Synthesis and multinuclear NMR study of Hg(II), Cd(II), and Pd(II) complexes with biphenylmethylenetriphenylphosphorane: X-ray crystal structure of $[\{C_6H_5C_6H_4CO\{(C_6H_5)_3P\}CH\}HgI_2]_2$

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Synthesis and multinuclear NMR study of Hg(II), Cd(II), and Pd(II) complexes with biphenylmethylenetriphenylphosphorane: X-ray crystal structure of [{C₆H₅C₆H₄CO{(C₆H₅)₃P}CH}HgI₂]₂

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Reactions of title ylide, {(C₆H₅)₃PCHCOC₆H₄C₆H₅)} (BPPPY), with mercury(II) halides in equimolar ratios in methanol yielded dinuclear complexes [(BPPPY)HgCl₂]₂ (**1**), [(BPPPY) HgBr₂]₂ (**2**), and [(BPPPY)HgI₂]₂ (**3**). Reactions of BPPPY with CdCl₂ in equimolar ratios gave [(BPPPY)CdCl₂]₂ (**4**). Reaction of PdCl₂ with BPPPY (1/2) in acetonitrile at room temperature gave *cis/trans* [PdCl₂{CH(PPh₃)COC₆H₄C₆H₅}₂] (**5**). The same reaction at reflux gave the orthopalladated complex [Pd{CH{P(2-C₆H₄)Ph}(COC₆H₄C₆H₅)}(μ-Cl)]₂ (**6**) along with the phosphonium salt [Ph₃PCHCOC₆H₄C₆H₅]Br. The compounds were characterized by elemental analysis, IR-, ¹H-, ¹³C-, and ³¹P-NMR spectroscopy. Single crystal X-ray analysis of **3** reveals the centrosymmetric dimeric structure containing the ylide and HgI₂. Crystallographic data for **3** are: crystal system, monoclinic; space group, *P 2₁/n*, *a* = 15.7744(7), *b* = 23.0288(9), *c* = 20.2867(9) Å, *β* = 112.237(3)°, *V* = 6821.4(5) Å³, and *Z* = 1.

Keywords: Phosphorus ylide; Dinuclear complexes; Orthopalladated; Single crystal structure

1. Introduction

Preparation and characterization of α-stabilized phosphorus ylides, and metal complexes incorporating these ylides, has attracted much attention. The utility of metalated phosphorus ylides in synthetic chemistry has been well documented [1, 2], driven primarily to develop new reagents for chemical synthesis that exhibit the enhanced properties [3–5]. Our work has been directed toward evaluating the ligating behavior of phosphorus ylides [6–8]. The juxtaposition of the keto group and carbanion in phosphorus ylides allows for the resonance delocalization of the ylidic electron density providing additional stabilization to the ylide species. The α-keto-stabilized phosphorus ylides R₃E = C(R′)COR″ (E = P, As; R, R′, R″ = H, alkyl or aryl groups) show high stability (which allow them to be easily handled in air) and ambidentate character as ligands (C- versus O-coordination). This ambidentate character can be

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rationalized in terms of resonance forms **a**–**c** (where **c** is represented by the *cis* and *trans geometrical* isomers).

$$R_3E=C\begin{smallmatrix}R'\\\\C-R''\\\\O\end{smallmatrix} \longleftrightarrow \overset{\oplus}{R_3E}-\overset{\ominus}{C}\begin{smallmatrix}R'\\\\C-R''\\\\O\end{smallmatrix} \longleftrightarrow \overset{\oplus}{R_3E}-C\begin{smallmatrix}R'\\\\C-R''\\\\\ominus O\end{smallmatrix} \text{ or } \overset{\oplus}{R_3E}-C\begin{smallmatrix}R'\\\\C-\ominus O\\\\R''\end{smallmatrix}$$

a   **b**   **c**
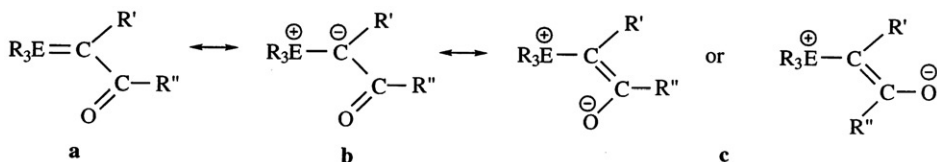
Forms **b** and **c** account for the metal C-coordination **A** and O-coordination **B** (in *cis* and *trans* forms), respectively.

A   Cisoid   **B**   Transoid
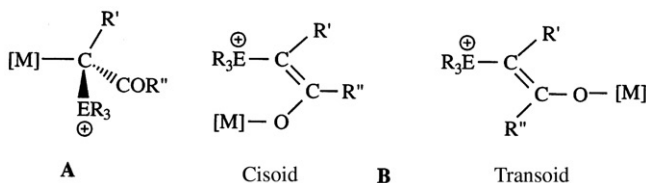
From the consideration of the HSAB rules [9], it can be hypothesized that the title ligands will coordinate soft metal ions *via* the soft ylidic carbon as opposed to the hard carbonyl oxygen atom. The reaction of $\{(p\text{-tolyl})_3\text{PCHCOOCH}_2\text{C}_6\text{H}_5\}$, BTPY, with mercury(II) halides have been reported by Sabounchei *et al.* [10] and characterized by IR-, ^{1}H-, ^{13}C-, and ^{31}P-NMR spectra. In the compounds reported to date, the chemical behavior of the α-keto phosphorus ylides has been clearly dominated by the C form [7, 8, 10–13] and very few examples of O-coordinated ylides are known [14–16]. One of the complexes previously formulated as $[\text{PtCl}_2\{\text{CH(PPh}_3)\text{C(O)Me}\}_2]_2$ was actually a mixture of the phosphonium salt $[\text{Ph}_3\text{PCH}_2\text{C(O)Me}]\text{Cl}$ and the *ortho*-metallated complex $[\text{Pt}\{\text{CH(P(2C}_6\text{H}_4)\text{Ph}_2\}\{\text{C(O)Me}\}(\mu\text{-Cl})]_2$ [17]. Although *ortho*-metallation reactions are common in the chemistry of platinum and this was not the first example of *ortho*-metallation of an ylide [18], we thought it of interest to study this reaction. In this work, we describe the preparation and spectroscopic characterization (IR and NMR) of the complexes of Hg(II), Cd(II), Pd(II), and the title ylide.

2. Experimental

2.1. Physical measurements and materials

Methanol and acetonitrile were distilled over magnesium powder and diethyl ether (Et$_2$O) over a mixture of sodium and benzophenone just before use. All other solvents were of reagent grade and used without further purification. Solution-state ^{1}H-, ^{31}P-, and ^{13}C-NMR spectra at an ambient temperature were obtained in DMSO-d$_6$ or CDCl$_3$ using FT-NMR Bruker 300 MHz and JEOL FX 90 Q spectrometers. Melting points were measured on a SMPI apparatus. Elemental analysis for C, H, and N were performed using a PE 2400 series analyzer. IR spectra were recorded on a Shimadzu 435-U-04 spectrophotometer from 550 to 4000 cm^{-1} with KBr disks. X-ray analysis was performed on a STOE IPDS-II diffractometer.

2.2. *Preparation of ylide ligand*

2.2.1. Synthesis of [(C$_6$H$_5$)$_3$PCHCOC$_6$H$_4$C$_6$H$_5$] (BPPPY). 2-Bromo-4-phenylaceto-phenone (1.1 mmol, 0.31 g) was dissolved in 20 mL of acetone and then a solution of triphenylphosphine (1.1 mmol, 0.30 g) in the same solvent (5 mL) was added dropwise at room temperature. The resulting brown solution was stirred for 10 h, pale brown solid (phosphonium salt) was filtered off, washed with diethyl ether, and dried under reduced pressure, 0.47 g (77%). Addition of the phosphonium salt (0.92 mmol, 0.47 g) to an aqueous solution of NaOH (0.5 mol) led to the elimination of HBr and gave the free ligand, biphenylmethylenetriphenylphosphorane (BPPPY). Yield 0.35 g (74%), m.p. 82–85°C. Anal. Calcd for C$_{32}$H$_{25}$OP (%): C, 79.78; H, 5.52. Found (%): C, 80.10; H, 5.61. IR (KBr) $\nu_{max} = 1568$ (C=O), 881 (P–C) cm^{-1}.

2.3. *Preparation of metal complexes*

2.3.1. General procedure for dinuclear Hg(II) and Cd(II) complexes. A solution (0.44 mmol, 0.12 g) of HgCl$_2$ in dry methanol (10 mL) was added to a solution (0.44 mmol, 0.20 g) of BPPPY in dry methanol and stirred for 12 h at room temperature. The white solution was concentrated to 2 mL and diethyl ether (15 mL) was added to precipitate the dinuclear complex which was recrystallized from chloroform–diethyl ether and dried in vacuum.

2.3.2. Data for [(BPPPY)HgCl$_2$]$_2$ (1). White solid. Yield 0.27 g (84%), m.p. 145–147°C. Anal. Calcd for C$_{64}$H$_{50}$Cl$_4$Hg$_2$O$_2$P$_2$ (%): C, 52.79; H, 3.46. Found (%): C, 52.11; H, 3.51. IR (KBr) $\nu_{max} = 1626$ (C=O), 819 (P–C) cm^{-1}.

2.3.3. Data for [(BPPPY)HgBr$_2$]$_2$ (2). Pale yellow solid. Yield 0.29 g (80%), m.p. 139–141°C. Anal. Calcd for C$_{64}$H$_{50}$Br$_4$Hg$_2$O$_2$P$_2$ (%): C, 47.05; H, 3.08. Found (%): C, 46.84; H, 3.24. IR (KBr) $\nu_{max} = 1628$ (C=O), 812 (P–C) cm^{-1}.

2.3.4. Data for [(BPPPY)HgI$_2$]$_2$ (3). Yellow solid. Yield 0.33 g (82%), m.p. 145–147°C. Anal. Calcd for C$_{64}$H$_{50}$I$_4$Hg$_2$O$_2$P$_2$ (%): C, 42.19; H, 2.77. Found (%): C, 41.86; H, 2.81. IR (KBr) $\nu_{max} = 1621$ (C=O), 806 (P–C) cm^{-1}.

2.3.5. Data for [(BPPPY)CdCl$_2$]$_2$ (4). White solid. Yield 0.12 g (60%), m.p. 107–110°C. Anal. Calcd for C$_{64}$H$_{50}$Cl$_4$Cd$_2$O$_2$P$_2$ (%): C, 60.07; H, 3.94. Found (%): C, 59.51; H, 3.81. IR (KBr) $\nu_{max} = 1672$ (C=O), 828 (P–C) cm^{-1}.

2.3.6. Synthesis of [PdCl$_2${CH(PPh$_3$)COC$_6$H$_4$C$_6$H$_5$}$_2$] (5). A solution (0.13 mmol, 0.01 g) of PdCl$_2$ in acetonitrile (15 mL) was added to a solution (0.13 mmol, 0.06 g) of BPPPY in dry acetonitrile (15 mL) and stirred for 15 min at room temperature. The brown solution was concentrated to 2 mL and diethyl ether (15 mL) was added to precipitate the brown complex. Yield 0.03 g (42%), m.p. 195–197°C (decomposition). Anal. Calcd for C$_{64}$H$_{50}$Cl$_2$PdO$_2$P$_2$ (%): C, 70.50; H, 4.62. Found (%): C, 70.19; H, 4.53.

IR (KBr) $\nu_{max} = 1621$ (C=O), 856 (P–C) cm^{-1}. ^{31}P-NMR (202.44 MHz, DMSO-d$_6$) $\delta_p = 16.01$ (*trans*, minor diastereoisomer), 16.41 (*trans*, major diastereoisomer), 29.54 (*cis*, minor diastereoisomer), 30.19 (*cis*, major diastereoisomer); ^{1}H-NMR (90 MHz, DMSO-d$_6$) $\delta_H = 4.54$ (br, 1H, CH, two diastereoisomers), 7.40–8.17 (24H, m, phenyl). ^{13}C-NMR (22.53 MHz, DMSO-d$_6$) $\delta_C = 42.90$ (br, CH, two diastereoisomers), 127.36 (d, $J = 150.42$, PPh$_3$(i)), 133.25 (d, $J = 6.03$, PPh$_3$(o)), 129.83 (br, PPh$_3$(m)), 133.58 (s, PPh$_3$(p)), 190.1 (CO).

2.3.7. Synthesis of [Pd{CH{C$_6$H$_4$(PPh$_2$)}COC$_6$H$_4$C$_6$H$_5$}(μ-Cl)]$_2$ (6). To a refluxing solution of PdCl$_2$ (0.44 mmol, 0.04 g) in acetonitrile (and so containing [PdCl$_2$ (NCCH$_3$)$_2$]), BPPPY (0.44 mmol, 0.20 g) was added and stirred for 8 h. The suspension was filtered and the solid was washed with diethyl ether (15 mL) to give **6** as a greenish-yellow solid, along with the phosphonium salt, [Ph$_3$PCHCOC$_6$H$_4$C$_6$H$_5$]Br. After washing with water, this impurity was removed. Yield 0.15 g (62%). m.p. 138–141°C (decomposition). Anal. Calcd for C$_{64}$H$_{48}$Cl$_2$Pd$_2$O$_2$P$_2$ (%): C, 64.34; H, 4.05. Found (%): C, 64.11; H, 3.88. IR (KBr) $\nu_{max} = 1671$ (C=O), 827 (P–C) cm^{-1}. ^{31}P-NMR (90 MHz, DMSO-d$_6$) $\delta_p = 21.80$ (s, orthopalladated complex).

2.4. *X-ray measurements*

A block colorless crystal of **3** having approximate dimensions of $0.36 \times 0.32 \times 0.22$ mm^3 was mounted on a glass fiber. All measurements were made on a STOE IPDS-II diffractometer with graphite monochromated Mo-Kα radiation ($\lambda = 0.7107$ nm). The data were collected at 298 K to a maximum θ value of 29.26 and in a series of ω scans in 1° oscillations with 60 s exposures. Of the 18,391 reflections that were collected, 52,781 were unique ($R_{int} = 0.0706$), equivalent reflections were merged. Data were collected and integrated using the STOE X-AREA [19] software package. The numerical absorption coefficient, μ, for Mo-Kα radiation is 6.459 mm^{-1}. A numerical absorption correction was applied using X-RED [20] and X-SHAPE [21] software, which resulted in transmission factors ranging from 0.248 to 0.115. The data were corrected for Lorentz and polarization effects. The structure was solved by direct [22] methods. All of the non-hydrogen atoms were refined anisotropically. Hydrogens were located in ideal positions. Anomalous description effects were included in F_{calc} [23], the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley [24]; values for the mass attenuation coefficient are those of Creagh and Habbell [25].

3. Results and discussion

The ligand was synthesized by treating 2-bromo-4-phenylacetophenone with triphenylphosphine and removing HBr from the phosphonium salt. The light-colored crystals are very soluble in chloroform, but with poor solubility in petroleum ether and *n*-hexane. Interaction of the ligand with HgX$_2$ (X = Cl, Br and I) in 1:1 molar ratio in methanol at room temperature yielded stable C-coordinated compounds in halo-bridged dimeric structures (scheme 1). The reaction of ylide with CdCl$_2 \cdot 2$H$_2$O in 1:1 molar ratio in methanol at room temperature also gave C-coordinated,
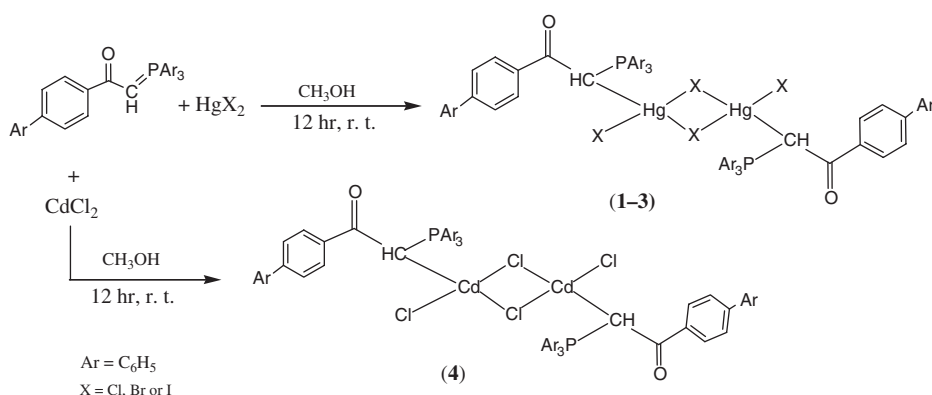
Scheme 1. Reaction of BPPPY with HgX_2 (X = Cl (**1**), Br (**2**) and I (**3**)) [10, 11] and $CdCl_2$ (**4**) [26].
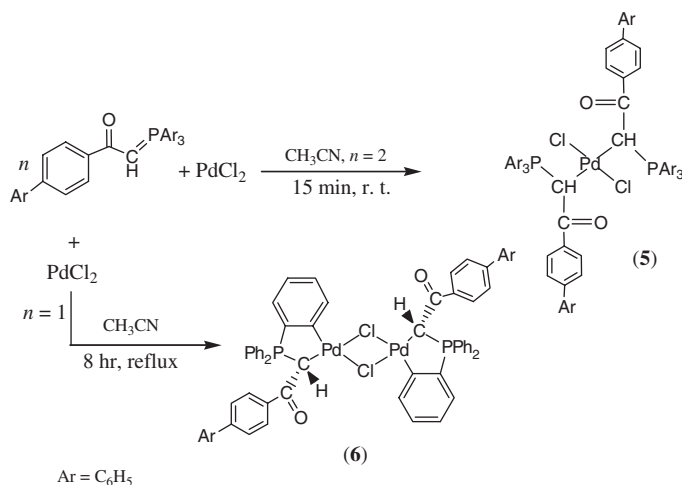
Scheme 2. Reaction of BPPPY with $PdCl_2$; (**5**) [$PdCl_2${CH(PPh$_3$)COC$_6$H$_4$C$_6$H$_5$}$_2$] and (**6**) [Pd{CH{C$_6$H$_4$(PPh$_2$)}COC$_6$H$_4$C$_6$H$_5$}(μ-Cl)]$_2$ [27, 28].

halo-bridged dimer (scheme 1). Reactions of Hg and Cd halides with phosphorus ylides were carried out at reflux. Reaction of ylide with $PdCl_2$ in a 2 : 1 molar ratio in CH_3CN at room temperature gave mononuclear **5**, while the reaction of ylide with $PdCl_2$ in 1 : 1 molar ratio in CH_3CN at reflux gave *ortho*-metalated **6** (scheme 2).

3.1. *IR spectra*

The ν(CO) at 1568 and 1615 cm^{-1} for BPPPY and BTPY, respectively, is sensitive to complexation as for other resonance stabilized ylides [29]. Coordination of ylide through carbon causes an increase in ν(CO), while O-coordination lowers ν(CO). Infrared spectra of complexes in the solid state show ν(CO) from 1568 to 1735 cm^{-1},

Table 1. ν(CO) of phosphoranes and their metal complexes.

Compound	ν(C=O) (cm^{-1})	Reference
Ph$_3$PCHCON(CH$_3$)$_2$	1530	[25]
APPY	1530	[30]
BPPY	1525	[31]
Ph$_3$PCHCOC$_6$H$_4$C$_6$H$_5$ (BPPPY)	1568	This work
(C$_6$H$_4$CH$_3$)$_3$PCHCOOCH$_2$C$_6$H$_5$ (BTPY)	1615	[10]
C-coordination		
[(BPPPY)HgCl$_2$]$_2$	1626	This work
[(BPPPY)HgBr$_2$]$_2$	1628	This work
[(BPPPY)HgI$_2$]$_2$	1621	This work
[(BPPPY)CdCl$_2$]$_2$	1672	This work
[(BPPPY)$_2$PdCl$_2$]	1621	This work
[Pd{C$_6$H$_4$-2-PPh$_2$C(H)COC$_6$H$_4$C$_6$H$_5$}(μ-Cl)]$_2$	1673	This work
O-coordination		
[(Sn(CH$_3$)$_3$BPPY]Cl	1480	[32]
[Pd(C$_6$F$_5$)(PPh$_3$)$_2$(APPY)]ClO$_4$	1513	[15]

APPY,   acetylmethylenetriphenylphosphorane   and   BPPY,   benzoylmethylenephenyl-phosphorane.

higher than the free ylide. The (P$^+$–C$^-$) which is also diagnostic for coordination occurs at 812 cm^{-1} in [(*p*-tolyl)$_3$PCHCOOCH$_2$C$_6$H$_5$] [10]. Here, ν(P$^+$–C$^-$) for all complexes shifted to lower frequencies, 803–821 cm^{-1}, suggesting some removal of electron density in the P–C bond. The infrared data of the ligand as well as the metal complexes are listed in table 1.

3.2. *Proton-1 spectra*

Signals due to methine proton, in CDCl$_3$ or DMSO-d$_6$, were broad and broad doublet in these complexes (figure S1(b)). In the ^{1}H-NMR spectra for **5**, the signal due to the methinic proton is a broad doublet, probably due to diastereoisomers. Similar behavior was observed for ylide complexes of platinum(II) chloride [31, 33]. The expected downfield shifts of ^{31}P- and ^{1}H- signals for PCH upon complexation were observed in the case of C-coordination (figure S2). The appearance of single signals for PCH in both the ^{31}P- and ^{1}H-NMR at ambient temperature indicates the presence of only one molecule for all complexes, as expected for C-coordination [6]. In this case, the C-coordination of the title ylide is in contrast to the O-coordination of the phosphorus ylide Ph$_3$PC(COMe)(COPh) (ABPPY) in a different Hg(II) complex [34]. The difference in coordination mode between ABPPY and the present ylide to Hg(II) can be rationalized in terms of the electronic properties, steric requirements, and size and shape of the ligand in the final bonding mode. The nucleophilicity of the carbanion in ABPPY is less than in our ylide, due to the additional delocalization of the ylide electron density in ABPPY, which is facilitated by the second carbonyl. This reduces the ability of ABPPY to bind *via* the ylidic carbon. Belluco *et al.* [35] have studied steric influences on the coordination modes of ylides to Pt(II) systems and concluded that the preferred coordination mode is *via* the ylidic carbon, but that steric hindrance around the metal center or the ylidic carbon may necessitate O-coordination. This trend is reflected here

Table 2. ^{1}H- and ^{31}P-NMR data of BPPPY and its complexes with Hg(II), Cd(II), and Pd(II).

Compound	δ (CH)	J_{PH} (Hz)	δ (phenyl)	δ (^{31}P)
BPPPY[a]	4.45(br)	–	7.35–8.03(m)	14.21(s)
[(BPPPY)HgCl$_2$]$_2$ (**1**)[b]	5.55(br)	–	7.40–8.17(m)	23.71(s)
[(BPPPY)HgBr$_2$]$_2$ (**2**)[b]	5.52(br)	–	7.32–8.20(m)	23.61(s)
[(BPPPY)HgI$_2$]$_2$ (**3**)[b]	5.27(d)	$^2J_{PH} = 10.7$	7.46–8.14(m)	21.75(s)
[(BPPPY)CdCl$_2$]$_2$ (**4**)[b]	6.22(d)	$^2J_{PH} = 13.4$	7.30–8.20(m)	21.70(s)
PdCl$_2$(BPPPY)$_2$ (**5**)[b]	4.55(bd)	$^2J_{PH} = 24.2$	7.48–8.11(m)	16.41(d)
				30.18(d)
6[b]	6.17(d)	$^2J_{PH} = 13.4$	7.21–8.21(m)	21.80(s)

$T = 298$ K; TMS $\delta = 0.00$ ppm. Br, broad; s, singlet; d, doublet; m, multiplet; and bd, broad doublet.
[a]In CDCl$_3$.
[b]In DMSO values (ppm) relative to internal TMS.

as these ylides are slightly less sterically demanding than ABPPY and are C-coordinated to Hg(II). O-coordination of the ylide sometimes leads to the formation of *cis* and *trans* isomers giving two different signals in the ^{31}P- and ^{1}H-NMR spectra [15, 36].

3.3. ^{31}P spectra

The presence of two chiral C centers (forming diastereoisomers) in **5** (figure S1a) is shown in the ^{1}H-, and ^{31}P-NMR spectra by two sets of signals with unequal populations for CH and PCH groups. *Cis* and *trans* geometry leads to the further peaks in the ^{31}P-NMR spectra: 16.42 and 30.18 ppm for **5** at 25°C [30, 37]. The peaks at 16.42 and 30.18 ppm (figure S1) for **5** indicate *trans* and *cis* diastereoisomer, respectively.

The proton decoupled ^{31}P{^{1}H}-NMR spectra show only sharp singlets for each isomer $\delta \approx 16$–30 ppm in these complexes. The ^{31}P chemical shift values for complexes appear downfield by about $\delta \approx 3$–15 ppm with respect to the parent ylide, indicating the coordination of the ylide [6, 7, 11]. The ^{1}H- and ^{31}P-NMR data for the mercury(II), palladium(II), and cadmium(II) complex along with those of the parent ylide are listed in table 2.

3.4. ^{13}C spectra

In ^{13}C-NMR spectra, higher shielding of the ylidic carbons compared to those of the parent ylide is expected, as observed for **5**. Such an upfield shift was observed in [PdCl(η^3-2-XC$_3$H$_4$)(C$_6$H$_5$)$_3$PCHCOR] (X = H, CH$_3$; R = CH$_3$, C$_6$H$_5$) and was attributed to change in the hybridization of the ylidic carbon on coordination [38]. Similar upfield shifts of 4–9 ppm were also observed [26] in the case of [(C$_6$H$_5$)$_3$PC$_5$H$_4$HgI$_2$]$_2$, and in our mercury complexes [11, 12]. The ^{13}C shifts of the complexes are listed in the "Supplementary material".

The CO in these complexes is around 190 ppm, higher than the 183.85 ppm for the same carbon in the parent ylide, indicating the shielding of the carbon of CO in **1**–**6**. No coupling to Hg was observed at room temperature in ^{1}H-, ^{13}C-, or ^{31}P-NMR spectra of all these complexes. Failure to observe satellites was previously noted in ylide

Table 3. Crystal data and structure refinement for **3**.

Empirical formula	$C_{68}H_{62}Hg_2I_4O_4P_2S_2$
Formula weight	1978.04
Temperature (K)	298(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P\,2_1/n$
Unit cell dimensions (Å, °)	
a	15.7744(7)
b	23.0288(9)
c	20.2867(9)
α	90
β	112.237(3)
γ	90
Volume (Å^3), Z	6821.4(5), 4
Calculated density (mg m^{-3})	1.926
Absorption coefficient (mm^{-1})	6.459
$F(000)$	752
Crystal size (mm^3)	$0.36 \times 0.32 \times 0.22$
θ range for data collection (°)	1.65–29.26
Limiting indices	$-21 \le h \le 21$; $-30 \le k \le 31$; $-27 \le l \le 27$
Reflections collected/unique	18,391/52,781
Independent reflection	52,781[R(int) = 0.0706]
Completeness to $\theta = 29.26$ (%)	98.9
Absorption correction	Numerical
Max. and min. transmission	0.248 and 0.115
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	18,391/0/743
Goodness-of-fit on F^2	1.094
Final R indices [$I > 2\sigma(I)$]	$R_1{}^a = 0.0700$, $wR_2{}^b = 0.1454$
R indices (all data)	$R_1 = 0.1125$, $wR_2 = 0.1642$
Largest difference peak and hole (e Å^{-3})	2.686 and -1.155

$^a R_1 = \Sigma \,||F_o| - |F_c||/\Sigma \,|F_o|$ for reflection with $I > 2\sigma(I)$ and $^b wR_2 = [\Sigma \,(w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

complexes of Hg(II) [10, 26] and Ag(I) [39] attributed to fast exchange of the ylide with the metal.

3.5. *X-ray crystallography*

Table 3 provides the crystallographic results and refinement information for **3**. The refinement was performed using the X-STEP32 [40] crystallographic software package. The molecular structure of **3** is shown in figure 1. Fractional atomic coordinates and equivalent isotropic displacement coefficients (U_{eq}) for the non-hydrogen atoms of **3** are shown in table S1. Table 4 lists key bond lengths and angles for **3**.

The Hg(II) in **3** has a tetrahedral coordination environment with one short Hg–I bond, a Hg–C bond and two asymmetric bridging Hg–I bonds at 2.7087(9) and 2.8131(7) Å. The short Hg–C bond length, 2.270(8) Å, compared to analogous distances in [BPPYHgI$_2$]$_2$ (**4**) [6] and [(C$_6$H$_5$)$_3$PC$_5$H$_4$HgI$_2$]$_2$ [38] (2.312(13) and 2.292(8) Å, respectively) is attributed to Hg(II) orbitals with high s character for bonding to ylidic carbon. The use of non-equivalent hybrid orbitals with high s character to bond to low electronegative atoms was proposed by Bent in the concept of isovalent hybridization to account for the variation in bond lengths and bond angles around a central atom.
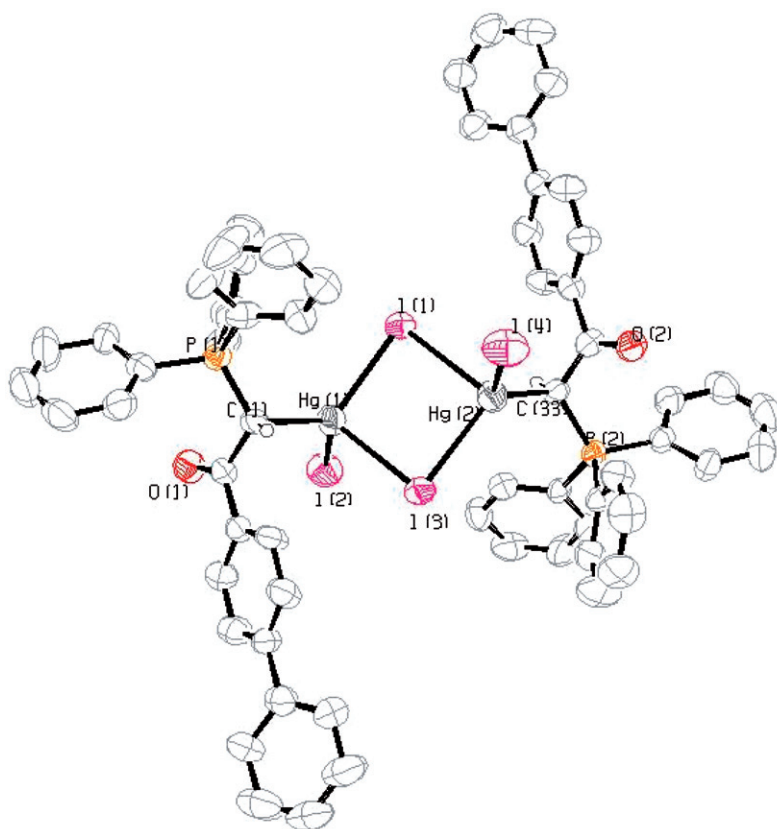
Figure 1.   Molecular structure of **3**. Hydrogens and DMSO have been omitted for clarity.

Table 4.   Selected bond lengths and angles for **3**.

C(1)–P(1)	1.771(8)	P(1)–C(1)–Hg(1)	113.2(4)
C(1)–Hg(1)	2.270(8)	C(1)–Hg(1)–I(2)	118.5(2)
I(1)–Hg(1)	2.8131(7)	C(1)–Hg(1)–I(1)	118.5(2)
I(2)–Hg(1)	2.7087(9)	I(2)–Hg(1)–I(3)	102.99(3)
I(3)–Hg(1)	3.0415(8)	I(1)–Hg(1)–I(3)	92.52(2)
I(1)–Hg(2)	3.0793(8)	I(3)–Hg(2)–I(1)	91.66(2)
I(3)–Hg(2)	2.8163(7)	I(4)–Hg(2)–I(1)	104.08(3)
I(4)–Hg(2)	2.6920(9)	C(33)–Hg(2)–I(1)	98.7(2)
		C(33)–Hg(2)–I(4)	124.5(2)

As expected on the basis of the same concept, Hg–C bonds in **3** are much shorter than in **4** because of the very low difference in electronegativity between carbon and iodine. The internuclear distances between mercury atoms were 3.951(5) and 4.014(1) Å in structures **3** and **4**, respectively, much longer than the sum of van der Waals radii (1.5 Å) [41], indicating the absence of significant bonding interactions between the mercury. Dimeric structures in Hg(II) ylide complexes may be explained by the preference of Hg(II) for four coordination and the stability of the 18 electron configuration around Hg(II).

4. Conclusions

Synthesis and characterization of a series of binuclear Hg(II) and Cd(II), mononuclear, and orthopalladate Pd(II) complexes of a phosphorus ylide are described. From physico-chemical and spectroscopic data we propose that BPPPY exhibits monodentate C-coordination to the metal center, further confirmed by the X-ray crystal structure of **3**.

Supplementary material

Crystallographic data for the structural analysis have been deposited at the Cambridge Crystallographic Data Centre, CCDC 745197. 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; Email: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk). Supplementary material contains two figures; ^{31}P-NMR of *trans* and *cis* isomers of **5** (a), ^{1}H-NMR of **3** (b) in DMSO-d$_6$ at 25°C (figure S1) and ^{31}P-NMR (a) and ^{1}H-NMR (b) of {(C$_6$H$_5$)$_3$PCHCOC$_6$H$_4$C$_6$H$_5$)}(BPPPY) in CDCl$_3$ at 25°C (figure S2). Atomic coordinates and equivalent isotropic displacement parameters (A$^2 \times 10^3$) for **3** U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor (table S1); ^{13}C-NMR data of complexes in DMSO-d$_6$ (table S2).

Acknowledgments

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