a clear solution was formed. Upon adding petroleum ether, a white solid was precipitated which was filtered off and recrystallized from benzene. The filtrate was found to contain some unreacted phosphine. The ^{1}H NMR spectrum of the solid product showed a doublet at 1.51 ppm (^3J(P–H) = 13.5 Hz) and a singlet at 1.96 ppm. However, the analytical data of the solid showed it to be an impure product.

Acknowledgment. Thanks are due to the National Research Council of Canada for financial assistance.

Registry No. $(t\text{-Bu})_3PZnCl_2$, 62882-82-0; $(t\text{-Bu})_3PZnBr_2$, 62882-81-9; $(t\text{-Bu})_3PZnI_2$, 62882-80-8; $(t\text{-Bu})_3PCdCl_2$, 62882-79-5; $(t\text{-Bu})_3PCdBr_2$, 62882-78-4; $(t\text{-Bu})_3PCdI_2$, 62882-77-3; $(t\text{-Bu})_3PCd(SCN)_2$, 62882-72-8; $((t\text{-Bu})_3PH)[(t\text{-Bu})_3PZnI_3]$, 62882-71-7; $((t\text{-Bu})_3PH)[(t\text{-Bu})_3PZn(SCN)_3]$, 62882-69-3; $(t\text{-Bu})_3PZn(SCN)_2$, 62882-67-1.

References and Notes

(1) C. A. Tolman, *Chem. Rev.*, **77**, 313 (1977).
(2) R. Mason, M. Textor, N. Al-Salem, and B. L. Shaw, *J. Chem. Soc., Chem. Commun.*, 292 (1976).
(3) A. J. Cheney and B. L. Shaw, *J. Chem. Soc., Dalton Trans.*, 860 (1972).
(4) A. J. Cheney, B. E. Mann, B. L. Shaw, and R. M. Slade, *J. Chem. Soc. A*, 3833 (1971).
(5) A. Immirzi, A. Musco, P. Zambelli, and G. Carturan, *Inorg. Chim. Acta*, **13**, L13 (1975).
(6) A. Immirzi and Z. Musco, *J. Chem. Soc., Chem. Commun.*, 400 (1974).
(7) A. Matsumoto, H. Yoshiska, K. Nakatsu, T. Yoshida, and S. Otsuka, *J. Am. Chem. Soc.*, **96**, 3323 (1974).
(8) E. C. Alyea, A. Costin, G. Ferguson, G. T. Fey, R. G. Goel, and R. J. Restivo, *J. Chem. Soc., Dalton Trans.*, 1294 (1975).
(9) E. C. Alyea, G. T. Fey, and R. G. Goel, *J. Coord. Chem.*, **5**, 143 (1976).
(10) G. B. Deacon, J. H. S. Green, and D. J. Harrison, *Spectrochim. Acta, Part A*, **24a**, 1921 (1968).
(11) F. G. Moers and J. P. Langhout, *Recl. Trav. Chim. Pays-Bas*, **92**, 996 (1973).
(12) R. C. Evans, F. G. Mann, H. S. Peiser, and D. Purdie, *J. Chem. Soc.*, 1209 (1940).
(13) G. E. Coates and D. Ridley, *J. Chem. Soc.*, 166 (1964).
(14) R. P. Taylor, D. H. Templeton, A. Zalkin, and W. De. W. Horrocks, Jr., *Inorg. Chem.*, **7**, 2629 (1968).
(15) C. A. Tolman, *J. Am. Chem. Soc.*, **92**, 2956 (1970).
(16) Y. Saito, M. Cordes, and K. Nakamoto, *Spectrochim. Acta, Part A*, **28a**, 1459 (1972).
(17) J. R. Ferraro, "Low Frequency Vibrations of Inorganic and Coordination Compounds", Plenum Press, New York, N.Y., 1971, p 177.
(18) J. Bradbury, K. P. Forest, P. H. Nuttall, and D. W. A. Sharp, *Spectrochim. Acta, Part A*, **23a**, 2702 (1967).
(19) I. R. Beattie and G. A. Ozin, *J. Chem. Soc. A*, 370 (1970).
(20) G. A. Ozin, *J. Chem. Soc. A*, 1307 (1970).
(21) A. H. Norbury, *Adv. Inorg. Chem. Radiochem.*, **17**, 23 (1975), and references therein.
(22) B. E. Mann, *Inorg. Nucl. Chem. Lett.*, **7**, 595 (1971).
(23) A. Yamasaki and E. Fluck, *Z. Anorg. Allg. Chem.*, **306**, 297 (1973).
(24) S. O. Grim, P. J. Lui, and R. L. Keiter, *Inorg. Chem.*, **13**, 342 (1974).