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New mercury(II) and cadmium(II) complexes with (*p*-methylbenzoyl)methylene triphenylphosphorane: Synthesis, spectroscopic and structural characterization

Seyyed Javad Sabounchei [a,*], Mohsen Ahmadi [a], Fateme Akhlaghi Bagherjeri [a], Farzaneh Hejazi [a], Keyhaneh Sanaie-Noorani [a], Hamid Reza Khavasi [b], Sepideh Samiee [c]

[a] *Faculty of Chemistry, Bu-Ali Sina University, 65174 Hamedan, Iran*
[b] *Department of Chemistry, Shahid Beheshti University, G.C., Evin, Tehran, Iran*
[c] *Department of Chemistry, Faculty of Science, Shahid Chamran University, Ahvaz, Iran*

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ABSTRACT

Reaction of $Ph_3PCHCOC_6H_4Me$ (**L**), with HgX_2 and $CdCl_2{\cdot}H_2O$ in methanol with equimolar ratios give binuclear complexes of the type $[MX(\mu\text{-}X)\{CH(PPh_3)C(O)C_6H_4Me\}]_2$ (M = Hg; X = Cl (**1**), Br (**2**), I (**3**), M = Cd; Cl(**4**)). The bridge-splitting reaction of binuclear complexes $[MX(\mu\text{-}X)\{CH(PPh_3)C(O)C_6H_4Me\}]_2$ by dimethyl sulfoxide (DMSO) yields the mononuclear complexes $[MX_2\{CH(PPh_3)C(O)C_6H_4Me\}(OSMe_2)]$ (M = Hg; X = Cl (**5**), Br (**6**), I (**7**), M = Cd; Cl (**8**)). The characterization of these complexes was carried out by elemental analysis and FT-IR, ^1H, ^{31}P, and ^{13}C NMR spectroscopies. C-coordination of ylide and O-coordination of DMSO are demonstrated by single-crystal X-ray analysis of mononuclear complex of $[HgBr_2\{CH(PPh_3)C(O)C_6H_4Me\}(OSMe_2)]$ (**6**). Complex **6** is monomeric with tetrahedral geometry around the metal ion.

1. Introduction

Phosphorus ylides are important reagents in organic chemistry, especially in the synthesis of naturally occurring products with biological and pharmacological activities [1]. The utility of metalated phosphorus ylides in synthetic chemistry has been well documented [2–4]. Ylides play in coordination chemistry other roles aside from its coordination to the metal [5]. Juxtaposition of the keto group and of the carbanion in the phosphorus ylides allows resonance delocalization of the ylidic electron density, providing additional stabilization to the ylide species. This so-called α-stabilization provides ylides with the potential to act as an ambidentate ligand and thus bond to a metal centre through the either carbon (B) or oxygen (A_1 and A_2) (Scheme 1). Although many bonding modes are possible for keto ylides [6], coordination through carbon is more predominant and observed with soft metal ions, e.g., Pd(II) [7], Pt(II) [7h,8], Ag(I) [9], Hg(II) [9d,10], Au(I) [11], Cd(II) [7i,9d,12], whereas O-coordination dominates when the metals involved are hard, e.g., Ti(IV), Zr(IV), and Hf(IV) [13].

Synthesis of complexes derived from phosphorus ylides and Hg(II) halides was initiated in 1965 by Nesmeyanov et al. [14] In 1975, Weleski et al. [15] proposed a symmetric halide-bridged dimeric structure for Hg(II) halide complexes, whereas Kalyanasundari et al. [10a] reported an asymmetric halide-bridged dimeric structure in 1995. In 1985, Sanehi et al. [16] reported a mononuclear Hg(II) complex of phosphorus ylides without any structural characterization. We have recently worked on the synthesis of mononuclear [9d,10b], binuclear [17–20] complexes derived from mercury (II) salts and phosphorus ylides.

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* Corresponding author.
E-mail address: jsabounchei@yahoo.co.uk (S.J. Sabounchei).

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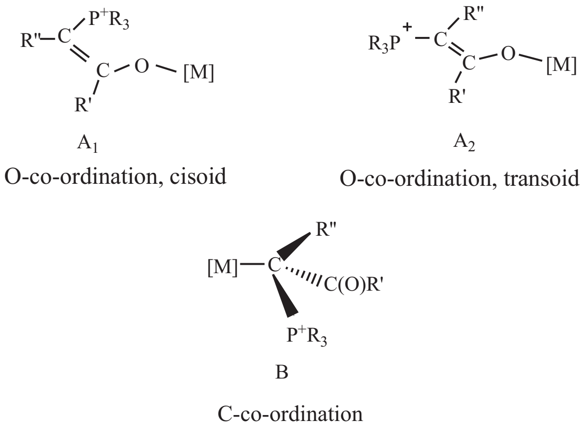


A₁
O-co-ordination, cisoid

A₂
O-co-ordination, transoid

B
C-co-ordination

Scheme 1. The possible bonding modes of an α-keto stabilized ylide to the metal center.

Based on the above backgrounds, we have focused on the synthesis, structure, and properties of coordination mononuclear Hg (II) and Cd (II) complexes with ambidentate phosphorus ylide as a ligand, and DMSO has been successfully utilized for the preparation of a series of complexes. In this study, we describe the preparation, structural and spectroscopic characterization of Hg(II) and Cd(II) complexes with the title ylide. Herein the structure of a new mononuclear mercury complex was reported and the single-crystal X-ray diffraction of **6** demonstrates the C-coordination of the ylide and O-coordination of the DMSO to the metal center.

2. Experimental

2.1. Materials and measurements

Methanol and dichloromethane were distilled over magnesium powder and diethyl ether (Et_2O) over a mixture of sodium and benzophenone just before use. All other solvents were reagent grade and used without further purifications. The ligand **L** was prepared and characterized according to the published procedure [17]. Melting points were measured on a SMPI apparatus. Elemental analyses for C, H and N were performed using a PerkinElmer 2400 series analyzer. Fourier transform IR spectra were recorded on a Shimadzu 435-U-04 spectrophotometer and samples were prepared as KBr pellets. ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded on a 300 MHz Bruker and 90 MHz Jeol spectrometer in DMSO-d_6 or $CDCl_3$ as a solvent at 25 °C. Chemical shifts (ppm) are reported according to internal TMS and external 85% phosphoric acid. Coupling constants are given in Hz.

2.2. Crystallographic data collection and structure determination

The single-crystal X-ray diffraction analyses of suitable crystal of **6** was performed on a STOE IPDS-II diffractometer at 298 K, using the graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The data collection was performed using the ω-scan technique and using the STOE X-AREA software package [21]. The crystal structure was solved by direct methods and refined by full-matrix least-squares on F^2 by SHELX [22] and using the X-STEP32 crystallographic software package [23]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were inserted at calculated positions using a riding mode with fixed thermal parameters.

2.3. Synthesis and characterization of compounds

2.3.1. $Ph_3PCHCOC_6H_4Me$ (L)

Selected IR data (KBr, ν/cm^{-1}), 1582 ($\nu_{C=O}$) and 895 ($\nu P^+–C^-$). 1H NMR ($CDCl_3$, ppm): $\delta = 2.38$ (s, 3H, CH_3), 4.32 (d, 1H, $^{2}J_{PH} = 23.29$ Hz, CH), 7.1–8.1 (m, 19H, arom). ^{31}P NMR ($CDCl_3$, ppm): $\delta = 12.98$. ^{13}C NMR ($CDCl_3$, ppm): $\delta = 21.48$ (s, CH_3), 45.63 (d, $^{1}J_{PC} = 70.42$ Hz, CH), 115.4 (d, $^{1}J_{PC} = 91.43$ Hz, PPh_3 (*i*)), 131.7 (d, $^{3}J_{PC} = 12.36$ Hz, PPh_3 (*m*)), 133.2 (d, $^{2}J_{PC} = 8.07$ Hz, PPh_3 (*o*)), 142.31 (s, PPh_3 (*p*)), 145.50 (s, COPh (*i*)), 126.19 (s, COPh (*m*)), 132.03 (s, COPh (*o*)), 128.7 (s, COPh (*p*)), 191.34 (s, CO).

2.3.2. $[HgCl(\mu\text{-}Cl)\{CH(PPh_3)C(O)C_6H_4Me\}]_2$ (1)

General procedure: To $HgCl_2$ (0.172 g, 0.63 mmol) dissolved in 5 mL of dried methanol was added **L** (0.250 g, 0.63 mmol) at room temperature. The mixture was stirred for 4 h. The white solid product was filtered, washed with diethyl ether and dried under reduced pressure. Yield: (84%); mp 208–210 °C; Selected IR data (KBr, ν/cm^{-1}), 1632 ($\nu_{C=O}$) and 817 ($\nu P^+–C^-$). ^{1}H NMR (DMSO-d_6, ppm): $\delta = 2.35$ (s, 3H, CH_3), 5.42 (d, 1H, $^{2}J_{PH} = 3.85$ Hz, CH), 6.94–8.12 (m, 19H, arom). ^{31}P NMR (DMSO-d_6, ppm): $\delta = 24.60$. ^{13}C NMR (DMSO-d_6, ppm): $\delta = 20.89$ (s, CH_3), 46.11 (d, $^{1}J_{PC} = 70.42$ Hz, CH), 122.91 (d, $^{1}J_{PC} = 89.99$ Hz, PPh_3 (*i*)), 129.21 (d, $^{3}J_{PC} = 12.36$ Hz, PPh_3 (*m*)), .17 (d, $^{2}J_{PC} = 9.77$ Hz, PPh_3 (*o*)), 134.33 (d, $^{4}J_{PC} = 9.84$ Hz, PPh_3 (*p*)), 142.46 (s, COPh (*i*)), 128.19 (s, COPh (*m*)), 133.38 (s, COPh (*o*)), 128.54 (s, COPh (*p*)), 190.87 (s, CO). Anal. calcd. (%) for $C_{54}H_{46}Cl_4Hg_2O_2P_2$ (1332): C, 48.69; H, 3.48. Found (%): C, 48.45, H, 3.54.

2.3.3. $[HgBr(\mu\text{-}Br)\{CH(PPh_3)C(O)C_6H_4Me\}]_2$ (2)

Yield: (85%); mp 197–199 °C. Selected IR data (KBr, ν/cm^{-1}), 1630 ($\nu_{C=O}$) and 814 ($\nu P^+\text{-}C^-$). ^{1}H NMR (DMSO-d_6, ppm): $\delta = 2.39$ (s, 3H, CH_3), 5.52 (br, 1H, CH), 7.04–8.24 (m, 19H, arom). ^{31}P NMR (DMSO-d_6, ppm): $\delta = 23.46$. ^{13}C NMR (DMSO-d_6, ppm): $\delta = 21.06$ (s, CH_3), 47.13 (d, $^{1}J_{PC} = 73.95$ Hz, CH), 123.01 (d, $^{1}J_{PC} = 89.52$ Hz, PPh_3 (*i*)), 129.27 (d, $^{3}J_{PC} = 12.43$ Hz, PPh_3 (*m*)), 133.23 (d, $^{2}J_{P}$C = 9.41 Hz, PPh_3 (*o*)), 133.44 (s, PPh_3 (*p*)), 142.41 (s, COPh (*i*)), 126.57 (s, COPh (*m*)), 131.97 (s, COPh (*o*)), 128.64 (s, COPh (*p*)), 190.75 (s, CO). Anal. calcd. (%) for $C_{54}H_{46}Br_4Hg_2O_2P_2$ (1510): C, 42.96; H, 3.07. Found (%): C, 43.21, H, 3.11.

2.3.4. $[HgI(\mu\text{-}I)\{CH(PPh_3)C(O)C_6H_4Me\}]_2$ (3)

Yield: (81%); mp 186–189 °C. Selected IR data (KBr, ν/cm^{-1}), 1621 ($\nu_{C=O}$) and 797 ($\nu P^+–C^-$). ^{1}H NMR (DMSO-d_6, ppm): $\delta = 2.34$ (s, 3H, CH_3), 5.25 (d, 1H, $^{2}J_{PH} = 8.44$ Hz, CH), 7.07–8.12 (m, 19H, arom). ^{31}P NMR (DMSO-d_6, ppm):

δ = 21.51. ^{13}C NMR (DMSO-d_6, ppm): δ = 20.83 (s, CH_3), 44.23 (d, $^1J_{PC}$ = 72.49 Hz, CH), 123.61 (d, $^1J_{PC}$ = 87.65 Hz, PPh_3 (*i*)), 128.93 (d, $^3J_{PC}$ = 12.57 Hz, PPh_3 (*m*)), 132.86 (d, $^2J_{PC}$ = 9.19 Hz, PPh_3 (*o*)), 135.07 (s, PPh_3 (*p*)), 141.34 (s, COPh (*i*)), 127.58 (s, COPh (*m*)), 132.86 (d, $^4J_{PC}$ = 9.19 Hz, COPh (*o*)), 128.25 (s, COPh (*p*)), 189.40 (d, $^2J_{PC}$ = 15.97 Hz, CO). Anal. calcd. (%) for $C_{54}H_{46}I_4Hg_2O_2P_2$ (1698): C, 38.20; H, 2.73. Found (%): C, 38.37, H, 2.67.

2.3.5. *[CdCl(μ-Cl){CH(PPh$_3$)C(O)C$_6$H$_4$Me}]$_2$* **(4)**

To $CdCl_2$. H_2O (0.150 g, 0.38 mmol) dissolved in 5 mL of dried methanol was added **L** (0.077 g, 0.38 mmol) at room temperature. The mixture was stirred for 12 h. The white solid product was filtered, washed with dietyl ether and dried under reduced pressure. Yield: (64%); mp 197–200 °C. Selected IR data (KBr, ν/cm^{-1}), 1653 ($\nu_{C=O}$) and 739 (νP$^+$–C$^-$). ^{1}H NMR (DMSO-d_6, ppm): δ = 2.30 (s, 3H, CH_3), 4.40 (d, 1H, $^2J_{PH}$ = 27.68 Hz, CH), 6.85–7.78 (m, 19H, arom). ^{31}P NMR (DMSO-d_6, ppm): δ = 16.35. ^{13}C NMR (DMSO-d_6, ppm): δ = 20.77 (s, CH_3), 44.56 (d, $^1J_{PC}$ = 72.56 Hz, CH), 121.30 (d, $^1J_{PC}$ = 90.31 Hz, PPh_3 (*i*)), 128.83 (d, $^3J_{PC}$ = 12.07 Hz, PPh_3 (*m*)), .66 (d, $^2J_{PC}$ = 10.36 Hz, PPh_3 (*o*)), 132134.08 (s, PPh_3 (*p*)), 153.23 (s, COPh (*i*)), 121.94 (s, COPh (*m*)), 126.60 (s, COPh (*o*)), 128.57 (s, COPh (*p*)), 183.66 (d, $^2J_{PC}$ = 2.43 Hz, CO). Anal. calcd. (%) for $C_{54}H_{46}Cd_2Cl_4O_2P_2$ (1156): C, 56.13; H, 4.01. Found (%): C, 56.22; H, 4.03.

2.3.6. *[HgCl$_2${CH(PPh$_3$)C(O)C$_6$H$_4$Me}(OSMe$_2$)]* **(5)**

General procedure: 0.150 g (0.1 mmol) of binuclear complex **1** was dissolved in DMSO (2 ml). The pale yellow crystals formed by the slow evaporation of the solvent over several days. Yield: (82%); Decomp. 183 °C. Selected IR data (KBr, ν/cm^{-1}), 1635 ($\nu_{C=O}$) and 825 (νP$^+$–C$^-$), ^{1}H NMR (DMSO-d_6, ppm): δ = 2.41 (s, 3H, CH_3), 5.36 (br, 1H, CH), 7.24–8.13 (m, 19H, arom). ^{31}P NMR (DMSO-d_6, ppm): δ = 22.03. ^{13}C NMR (DMSO-d_6, ppm): δ = 22.25 (s, CH_3), 47.89 (d, $^1J_{PC}$ = 74.14 Hz, CH), 122.21 (d, $^1J_{PC}$ = 90.09 Hz, PPh_3 (*i*)), 130.14(d, $^3J_{PC}$ = 11.64 Hz, PPh_3 (*m*)), 133.72 (d, $^2J_{PC}$ = 10.0 Hz, PPh_3 (*o*)), 133.93 (s, PPh_3 (*p*)), 143.21 (s, COPh (*i*)), 127.64 (s, COPh (*m*)), 132.0 (s, COPh (*o*)), 128.19 (s, COPh (*p*)), 189.58 (s, CO). Anal. calcd. (%) for $C_{29}H_{29}HgCl_2O_2PS$ (744): C, 46.81; H, 3.93. Found (%): C, 46.72; H, 3.80.

2.3.7. *[HgBr$_2${CH(PPh$_3$)C(O)C$_6$H$_4$Me}(OSMe$_2$)]* **(6)**

Yield: (95%); Decomp. 196 °C. Selected IR data (KBr, ν/cm^{-1}), 1628 ($\nu_{C=O}$) and 819 (νP$^+$–C$^-$). ^{1}H NMR (DMSO-d_6, ppm): δ = 2.42 (s, 3H, CH_3), 5.65 (br, 1H, CH), 7.42–8.30 (m, 19H, arom). ^{31}P NMR (DMSO-d_6, ppm): δ = 21.65. ^{13}C NMR (DMSO-d_6, ppm): δ = 21.06 (s, CH_3), 47.13 (d, $^1J_{PC}$ = 73.95 Hz, CH), 123.01 (d, $^1J_{PC}$ = 89.52 Hz, PPh_3 (*i*)), 129.27 (d, $^3J_{PC}$ = 12.43 Hz, PPh_3 (*m*)), 133.23 (d, $^2J_{PC}$ = 9.41 Hz, PPh_3 (*o*)), 133.44 (s, PPh_3 (*p*)), 142.41 (s, COPh (*i*)), 126.57 (s, COPh (*m*)), 131.97 (s, COPh (*o*)), 128.64 (s, COPh (*p*)), 190.75 (s, CO). Anal. calcd. (%) for $C_{29}H_{29}HgBr_2O_2PS$ (833): C, 41.82; H, 3.5. Found (%): C, 42.01; H, 3.4.

2.3.8. *[HgI$_2${CH(PPh$_3$)C(O)C$_6$H$_4$Me}(OSMe$_2$)]* **(7)**

Yield: (71%); Decomp. 224 °C. Selected IR data (KBr, ν/cm^{-1}), 1628 ($\nu_{C=O}$) and 832 (νP$^+$-C$^-$). ^{1}H NMR (DMSO-d_6, ppm): δ = 2.39 (s, 3H, CH_3), 5.19 (br, 1H, CH), 7.35–8.23 (m, 19H, arom). ^{31}P NMR (DMSO-d_6, ppm): δ = 21.15. ^{13}C NMR (DMSO-d_6, ppm): δ = 21.0 (s, CH_3), 48.58 (d, $^1J_{PC}$ = 72.85 Hz, CH), 123.29 (d, $^1J_{PC}$ = 90.68 Hz, PPh_3 (*i*)), 129.84 (d, $^3J_{PC}$ = 14.01 Hz, PPh_3 (*m*)), 134.28 (d, $^2J_{PC}$ = 11.51 Hz, PPh_3 (*o*)), 134.72 (s, PPh_3 (*p*)), 142.39 (s, COPh (*i*)), 127.18 (s, COPh (*m*)), 132.65 (s, COPh (*o*)), 129.46 (s, COPh (*p*)), 192.11 (s, CO). Anal. calcd. (%) for $C_{29}H_{29}HgI_2O_2PS$ (927): C, 35.57; H, 3.15. Found (%): C, 35.12; H, 3.11.

2.3.9. *[CdCl$_2${CH(PPh$_3$)C(O)C$_6$H$_4$Me}(OSMe$_2$)]* **(8)**

Yield: (65%); Decomp. 183–185 °C. Selected IR data (KBr, ν/cm^{-1}), 1635 ($\nu_{C=O}$) and 828 (νP$^+$-C$^-$). ^{1}H NMR (DMSO-d_6, ppm): δ = 2.12 (s, 3H, CH_3), 5.0 (br, 1H, CH), 7.33–8.12 (m, 19H, arom). ^{31}P NMR (DMSO-d_6, ppm): δ = 23.12. ^{13}C NMR (DMSO-d_6, ppm): δ = 19.68 (s, CH_3), 49.32 (d, $^1J_{PC}$ = 75.61 Hz, CH), 124.21 (d, $^1J_{PC}$ = 92.59 Hz, PPh_3 (*i*)), 130.24 (d, $^3J_{PC}$ = 15.14 Hz, PPh_3 (*m*)), 134.18 (d, $^2J_{PC}$ = 13.84 Hz, PPh_3 (*o*)), 135.62 (s, PPh_3 (*p*)), 143.08 (s, COPh (*i*)), 127.84 (s, COPh (*m*)), 133.12 (s, COPh (*o*)), 129.82 (s, COPh (p)), 187.13 (s, CO). Anal. calcd. (%) for $C_{29}H_{29}CdCl_2O_2PS$ (656): C, 53.10; H, 4.46. Found (%): C, 52.41; H, 4.44.

3. Results and discussion

3.1. *Chemistry*

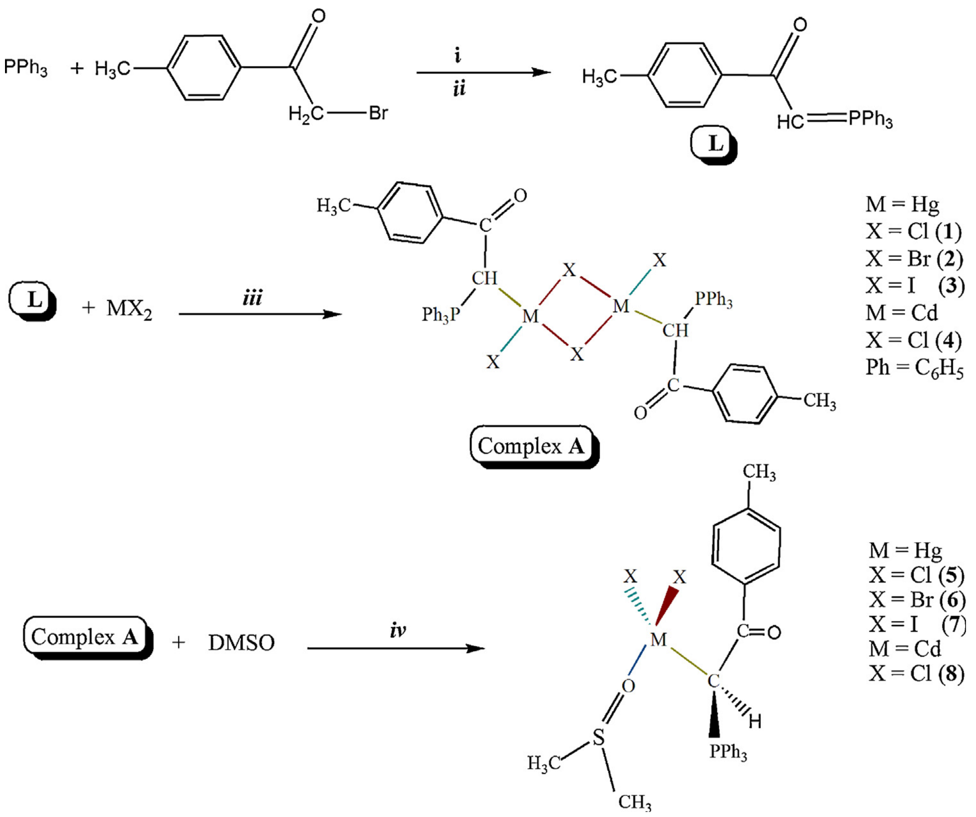
In this study, four binuclear complexes and four mononuclear complexes with the ambidentate phosphorus ylide (*p*-methylbenzoyl)methylene triphenylphosphorane were synthesized and investigated by physicochemical techniques. Reaction of **L** with MX_2 (M = Hg; X = Cl, Br and I and M = Cd; X = Cl) in methanol (1:1) yielded the binuclear complexes (Scheme 2) [10a,17]. The bridge-splitting reaction of binuclear complexes [MX(μ-X){CH(PPh$_3$)C(O)C$_6$H$_4$Me}]$_2$ by DMSO yields the mononuclear complexes [MX$_2${CH(PPh$_3$)C(O)C$_6$H$_4$-Me}(OSMe$_2$)] (Scheme 2) [13].

3.2. *IR studies*

The ν (C=O) band, which is sensitive to complexation, occurs at 1582, in the parent ylides (**L**) [17–20,23]. Coordination of ylide through the carbon atom causes an increase in the ν (C=O) band, whereas for O-coordination a lowering of the ν (C=O) band is expected [10b]. Thus the IR absorption bands for the complexes at higher frequencies indicate that C-coordination has occurred. The ν(P–C) band frequencies, which are also diagnostic of the coordination mode, occur at 895 in the parent ylides (**L**), and are shifted to lower frequencies for the complexes, suggesting some removal of the electron density of the P–C bonds [24]. It should be noted that there is no significant difference in the IR absorption band between binuclear and related mononuclear complexes.

3.3. *NMR studies*

In the ^{1}H NMR spectra, methinic protons exhibit doublet or broad doublet signals. Similar behavior was



Scheme 2. Synthetic route for the preparation of Hg(II) and Cd(II) complexes. Reagents and conditions: i: in acetone, using dry nitrogen atmosphere, 10 h at 25 °C; ii: in an aqueous solution of NaOH (0.5 mol), 2 h in 40 °C; iii: in methanol, for binuclear Hg complexes, 4 h at 25 °C; for binuclear Cd complexes, 12 h at 25 °C; iv: in dimethyl solfoxide, 3 days at 25 °C.

observed earlier in the case of ylide complexes of platinum(II) chloride [25]. The expected downfield shifts of ^{31}P and ^{1}H signals for the PCH group upon complexation in the case of C-coordination were observed in their corresponding spectra. It must be noted that O-coordination of the ylide generally leads to the formation of cisoid and transoid isomers, giving rise to two different signals in ^{31}P and ^{1}H NMR (Scheme 1) [7h]. The downfield shifts of the CH proton upon coordination in the ^{1}HNMR spectra show the coordination of the ylides through methinic carbon atoms. The proton-decoupled ^{31}P NMR spectra show only one sharp singlet between δ 16.2–24.6 ppm for the complexes of Hg(II) halides and $CdCl_2.H_2O$. Chemical shift values for the complexes appear to be downfield by about δ 2–10 ppm with respect to the parent ylide (δ 14.10 ppm for **L**), indicating that coordination of the ylide has occurred.

The most interesting aspect of the ^{13}C NMR spectra of the complexes is the up-field shift of the signals due to the ylidic carbon. Similar up-field shifts of 2–3 ppm with reference to the parent ylide were also observed in the case of the mercury cyclopentadienyl complex [26] and in our synthesized Hg(II) complexes [9d,10b]. The ^{13}C shifts of the CO group in the complexes are lower than noted for the same carbon in the parent ylide, indicating much lower shielding of the carbon of the CO group in these complexes.

3.4. X-ray structure analysis

Table 1 provides the crystallographic results and refinement information for complex **6**. The molecular structure is shown in Fig. 1. Pertinent bond distances and angles for **6** are given in Table 2. The fractional atomic coordinates and equivalent isotropic displacement coefficients (U_{eq}) for the non-hydrogen atoms of the complex are shown in the supplementary material. The Hg(II) centre in complex **6** is coordinated by one carbon from ylide, one oxygen of coordinated DMSO and two bromo atoms in a distorted tetrahedral geometry. The two different Hg–Br distances in **6** (2.6166(10) and 2.5204(9) Å) are less than those found in the mononuclear complex of $[HgBr_2(PPh_3)_2]$ (2.633(6) and 2.626(8) Å) [27], indicating relatively strong Hg–Br bonds in **6**. The difference between two distances in these complexes might be arising from steric effects of the large ylidic groups. The angles around mercury vary from 88.3(3) to 138.80(17), indicating a much distorted tetrahedral environment. This distortion must be due to the higher s character of the sp^{3} hybrid mercury orbitals involved in the above bonds and the steric effects of phosphine group causing the C–H–Br angle to be larger. In complex **6**, a medium intermolecular interactions, including C–H (25) Phenyl....Br (1) (3.044 Å) (symmetry operations used: 1.5–*x*, –½+*y*, ½–*z*), determine the structural assembly in this compound (Fig. 2).

Table 1
Crystal data and refinement details for **6**.

Identification code	**6**
Empirical formula	$C_{29}H_{29}Br_2Hg_1O_2P_1S_1$
Formula weight	832.95
Temperature	298(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2/_1n$
Unit cell dimensions	$a = 16.7187(16)$ Å $b = 10.7949(6)$ Å $c = 18.6553(18)$ Å $\beta = 115.677(7)^\circ$
Volume (Å^3)	3034.4(4)
Z, calculated density (mg/m$_3$)	4,1.823
Absorption coefficient (mm^{-1})	7.851
F(000)	1600
Crystal size (mm)	$0.30 \times 0.15 \times 0.10$ mm
θ, range for data collection (°)	2.17–29.25
Limiting indices	$-18 \leq h \leq 22$ $-12 \leq k \leq 14$ $-25 \leq l \leq 25$
Reflections collected/unique	21,289/8119 [R(int) = 0.0919]
Completeness	98.4%
Absorption correction	Numerical
Max. and min. transmission	0.450 and 0.250
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	8119/0/325
Goodness-of-fit on F^2	0.899
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0543$, $wR_2 = 0.1073$
R indices (all data)	$R_1 = 0.1165$, $wR_2 = 0.1254$
Largest diff. peak and hole (eÅ^3)	1.818 and −0.945

Table 2
Selected bond lengths (Å) and angles (°) for **6**[a].

Bond lengths	
Hg(1)–C(1)	2.221 (7)
Hg(1)–Br(1)	2.6166 (10)
Hg(1)–Br(2)	2.5204 (9)
Hg(1)–O(2)	2.540 (7)
P(1)–C(1)	1.788 (7)
O(1)–C(2)	1.230 (8)
C(1)–C(2)	1.498 (10)
O(2)–S(1)	1.412 (8)
Bond angles	
Br(2)–Hg(1)–Br(1)	106.33 (3)
C(1)–Hg(1)–Br(2)	138.80 (17)
C(1)–Hg(1)–Br(1)	113.13 (17)
C(1)–Hg(1)–O(2)	88.3 (3)
O(2)–Hg(1)–Br(2)	91.3 (2)
O(2)–Hg(1)–Br(1)	106.9 (4)
C(2)–C(1)–P(1)	112.8 (5)
C(2)–C(1)–Hg(1)	109.3 (4)
P(1)–C(1)–Hg(1)	110.5 (3)

[a] See Fig. 1 for the atom numbering.

The stabilized resonance structure for the parent ylides is destroyed by the complex formation 6; thus, the C(H)–C bond length 1.498(10) Å is significantly longer than the corresponding distance found in the similar uncomplexed phosphorane (1.407(8) Å [28] and 1.401(2) Å) [29]. On the other hand, the bond length of P–C(H) in the similar ylide is 1.7194(17) Å [30], which shows that the corresponding bond is considerably elongated to 1.788(7) Å. The C-coordination of the title ylide is in contrast to the O-coordination of the phosphorus ylide $Ph_3PC(COMe)(COPh)$ (ABPPY) in a different Hg(II) complex [30]. The difference in coordination mode between ABPPY and these ylides to Hg(II) can be rationalized in terms of the electronic properties and steric requirements of the ylides. The lower electronic density at the ylidic C atom in doubly stabilized ylides compared to simple stabilized ylides has been calculated by DFT (density functional theory) methods recently [31]. It was also demonstrated in the same paper that these factors are not solely responsible for the bonding

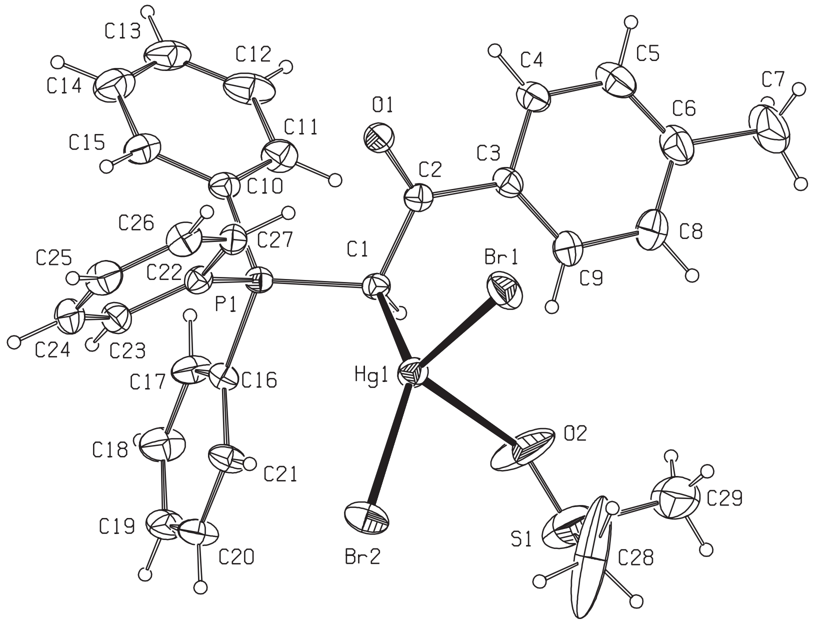


Fig. 1. ORTEP view of the asymmetric unit of **6** (30% probability level) showing the numbering scheme.

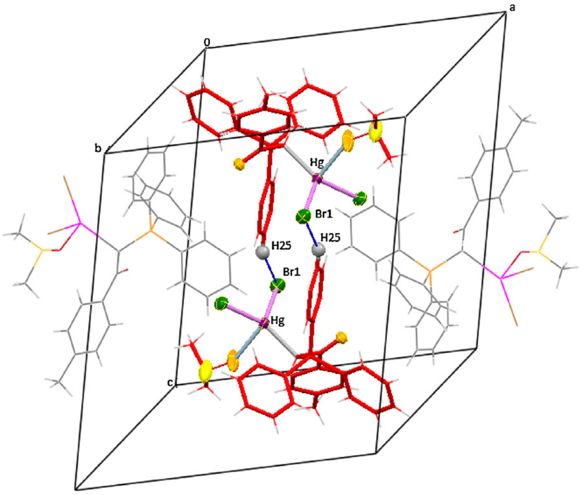


Fig. 2. A representation of complex **6** packing showing the association of the adjacent molecules through H (25) Phenyl….Br (1) interactions. Dotted lines represent the short contacts. For visualization of colors, see the online version of this article.

properties of doubly stabilized ylides. For "simple"stabilized ylides, the C- vs. O-bonding is also a very delicate balance of steric and electronic properties [32]. In this balance it is necessary to consider not only the size and shape of the ligand in the final bonding mode, but also the electronic nature of the metal (Pd, Pt, Ru, Au, etc.) and the donor atoms (C, O, N, etc.) and even the position of the coordination site (trans to a C atom, trans to a N atom, trans to an O atom, and so on). All these facts must be considered as a whole in order to account for the final bonding mode of a given ylide. The nucleophilicity of the carbanion in ABPPY is less than in our ylides; this is due to the additional delocalization of the ylide electron density in ABPPY, which is facilitated by the second carbonyl group. This will reduce the ability of ABPPY to bind via the ylidic carbon. Belluco et al. have studied steric influences on the coordination modes of ylide molecules to Pt(II) systems [8a]. These authors concluded that the preferred coordination mode is via the ylidic carbon, but that steric hindrance around the metal centre or the ylidic carbon will necessitate O-coordination. Indeed, this trend is reflected here, these ylides are slightly less sterically demanding than ABPPY and are C-coordinated to Hg(II).

Literature data show that the coordination mode of dimethylsulfoxide (DMSO) to relatively soft metal atoms depends on both electronic and steric factors deriving from the DMSO moderate π-acceptor properties and its greater steric demand, in the case of S-bonding [33]. In the case of ruthenium(II) complexes, coordination through sulfur (DMSO–S) seems to be preferred over coordination through oxygen (DMSO–O) to get stable species, unless ligand overcrowding occurs [34] or DMSO is trans to strong p-acceptors like CO [35] and NO [36]. Although on the basis of the Hard-Soft-Acid-Base principle, S-bonding is preferred by 'soft' metal ions, but with bulky ligands like present phosphorus ylides, steric effects can induce O-bonding. It may also be seen that for 'soft' metal ions, such as Ag(I), Cd(II), and Hg(II), there is evidence of a prevalence of O-bonded species, even in the absence of π-accepting or bulky ligands. This suggests that a particular electronic structure is required in order to favor the metal–sulfur bond over the metal–oxygen one [33]. Bulkiness of present ylides and the absence of the above influences in the structure shown on Fig. 2 lead to preferring O-bonding. An overestimate is found for the calculated S–O distance in 'free' DMSO (1.509 Å), which results in a value 0.018 Å longer than the experimental reference one of 1.492(1) Å [37]. The significant elongation of the S–O distance upon O-coordination is further confirmed by the recent X-ray structure determination of disulfoxide and related copper(II) complexes, where the average S–O distances are of 1.487(4) Å (free) and 1.520(3) Å (O-bonded) [38]. It is worth noting that in **6** the S–O bond distance of 1.412(8) Å is about 0.080 Å lower than the experimental reference value of 1.492(1) Å for free DMSO ligand [37]. To get an idea about the nature of this distance, a Cambridge Structural Database (CSD) search was carried out with the help of the Vista program (version 2.1) in the November 2010 release of the CSD version 5.32 (ref: The Cambridge Crystallographic Data Center, Cambridge, UK, 2010.). The result of this search on S–O distances for O-coordinated DMSO to any metal shows that only 18 complexes have shorter distance than 1.413 Å.

4. Conclusion

The present study describes the synthesis and characterization of mono- and dinuclear Hg(II) and Cd(II) complexes of (*p*-methylbenzoyl)methylene triphenylphosphorane as a ligand. On the basis of the physicochemical and spectroscopic data, we propose a monodentate C-coordination to the metals, which is further confirmed by the X-ray crystal structure of **6**.

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Appendix A. Supplementary data

CCDC 805758 contains the supplementary crystallographic data for complex **6**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.crci.2013.03.015.

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