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Phosphorus-31 and Cadmium-113 NMR Studies of Some Cadmium(II) Complexes Containing Tricyclohexylphosphine and Tributylphosphine

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Abstract

Phosphorus-31 and cadmium-113 NMR spectroscopy has been used to study the interaction between tertiary phosphines ($P(c\text{-}C_6H_{11})_3$ and PBu_3) and $Cd(O_3SCF_3)_2$, $Cd(ClO_4)_2$, $Cd(CF_3COO)_2$ and $Cd(SCN)_2$ salts in solution. The NMR data imply the formation in solution of novel 1:1 adducts CdX_2(phos) (X = O_3SCF_3, ClO_4, CF_3COO, phos = $P(c\text{-}C_6H_{11})_3$, PBu_3) in which there is substantial interaction between the anions and cadmium. Data are also presented for mixed phosphine complexes $CdX_2[P(c\text{-}C_6H_{11})_3][PBu_3]$ (X = O_3SCF_3, ClO_4, NO_3, CF_3COO, CH_3COO, Cl, Br, I, SCN). The two bond coupling constants $^2J(P'-P)$ of these mixed phosphine complexes decrease as the coordination ability of the anion increases and cover the narrow range from 95 Hz to 66 Hz.

Introduction

Phosphorus-31 and cadmium-113 NMR measurements have been used previously to investigate phosphine complexes of cadmium(II) in solution [1, 4]. These studies have shown the sensitivity of one bond cadmium–phosphorus couplings, $^1J(Cd-P)$, and cadmium-113 chemical shifts, $\delta(^{113}Cd)$, to structural changes about the metal resulting from variation of the number of coordinated phosphines and involvement of anion in coordination to cadmium, in a fashion similar to that observed for analogous mercury(II) complexes [2, 3].

There are still few literature values for two bond phosphorus–phosphorus coupling through a metal atom. These couplings should reflect the nature of the phosphorus–metal bond and possibly the geometry about the metal atom. Recently $^2J(P'-P)$ coupling constants were reported for a series of mercury(II) complexes $HgX_2[P(c\text{-}C_6H_{11})_3][PBu_3]$ (X = O_3SCF_3, ClO_4, NO_3, CF_3COO, CH_3COO, Cl, Br, I, SCN) in dichloromethane solution [5]. The magnitude of the two bond coupling constants $^2J(P'-P)$ of these asymmetric complexes reflect changes in stereochemistry caused by the various coordination abilities of the anions. Phosphorus-31 and cadmium-113 NMR parameters are now reported for adduct formation between the phosphines PBu_3 and $P(c\text{-}C_6H_{11})_3$ with the cadmium salts $Cd(O_3SCF_3)_2$, $Cd(ClO_4)_2$, $Cd(CF_3COO)_2$ and $Cd(SCN)_2$ in a variety of solvents. Data are also presented for the formation of a series of mixed-phosphine adducts $CdX_2[P(c\text{-}C_6H_{11})_3][PBu_3]$ (X = ClO_4, O_3SCF_3, NO_3, CF_3COO, CH_3COO, Cl, Br, I, SCN).

Results and Discussion

The phosphorus-31 and cadmium-113 spectra of methanol solutions containing equimolar quantities of $Cd(O_3SCF_3)_2(DMSO)_6$ and either tributylphosphine, PBu_3, or tricyclohexylphosphine, $P(c\text{-}C_6H_{11})_3$, are consistent with the formation of 1:1 adducts. In each case cooling is required to establish cadmium–phosphorus coupling and at these low temperatures each phosphorus-31 spectrum contains a single resonance accompanied by cadmium-111 and cadmium-113 satellites. Each cadmium-113 spectrum comprises a doublet with the coupling constant, $J(Cd-P)$, equal to that derived from the corresponding phosphorus-31 spectrum. An equimolar mixture of $Cd(O_3SCF_3)_2(DMSO)_6$ and PBu_3 is not completely soluble in dichloromethane solution. The phosphorus-31 spectrum of this mixture at –70 °C shows three resonances accompanied by cadmium-111 and cadmium-113 satellites whilst the cadmium-113 spectrum contains a doublet, a triplet and a quartet. These results are consistent with the formation of 1:1, 1:2 and 1:3 adducts between $Cd(O_3SCF_3)_2$ and PBu_3 with the 1:3 species being present in the highest concentration. The position of the equilibrium is obviously affected by the poor solubility of this system in dichloromethane. Similarly, an equimolar mixture of $Cd(O_3SCF_3)_2(DMSO)_6$ and $P(c\text{-}C_6H_{11})_3$ is poorly soluble in dichloromethane solution. The phosphorus-31 and cadmium-113 spectra of this solution show the presence of both 1:1 and 1:2 adducts.

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TABLE I. NMR Parameters for Adducts of PBu_3 and $P(c\text{-}C_6H_{11})_3$ with Various Cadmium(II) Salts.

Species	Solvent	$\delta(^{31}P)$ (ppm)	$\delta(^{113}Cd)^a$ (ppm)	$J(^{113}Cd-P)$ (Hz)	Temperature (°C)
$Cd(O_3SCF_3)_2[P(c\text{-}C_6H_{11})_3]_n$					
n = 1	DCM	20.1	160(d)	2540	−70
	MeOH	20.6	150(d)	2580	−60
	acetone	18.9	160(d)	2500	−50
n = 2	DCM	23.4	357(6)	2180	−60
	MeOH	23.0	352(t)	2170	−60
	acetone	23.5	354(t)	2145	−50
$Cd(O_3SCF_3)_2(PBu_3)_n$					
n = 1	DCM	−13.7	167(d)	2630	−70
	MeOH	−13.4	155(d)	2730	−70
	acetone	−14.1	167(d)	2610	−50
n = 2	DCM	−6.2	379(t)	2250	−60
	MeOH	−6.7	385(t)	2270	−70
	acetone	−6.5	371(t)	2250	−50
n = 3	DCM	−10.5	505(t)	1730	−60
	MeOH	−10.3	507(t)	1720	−70
	acetone	−10.0	509(t)	1690	−50
$Cd(ClO_4)_2[P(c\text{-}C_6H_{11})_3]_n$					
n = 1	DCM	Not soluble			
	MeOH	22.6	156(d)	2680	−70
	acetone	25.7	170(d)	2800	−70
n = 2	DCM	28.1	397(t)	2240	−70
	MeOH	32.8	430(t)	2140	−60
	acetone	30.3	402(t)	2160	−50
$Cd(ClO_4)_2(PBu_3)_n$					
n = 1	DCM	Not soluble			
	MeOH	−11.2	163(d)	2960	−60
	acetone	−10.4	160(d)	2960	−50
n = 2	DCM	−4.6	354(t)	2500	−70
	MeOH	−5.1	361(t)	2480	−50
	acetone	−4.4	363(t)	2450	−50
n = 3	DCM	−8.7	506(q)	1700	−80
	MeOH	−8.6	493(q)	1690	−50
	acetone	−8.4	520(q)	1680	−50
$Cd(CF_3COO)_2[P(c\text{-}C_6H_{11})_3]_n$					
n = 1	DCM	26.5	not found	2720	−60
	MeOH	22.4	181(d)	2650	−70
n = 2	DCM	24.9	428(t)	2000	−70
	MeOH	25.3	not found	2050	−70
$Cd(CF_3COO)_2(PBu_3)_n$					
n = 1	DCM	−11.2	194(d)	2670	−70
	MeOH	−13.0	170(d)	2690	−70
n = 2	DCM	−7.6	431(t)	2080	−70
	MeOH	−7.5	386(t)	2180	−70

(continued on facing page)

TABLE I. *(continued)*

Species	Solvent	$\delta(^{31}P)$ (ppm)	$\delta(^{113}Cd)^a$ (ppm)	$J(^{113}Cd-P)$ (Hz)	Temperature (°C)
n = 3	DCM	−12.9	485(q)	1720	−70
	MeOH	−11.9	486(q)	1700	−70
$Cd(SCN)_2[P(c\text{-}C_6H_{11})]_n$					
n = 2	DCM	26.5	549(t)	1845	−70
	acetone	26.4	not found	1830	−70
$Cd(SCN)_2(PBu_3)_n$					
n = 1	DCM	Not soluble			
	MeOH	−14.0	313(d)	2250	−70
n = 2	DCM	Not soluble			
	MeOH	−8.7	523(t)	2000	−70
	acetone	−9.1	503(t)	2010	−70
n = 3	DCM	−12.4	538(q)	1685	−100
	MeOH	−11.7	544(q)	1670	−70
	acetone	−12.4	534(q)	1690	−70

[a] (d) = doublet, (t) = triplet, (q) = quartet.

The two phosphines also react similarly with cadmium(II)perchlorate, each giving 1:1 adducts in methanol solution. Subsequently all of the 1:1 adducts were studied in a range of solvents in order to determine the importance of solvent effects on the stabilisation of 1:1 adducts. These results (Table I) show comparative minor changes with variation of solvent and imply that these solvents are not significantly involved in first-shell coordination to cadmium. In fact the changes in NMR parameters associated with variation of solvent are appreciably smaller than changes associated with variation of the counter ion in a series of cadmium salts in aqueous solution [6, 7].

The coupling constants, *J*(Cd–P), and cadmium-113 chemical shifts for the 1:1 adducts $Cd(O_3SCF_3)_2(phos)$ and $Cd(ClO_4)_2(phos)$ (where phos = PBu_3, $P(c\text{-}C_6H_{11})_3$) are similar to values observed for the analogous 1:1 adducts of $Cd(NO_3)_2$ with the same phosphines [4]. Involvement of the nitrate and acetate in coordination to cadmium has been shown to be significant in solution for the 1:1 adducts $Cd(NO_3)_2(phos)$ and $Cd(OOCCH_3)_2(phos)$ with acetate being more strongly involved than nitrate [4]. The present results imply that in solution perchlorate and trifluoromethylsulphonate interact differently with cadmium in these 1:1 adducts, the degree of interaction being somewhere between that observed for nitrate and acetate. It may be that these differences result from varying degrees of ion pair formation because of the different solvation spheres of each of the two anions. Such differences in ion pair formation might result in different amounts of effective electron density being conferred to the cadmium atom via dipolar interactions and hence explain the different NMR parameters observed for the perchlorate and trifluoromethylsulphonate adducts. Alternatively, it is more likely that perchlorate is actually coordinated to cadmium in solution.

The 1:1 adducts $Cd(O_3SCF_3)_2(phos)$ and $Cd(ClO_4)_2(phos)$ react in solution with further phosphine to give corresponding 1:2 adducts. The reacions are not quantitative. The coupling constants J(Cd–P) decrease and the cadmium-113 chemical shifts move to higher frequency with the addition of a second phosphine molecule. Somewhat surprisingly, addition of a second molecule of phosphine is accompanied by phosphorus-31 chemical shifts moving to higher frequency. Similar shifts of phosphorus-31 resonances to higher frequency have been observed in the formation of 1:2 adducts of mercury(II)phosphite complexes [11], mercury(II)-phosphine complexes [3] and some other cadmium(II)phosphine complexes [4] from the 1:1 adducts and imply that in all these cases the anion is involved in coordination in substantially different manners in the 1:1 and 1:2 adducts.

The NMR parameters for the 1:2 adducts $Cd(O_3SCF_3)_2(phos)_2$ and $Cd(ClO_4)_2(phos)_2$ are again significantly different for the two anions and suggest that the trifluoromethylsulphonate and perchlorate are involved in different degrees of coordination to cadmium. Infrared measurements on the 1:2 adduct with triphenylphosphine, $Cd(ClO_4)_2[P(C_6H_5)_3]_2$, suggest that the perchlorate ions act as bidentate ligands and that the complex contains octahedrally coordinated cadmium in the solid state as well as in dichloromethane solution [12]. Likewise the structures of $Cd(NO_3)_2[P(C_6H_5)_3]_2$ and $Cd(CF_3COO)_2[P(C_6H_5)_3]_2$ do not seem to be altered in going from solid state to solution but here the actual bonding mode of the anions is not as clearly defined as for the perchlorate analogue [12]. Therefore it seems reasonable to propose that the observed differences in NMR parameters for 1:2 phosphine adducts involving $Cd(ClO_4)_2$ and $Cd(O_3SCF_3)_2$ are due to perchlorate being substantially coordinated to cadmium in solution with the trifluoromethylsulphonate showing little or no interaction to cadmium. We have so far been unable to isolate solid samples of either $Cd(ClO_4)_2$(phos) or $Cd(O_3SCF_3)_2$(phos). It is interesting to note that there is no evidence for the formation of 1:1 adducts with these phosphines and either $Hg(O_3SCF_3)_2$ or $Hg(ClO_4)_2$ [5] although a 1:1 adduct of $Hg(ClO_4)_2$ with triphenylphosphine has been reported [10].

The 1:2 adducts involving $P(c\text{-}C_6H_{11})_3$ do not undergo any further reaction in solution with additional quantities of $P(c\text{-}C_6H_{11})_3$, presumably because of the large cone angle of the phosphine. However, addition of further PBu_3 to 1:2 adducts $Cd(O_3SCF_3)_2(PBu_3)_2$ and $Cd(ClO_4)_2(PBu_3)_2$ leads to the formation of the analogous 1:3 adducts in solution. The NMR parameters for the 1:3 adducts $Cd(O_3SCF_3)_2(PBu_3)_3$ and $Cd(ClO_4)_2(PBu_3)_3$ are very similar (Table I) probably because neither trifluoromethylsulphonate nor perchlorate are any longer involved in coordination to cadmium in these adducts.

Both phosphines react with $Cd(CF_3COO)_2$ in methanol to give 1:1 and 1:2 adducts. Only the 1:2 adduct $Cd(CF_3COO)_2(PBu_3)_2$ reacts with further phosphine in solution to give a 1:3 adduct, $Cd(CF_3COO)_2(PBu_3)_3$. This behaviour is different to reaction of PBu_3 with $Cd(CH_3COO)_2$ where, under similar conditions, a maximum of two phosphine molecules coordinate in solution [4]. This observation implies that the trifluoroacetate anion is less strongly coordinated to cadmium than acetate. A comparison of the NMR parameters for $Cd(CF_3COO)_2(PBu_3)_3$ with those for $Cd(ClO_4)_2(PBu_3)_3$ or $Cd(O_3SCF_3)_2(PBu_3)_3$, suggests that the trifluoroacetate anion is more strongly coordinated than either perchlorate or trifluoromethylsulphonate.

Reactions of cadmium(II)thiocyanate with a variety of tertiary phosphines give isolable 1:1 adducts which are poorly soluble, probably because of the polymeric structure of these compounds [16]. Attempts to prepare adducts containing more than one mole equivalent of phosphine resulted only in mixtures containing the 1:1 adduct and unreacted phosphine [16]. We have also found that equimolar equivalents of $Cd(SCN)_2$ and $P(c\text{-}C_6H_{11})_3$ are insufficiently soluble to record NMR spectra. However a dichloromethane solution containing $Cd(SCN)_2$ and $P(c\text{-}C_6H_{11})_3$ (1:2) is more soluble and the phosphorus-31 spectrum of this solution shows a single resonance with coupling to cadmium-111 and cadmium-113 at −70 °C. The cadmium-113 shows a triplet confirming that, in solution, two phosphines are in fact coordinated to cadmium.

Tributylphosphine adducts are more soluble and the phosphorus-31 spectrum of an equimolar solution of $Cd(SCN)_2$ and PBu_3 in methanol shows two resonances each accompanied by cadmium satellites. The corresponding cadmium-113 spectrum, at −70 °C, shows a triplet, a doublet and a singlet which is consistent with an equilibrium mixture of 1:2 and 1:1 adducts together with unreacted $Cd(SCN)_2$. The addition of further quantities of PBu_3 to this solution results in the disappearance of the singlet and doublet from the cadmium-113 spectrum and the appearance of a quartet. The cadmium-113 spectrum of a solution containing $Cd(SCN)_2$ and PBu_3 in the ratio 1:5 shows only the quartet due to the 1:3 adduct $Cd(SCN)_2(PBu_3)_3$.

The phosphorus-31 and cadmium-113 spectra of a methanol solution containing equimolar quantities of CdX_2, $P(c\text{-}C_6H_{11})_3$ and PBu_3 (X = Cl, Br, I, SCN) show the presence of $CdX_2[P(c\text{-}C_6H_{11})_3]_2$, $CdX_2(PBu_3)_2$ and the mixed phosphine complex $CdX_2[P(c\text{-}C_6H_{11})_3][PBu_3]$ in approximate statistical distributions. Similarly, solutions containing equimolar quantities of $CdX_2[P(c\text{-}C_6H_{11})_3]_2$ and $CdX_2(PBu_3)_2$ (X = NO_3, CH_3COO, CF_3COO) lead to the formation of mixed phosphine species but in these cases significant amounts of 1:1 adducts CdX_2(phos) were also observed. The mixed species $Cd(O_3SCF_3)_2[P(c\text{-}C_6H_{11})_3][PBu_3]$ was formed by mixing equimolar quantities of $Cd(O_3SCF_3)_2(DMSO)_6$ [13], $P(c\text{-}C_6H_{11})_3$ and PBu_3. The mixed species $Cd(ClO_4)_2[P(c\text{-}C_6H_{11})_3][PBu_3]$ was observed in an equimolar mixture of $Cd(ClO_4)_2(PBu_3)_2$ and $Cd(ClO_4)_2[P(c\text{-}C_6H_{11})_3]_2$. The mixed phosphine species were not isolable. With the exception of the mixture involving the iodine anion, cooling is required to slow phosphine exchange sufficiently to observe cadmium-111 and cadmium-113 satellites in the phosphorus-31 spectra.

The phosphorus-31 spectrum of each of the mixtures studied comprises two singlets (each with cadmium-111 and cadmium-113 satellites) due to $CdX_2[P(c\text{-}C_6H_{11})_3]_2$ and $CdX_2(PBu_3)_2$ as well as an ABX spectrum due to the mixed-phosphine species $CdX_2[P(c\text{-}C_6H_{11})_3][PBu_3]$. The ABX spectrum was adequately solved by a simple first order treatment. The corresponding cadmium-113 spectra each contain two triplets due to $CdX_2[P(c\text{-}C_6H_{11})_3]_2$ and $CdX_2[PBu_3]_2$ as well as a doublet of doublets arising from the $CdX_2[P(c\text{-}C_6H_{11})_3][PBu_3]$ species. Analysis of these spectra give the results presented in Table II.

The data in Table II show that the cadmium-113 chemical shifts generally move to higher frequency with increasing donor ability of the anion, X. These shifts are accompanied by decreases in ^1J(Cd–P) values. Although there is a paucity of crystal struc-

TABLE II. NMR Parameters for $CdX_2P'P$ (where $P' = P(c\text{-}C_6H_{11})_3$, $P = PBu_3$) in Dichloromethane Solution.

X	$\delta(^{31}P')$ (ppm)	$\delta(^{31}P)$ (ppm)	$J(P'-P)$ (Hz)	$J(Cd-P')$ (Hz)	$J(Cd-P)$ (Hz)	$\delta(^{113}Cd)$ (ppm)	Temp. (°C)
O_3SCF_3	27.6	−10.1	85	2250	2200	383	−80
ClO_4	30.5	−5.0	95	2360	2360	367	−70
NO_3	29.2	−6.5	83	2220	2180	356	−70
CF_3COO	28.5	−8.2	85	2060	2060	452	−70
CH_3COO	25.2	−10.5	87	1990	1925	411	−70
Cl	25.7	−11.7	85	1780	1650	656	−70
Br	19.3	−16.9	77	1480	1630	623	−40
I	10.5	−25.6	66	1460	1280	537	0
SCN	29.5	−8.8	81	1940	1930	540	−70

ture data for appropriate solid state complexes these changes would appear to reflect changes in effective geometry about cadmium, probably going from approximately linear when $X = O_3SCF_3$, to approximately tetrahedral when X = halide. These observations are similar to earlier reports for analogous mercury phosphine complexes [5, 14, 15], correlating decreasing one bond mercury–phosphorus coupling with decreasing P–Hg–P angles. It would seem reasonable that a similar correlation exists for the cadmium complexes. Furthermore such a correlation also appears to hold true for two bond couplings, $^2J(P-P')$ which also decrease as the donor ability of the anion increases although the $^2J(P-P')$ values cover only the narrow range 95 Hz to 66 Hz.

Experimental

Nuclear Magnetic Resonance Spectrometry

All NMR spectra were recorded on a JEOL FX-100 spectrometer, phosphorus-31 at 40.26 MHz and cadmium-113 at 22.04 MHz using external ^7Li lock. Phosphorus-31 spectra were referenced against external 85% H_3PO_4 and cadmium-113 against external 4.5 M cadmium nitrate in water. A JEOL NM 5471 controller was used for temperature control.

Preparations

Tributylphosphine, PBu_3 and tricyclohexylphosphine, $P(c\text{-}C_6H_{11})_3$, were purchased from Strem Chemicals Inc., Newburyport, Mass., U.S.A. and used without further purification. Preparation of phosphine complexes of cadmium was as previously described [1–4, 13].

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