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Synthesis, crystal and molecular structures of pyridine adducts of the zinc and cadmium bis-1,2,4-triphospholyl complexes $[M(\eta^1\text{-}P_3C_2^tBu_2)_2(NC_5H_5)_n]$ ($M = Zn$, $n = 2$; $M = Cd$, $n = 3$)

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Abstract

The reaction between zinc or cadmium dichloride and the triphospholyl anion $P_3C_2^tBu_2^-$ in each case leads to highly insoluble orange compounds, the structures of which are believed to be polymeric. Subsequent treatment with pyridine leads to the monomeric complexes $[M(\eta^1\text{-}P_3C_2^tBu_2)_2(NC_5H_5)_n]$ ($M = Zn$, $n = 2$; $M = Cd$, $n = 3$). Both complexes, which are fluxional in solution even at low temperature, have been fully characterised by multinuclear NMR spectroscopy and single crystal X-ray diffraction studies. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Triphospholyl; Cd NMR; Complexes; Zinc; Cadmium; Fluxional

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1. Introduction

A rich new area of organometallic chemistry has been recently developed in which phosphorus atoms replace CH-fragments in the more familiar unsaturated organic ligands. There is now an extensive range of phospha-organometallic compounds containing phospha-alkynes, phospha-alkenes, phospha-dienes, phospha-allyls, phospha-cyclobutadienes, phospha-cyclopentadienyls and phospha-arenes as well as tetraphosphacubanes and tetraphospha-barrelenes. The area has recently been comprehensively reviewed [1–12].

Cyclopentadienyl ring anions in which one or more CR units are replaced by phosphorus atoms have been the most extensively studied, in particular the 1,3-di- and 1,2,4-triphospholyl anions, $P_2C_3^tBu_3^-$ and $P_3C_2^tBu_2^-$. Both rings can exhibit η^5-ligation through their delocalised 6π aromatic systems and hence parallel the well-known cyclopentadienyl ligand in the formation of metallocene-like sandwich compounds. A wide range of such polyphospholyl compounds have been reported typified by the tetra-phosphametallocenes $[M(\eta^5\text{-}P_2C_3^tBu_3)_2]$ ($M = Sc$, Fe, Ni, Pd, Pt, Yb), penta-phosphametallocenes $[M'(\eta^5\text{-}P_3C_2^tBu_2)(\eta^5\text{-}P_2C_3^tBu_3)]$ ($M' = V$, Cr, Fe, Ru), $[M''(\eta^5\text{-}P_3C_2^tBu_2)(\eta^3\text{-}P_2C_3^tBu_3)]$ ($M'' = Ni$) and the hexa-phosphametallocenes $[M'''(\eta^5\text{-}P_3C_2^tBu_2)_2]$ ($M''' =$ Ti, V, Cr, Mn, Fe, Ru) [13–24] (Fig. 1). Photoelectron measurements and density functional calculations have revealed important details about the electronic structures of $[M(\eta^5\text{-}P_3C_2^tBu_2)_2]$ ($M = Ti$, Fe) [25,26].

Synthetic routes involve treatment of the appropriate transition metal halide with an alkali metal salt of the $P_2C_3^tBu_3^-$ or $P_3C_2^tBu_2^-$ anions or via metal vapour synthesis directly from the transition metal and the phosphaalkyne $P{\equiv}C^tBu$. The recent synthesis of $KP_2C_3^tBu_3$ via phosphorus atom extrusion from the 1,3,5-triphosphabenzene $P_3C_3^tBu_3$ on treatment with potassium [27] offers further synthetic potential for the former route, while Zenneck and coworkers [28–30] have utilised $Ph_3SnP_3C_2^tBu_2$ as a convenient ring-transfer reagent to synthesise the paramagnetic hexa-phosphamanganocene, $[Mn(\eta^5\text{-}P_3C_2^tBu_2)_2]$.

In contrast to the studies on transition metal compounds analogous main group element chemistry has been much less developed, although compounds of the type $[M(\eta^5\text{-}P_3C_2^tBu_2)]$ and $[M(\eta^5\text{-}P_2C_3^tBu_3)]$ [31,32] have been described (Fig. 2), which are of special interest as potential single source precursors of InP [33] as well as $[M'(\eta^5\text{-}P_3C_2^tBu_2)_2]$ ($M' = Sr$, Pb) [34,35].

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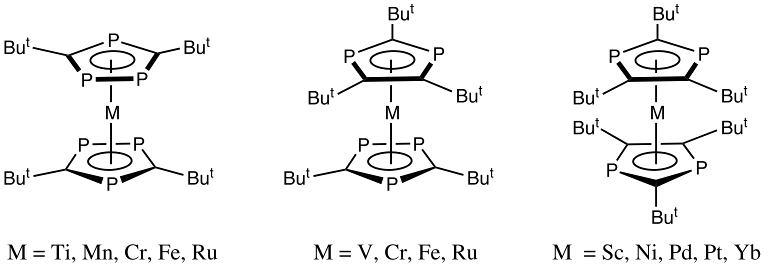


Fig. 1. Typical transition metal $P_3C_2Bu^t_2$ and $P_2C_3Bu^t_3$ complexes.

In this paper, we report our studies on Zn and Cd 1,2,4-triphospholyl compounds and present full structural characterisation of the complexes [M(η^1-$P_3C^t_2Bu_2$)$_2$(NC_5H_5)$_n$] (M = Zn, $n = 2$; M = Cd, $n = 3$).

2. Results and discussion

Treatment of two equivalents of K[$P_3C^t_2Bu_2$] **1**, with $ZnCl_2$ or $CdCl_2$ in THF, followed by subsequent treatment with pyridine led to the moisture sensitive complexes [Zn(η^1-$P_3C^t_2Bu_2$)$_2$(NC_5H_5)$_2$] **2** (36% yield) and [Cd(η^1-$P_3C^t_2Bu_2$)$_2$(NC_5H_5)$_3$] **3** (43% yield), respectively, after recrystallisation (Scheme 1).

Before pyridine treatment was carried out, the only isolable products from the above reactions were orange powders in both cases, which were soluble only in pyridine and were completely insoluble in other common solvents. It seems likely that these compounds possess a polymeric structure in which the lone-pairs of the phosphorus centres act as donors, joining the individual molecules together in essentially infinite polymeric chains. Treatment with pyridine breaks up these chains forming the monomeric adducts **2** and **3** which were isolated and fully characterised. Despite repeated attempts, the exact natures of the orange powders could not be determined, although we have observed similar behaviour in the very recently reported hexa-phosphastrontocene [{Sr(η^5-$P_3C^t_2Bu_2$)$_2$}$_\infty$] which exists as a polymeric chain structure which easily dissociates in the presence of Lewis bases such as THF, pyridine and pyrazine [35].

The solution $^{31}P\{^1H\}$-NMR spectrum of **2** displays an AB_2 spin system at 182.0 and 276.3 ppm with a typical $^2J_{PP}$ coupling constant of 44.7 Hz. The presence of only two different phosphorus environments implies either η^5-ligation or that the triphospholyl rings are fluxional and the zinc centre is rapidly exchanging between two η^1-ligated sites on adjacent phosphorus centres. Variable temperature NMR studies indicate that this exchange process is extremely rapid and no coalescence point could be obtained. Even at the solvent limiting temperature of ca. −95 °C, only two resonances still remained, (albeit with considerable broadening), rather than the three resonances expected for the rigid η^1-structure that subsequently was established in the solid state by a single crystal X-ray diffraction study (vide infra).

Similar fluxional behaviour has been previously observed by us in the compounds *trans*-[MCl(η^1-$P_3C^t_2Bu_2$)(PEt_3)$_2$] [36] (M = Pt, Pd) and by Zenneck and coworkers [30] in [SnR_3(η^1-$P_3C^t_2Bu_2$)] (R = Me, ^{n}Bu, Ph), although in both these cases signal coalescence was observed and values of $\Delta G^{\neq}$ of activation could be established. In accord with the $^{31}P\{^1H\}$ spectral data, the ^1H-NMR spectrum of **2** consists only of a single resonance at 1.95 ppm corresponding to two apparently equivalent ^{t}Bu groups, as well as exhibiting resonances for the ligated pyridine molecules at the expected shifts. Like the ^{31}P-NMR signals, no low temperature resolution could be observed. The molecular structure of **2** is shown in Fig. 3 and relevant bond angles and distances are listed in Table 1.

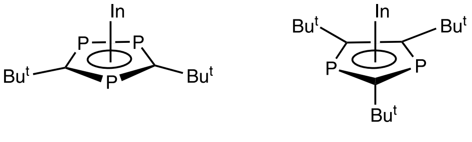
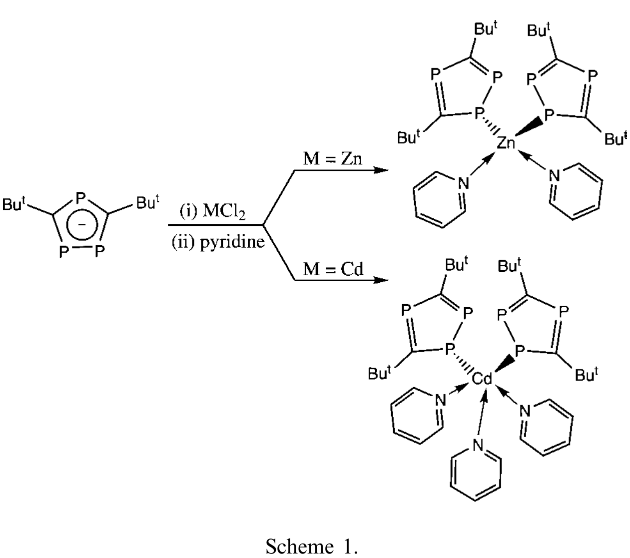


Fig. 2. η^5-$P_3C_2Bu^t_2$ and η^5-$P_2C_3Bu^t_3$ complexes of indium (I).



Scheme 1.

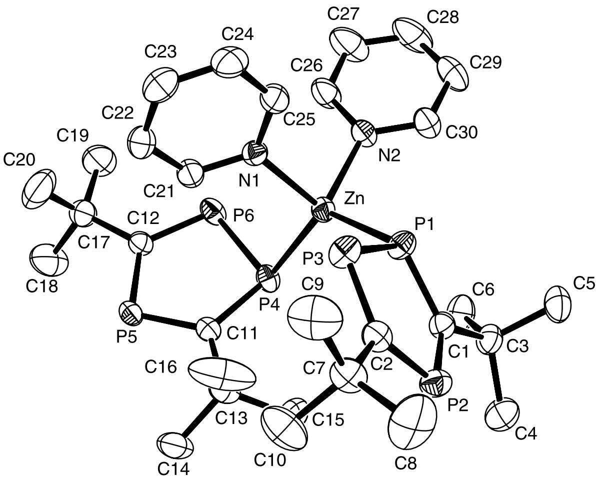


Fig. 3. ORTEP diagram of the molecular structure of **2**.

Table 1
Bond lengths (Å) and bond angles (°) for **2**

Bond lengths			
Zn–P(4)	2.3861(7)	P(5)–C(11)	1.723(3)
Zn–P(1)	2.3730(7)	C(11)–P(4)	1.767(2)
Zn–N(1)	2.067(2)	P(1)–P(3)	2.1082(10)
Zn–N(2)	2.080(2)	P(3)–C(2)	1.727(3)
P(4)–P(6)	2.1159(10)	C(2)–P(2)	1.764(3)
P(6)–C(12)	1.723(3)	P(2)–C(1)	1.726(3)
C(12)–P(5)	1.758(4)	C(1)–P(1)	1.757(3)
Bond angles			
P(3)–P(1)–Zn	105.71(3)	P(6)–P(4)–Zn	99.68(3)
P(3)–P(1)–C(1)	102.48(9)	P(6)–P(4)–Zn	101.09(9)
Zn–P(1)–C(1)	122.69(9)	Zn–P(4)–C(11)	115.39(8)
N(1)–Zn–N(2)	96.59(9)	N(1)–Zn–P(4)	109.83(6)
N(2)–Zn–P(1)	108.21(6)	N(1)–Z–P(1)	101.87(6)
P(4)–Zn–P(1)	125.30(3)	N(2)–Zn–P(4)	110.92(6)

The structure of **2** consists of discrete monomeric units, each with a distorted tetrahedral zinc centre bearing two η^1-ligated 1,2,4-triphospholyl rings and two donor pyridine molecules. The intra-ring bond distances are consistent with partial delocalisation of the phosphorus lone-pairs within the rings. The mean of the carbon–phosphorus double bond distances (P6–C12, P5–C11, P3–C2, P2–C1) (1.725 Å), lies midway between the expected values for fully localised phosphorus–carbon double and phosphorus–carbon single bonds (typically 1.61–1.71 and 1.85 Å, respectively). Similarly, the carbon–phosphorus single bond distances for C1–P1, C2–P2, C11–P4 and P5–C12 range between 1.757(3) and 1.767(2) Å which are notably shorter than expected for formally single phosphorus–carbon bonds. Moreover, the sum of the angles at the saturated phosphorus centres (330.81° at P1 and 316.16° at P4) are between those of the planar saturated P centre (sum of angles = 359°) in the highly aromatic triphosphole $P_3C_2(SiMe_3)_2R$ ($R = CH(SiMe_3)_2$) [37] and 303° in 1-benzylphosphole in which only weak electron delocalisation is observed [38]. The Zn–N distances of 2.067(2) and 2.080(2) Å are unremarkable and are comparable with those in many structurally characterised pyridine zinc complexes which are typically ca. 2.0–2.1 Å.

The cadmium complex **3** shows similar solution NMR characteristics to **2**. The ${}^{31}P\{{}^{1}H\}$-NMR spectrum consists of a doublet at 186.5 ppm and a triplet at 294.5 ppm with a ${}^{2}J_{PP}$ coupling of 45.9 Hz, whilst the ^{1}H-NMR spectrum displays a single ^{t}Bu resonance at 1.76 ppm as well as resonances corresponding to the coordinated pyridine molecules. Like **2**, complex **3** is highly fluxional in solution and no coalescence of either the ^{31}P- or ^{1}H-NMR resonances was observed even at −95 °C. The ^{113}Cd-NMR spectrum of **3** was also recorded and showed a single broad resonance at −336.1 ppm, but no discernable ${}^{1}J_{CdP}$ coupling could be measured. The molecular structure of **3** which was determined by a single crystal X-ray diffraction study is shown in Fig. 4 and relevant bond distances and angles are shown in Table 2.

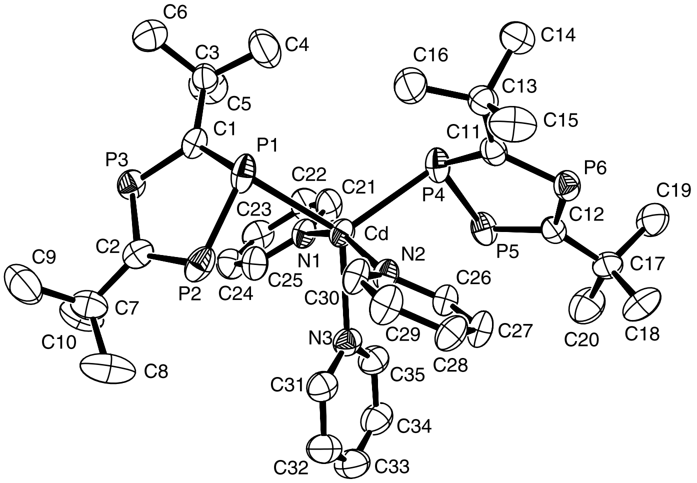


Fig. 4. ORTEP diagram of the molecular structure of **3**.

Table 2
Bond lengths (Å) and bond angles (°) for **3**

Bond lengths			
Cd–P(4)	2.6018(11)	C(2)–P(2)	1.730(4)
Cd–P(1)	2.6317(11)	P(2)–P(1)	2.1156(18)
Cd–N(1)	2.398(3)	P(4)–C(11)	1.754(4)
Cd–N(2)	2.399(3)	C(11)–P(6)	1.724(4)
Cd–N(3)	2.423(3)	P(6)–C(12)	1.747(4)
P(1)–C(1)	1.757(14)	C(12)–P(5)	1.727(4)
C(1)–P(3)	1.714(4)	P(5)–P(4)	2.1080(16)
P(3)–C(2)	1.747(4)		
Bond angles			
C(1)–P(1)–Cd	114.36(12)	C(11)–P(4)–Cd	116.36(12)
C(1)–P(1)–P(2)	99.79(14)	P(5)–P(4)–Cd	98.80(5)
P(2)–P(1)–Cd	87.58(5)	P(5)–P(4)–C(11)	100.72(14)
N(1)–Cd–N(2)	158.78(11)	N(3)–Cd–P(4)	118.17(8)
N(1)–Cd–N(3)	79.61(11)	N(1)–Cd–P(1)	95.52(8)
N(2)–Cd–N(3)	79.17(11)	N(2)–Cd–P(1)	96.90(7)
N(1)–Cd–P(4)	95.87(8)	N(3)–Cd–P(1)	125.74(8)
N(2)–Cd–P(4)	94.03(7)	P(4)–Cd–P(1)	116.08(4)

In the solid state, complex **3** like **2** is monomeric, the cadmium atom lying in a distorted trigonal bipyramidal environment where N1 and N2 can be viewed as the axial positions and P1, P4 and N3 as the equatorial positions. The sum of the angles subtended by the three axial ligands and the central metal is almost 360° whilst the metal axial–ligand vectors subtend an angle of 158° at the cadmium centre. The cadmium atom in **3** bears two η^1-ligated triphospholyl rings, but unlike its zinc analogue **2**, **3** possesses three donor pyridine molecules, making it a rare example of a five-coordinate monomeric cadmium complex. The structure of **3** also contrasts with that of the related cyclopentadienyl complex $[Cd(\eta^1\text{-}C_5H_5)_2(NC_5H_5)_2]$ **4** [39] which has only two ligated pyridine molecules. Since this is contrary to that expected on steric grounds, it seems likely that the extra coordination of pyridine in **3** may be attributed to the known overall greater electron withdrawing effect of the 1,2,4-triphospholyl rings compared with the cyclopentadienyl ring [2], making the cadmium more electrophilic in the case of **3**. The saturated phosphorus centres in **3** are somewhat more pyramidalised than in **2**, the sum of the angles being 301.73° at P1 and 315.88° at P4. Additionally, the intra-ring bond distances are indicative of only slight electron delocalisation. The Cd–N distances of 2.398(3), 2.399(3) and 2.423(3) Å are similar to those in related complexes, which typically range from 2.30 to 2.46 Å. In view of the generation of InP from $[In(\eta^1\text{-}P_3C^t_2Bu_2)]$ [33], we are currently examining the suitability of complexes **2** and **3** as possible single source precursors to their corresponding metal phosphides.

3. Experimental

3.1. General remarks

All procedures were conducted using conventional Schlenk and glove box techniques under an atmosphere of high purity Ar or nitrogen. Toluene and THF were dried by refluxing over sodium–potassium alloy and were distilled and degassed before use. Pyridine was distilled from CaH_2 immediately before use. ^{1}H-, ^{31}P{^{1}H}- and ^{13}C-NMR spectra were recorded on either a Bruker AMX-500 or DPX-300 spectrometer in C_5D_5N and were referenced to the residual ^{1}H resonances of the solvent, the ^{13}C resonances of the deuterated solvent or to external 85% H_3PO_4 ($\delta = 0.0$, ^{31}P-NMR), respectively. EIMS were recorded on a VG Autospec instrument at 70 eV. Microanalyses were performed by Labor Pascher, Remagen, Germany. Anhydrous $ZnCl_2$ and $CdCl_2$ were commercial samples and were used as received. $KP_3C^t_2Bu_2$ was synthesised by the literature procedure [31].

3.2. Syntheses $[Zn(\eta^1\text{-}P_3C^t_2Bu_2)_2(NC_5H_5)_2]$ (**2**)

To a solution of $ZnCl_2$ (0.126 g, 0.93 mmol) in THF (30 cm^3) was added dropwise a solution of $[K][P_3C^t_2Bu_2]$ (0.5g, 1.85 mmol) in THF (20 cm^3) with rapid stirring at ambient temperature. The resulting solution was stirred for 18 h and then filtered and volatiles removed in vacuo to afford an orange powder. The powder was heated to 60 °C for 24 h in a mixture of toluene and pyridine. Volatiles were again removed and the yellow oily residue recrystallised from toluene at −18 °C to afford **2** as a yellow crystalline solid (0.23 g, 36%) which decomposed gradually on heating from ca. 140 °C. The crystals were suitable for the X-ray diffraction study.

^{31}P{^{1}H}-NMR: δ 182.0 (d, $^2J_{PP} = 44.7$ Hz), 276.3 (t, $^2J_{PP} = 44.7$ Hz). ^{1}H-NMR: δ 1.95 (s, 36H, ^{t}Bu), 7.19 (4H, py), 7.55 (2H, py), 8.71 (4H, py). ^{13}C-AMXX′ spin system 37.3 (unresolved multiplet $C(\mathit{C}H_3)_3$), 41.5 ($^2J_{PmC} = 21.40$ Hz, $\Sigma^3J_{PxC} + {}^2J_{Px'C} = 12.69$ Hz, $\mathit{C}(CH_3)_3$), 211.1 ($^1J_{PmC} = 63.3$ Hz,, $\Sigma^2J_{PxC} + {}^1J_{Px'C} = 65.5$ Hz P*C*P). EIMS (70 eV), *m*/*z*: 526 (25%, $[M - 2py]^+$), 464 (58%, $[P_3C_2Bu_2H]_2^+$), 231 (59%, $[P_3C^t_2Bu_2]^+$), 57 (100%, $[^tBu]^+$). Microanalysis. Anal. Found: C, 52.69; H, 6.76; N, 4.03. Calc. for $C_{30}H_{46}N_2P_6Zn$: C, 52.53; H, 6.76; N, 4.08%.

3.3. $[Cd(\eta^1\text{-}P_3C^t_2Bu_2)_2(NC_5H_5)_3]$ (**3**)

To a solution of $CdCl_2$ (0.170 g, 0.93 mmol) in THF (30 cm^3) was added dropwise a solution of the salt $[K][P_3C^t_2Bu_2]$ (0.5 g, 1.85 mmol) in THF (20 cm^3) with rapid stirring at ambient temperature. The resulting solution was stirred for 18 h and then filtered and volatiles were removed in vacuo to afford an orange powder which was washed with toluene. The powder was then heated to 60 °C for 24 h in a mixture of pyridine and toluene. Volatiles were again removed and the yellow oily residue recrystallised from a pyridine/toluene mixture at −40 °C to afford **3** as an orange crystalline solid (0.26 g, 43%) which decomposed gradually on heating from ca. 100 °C.

^{31}P{^{1}H}-NMR: δ 186.5 (d, $^2J_{PP} = 45.9$ Hz), 294.5 (t, $^2J_{PP} = 45.9$ Hz). ^{1}H-NMR: δ 1.76 (s, 36H, ^{t}Bu), 7.19 (6H, py), 7.55 (3H, py), 8.71 (6H, py). ^{13}C-AMXX′ spin system, 37.24 ($^3J_{PmC} = 11.2$ Hz, $\Sigma^4J_{PmC} + {}^3J_{PxC} = 10.2$ Hz C(CH$_3$)$_3$), 41.6 ($^2J_{PmC} = 21.4$ Hz, $\Sigma^3J_{PxC} + {}^2J_{Px'C} = 12.2$ Hz C(CH$_3$)$_3$), 214.9 ($^1J_{PmC} = 64.1$ Hz, $\Sigma^2J_{PxC} + {}^1J_{Px'C} = 75.3$ Hz, PCP).^{113}Cd −336.1 (broad unresolved resonance). EIMS 576 (<1%, [M − 3py]$^+$), 462 (95%, $[P_3C_2^tBu_2]_2^+$), 231 (100%, $[P_3C_2^tBu_2]^+$), 57 (90%, [^{t}Bu]$^+$). Microanalysis. Anal. Found: C 51.77; H, 6.33; N, 5.08. Calc. for $C_{35}H_{51}N_3P_6Cd$: C, 51.76; H, 6.30; N, 5.17%.

3.4. Crystallography

Crystals of **2** and **3** suitable for X-ray analysis were grown from toluene or pyridine, respectively. Intensity data were measured on a Kappa CCD area detector at 173(2) K using Mo–K$_\alpha$ radiation ($\lambda = 0.71073$ Å). Both structures were solved and refined using the SHELX-97 suite of programs [40] and WINGX [41]. An empirical absorption correction was applied in both cases. The structure of **3** contains two disordered pyridine solvate molecules per molecule of the complex. Details of crystal data are collected in Table 3.

Table 3
Crystallographic data and structural parameters for complexes **2** and **3**

	2	**3**
Empirical formula	$C_{30}H_{46}N_2P_6Zn$	$C_{35}H_{51}N_3P_6Cd.2$-(C_5H_5N)
Formula weight	685.88	970.21
Crystal system	Monoclinic	Monoclinic
Space group	*C*2/*c* (no. 15)	*C*2/*c* (no. 15)
Unit cell dimensions		
a (Å)	33.9664(10)	38.6234(10)
b (Å)	11.5953(4)	12.4688(5)
c (Å)	19.6712(5)	22.2422(8)
β (°)	109.182(2)	108.784(2)
V (Å^3)	7317.4(4)	10141.1(6)
Z	8	8
μ (mm^{-1})	0.96	1.27
Crystal size (mm)	0.4 × 0.3 × 0.2	0.3 × 0.2 × 0.05
Reflections collected	21 382	25 735
Independent (R_{int})	8647 (0.045)	8872 (0.063)
R_1 $I>2\sigma I$	0.044	0.045
wR_2 $I>2\sigma I$	0.097	0.091
R_1 all data	0.056	0.080
wR_2 all data	0.103	0.104

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 157794 and 157795 for compounds **2** and **3**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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