

# Subtlety in the reactivity of a diketo phosphorus ylide towards mercuric halides: the unprecedented O-coordination of $\alpha$ -acetyl- $\alpha$ -benzoylmethylenetriphenylphosphorane to Hg(II)<sup>†</sup>

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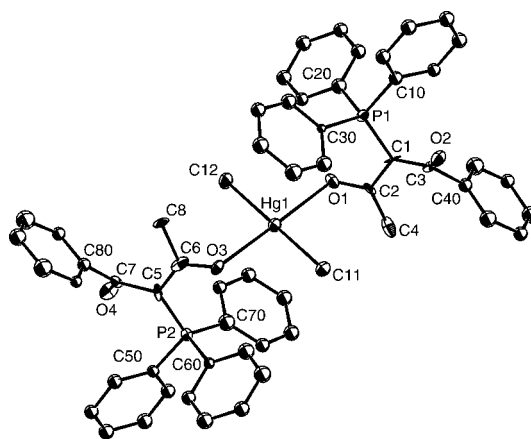
The reactions of the title ylide with HgX<sub>2</sub> (X = Cl, Br or I) lead to the regiospecific binding of the acetyl oxygen to soft Hg(II), producing a chloro complex with (2 + 2) coordination and isostructural dimeric bromo and iodo complexes containing halogen bridges with tetrahedral configurations around the metal centres.

The ambidentate resonance stabilized ylide, Ph<sub>3</sub>PCHCOPh coordinates through carbon and oxygen to Hg(II)<sup>1,2</sup> and U(VI),<sup>3</sup> respectively. The diketo ylide,  $\alpha$ -acetyl- $\alpha$ -benzoylmethylenetriphenylphosphorane (ABPPY) has an additional oxygen site for coordination and can utilize different bonding modes. The symmetrical bidentate O-coordination of the carbonyl groups had been recently observed by us in its reaction with uranyl nitrate.<sup>3</sup> We present herein the regiospecific coordination of the diketo ylide to the soft metal center, Hg(II) via the acetyl oxygen. This paper represents the first report of O-coordination of any keto phosphorus ylide to Hg(II).

The parent ylide was prepared by the action of acetic anhydride on Ph<sub>3</sub>PCHCOPh and spectrally characterized as published.<sup>4</sup> The action of HgX<sub>2</sub> on an equimolar methanolic solution of the ylide afforded the complexes HgCl<sub>2</sub>(ABPPY)<sub>2</sub> (**1**), [HgBr<sub>2</sub>(ABPPY)]<sub>2</sub> (**2**) and [HgI<sub>2</sub>(ABPPY)]<sub>2</sub> (**3**) which were formed as crystals, on cooling the concentrated solution. Elemental analyses of the products revealed their stoichiometry. In the FTIR spectra of the products, the  $\nu_{\text{CO}}$  for the COMe group observed at 1537 cm<sup>-1</sup> for ABPPY is shifted to 1526, 1573 and 1575 cm<sup>-1</sup> in **1**, **2** and **3**, respectively. The corresponding frequencies for the CPh group occur at 1566, 1568, 1600 and 1596 cm<sup>-1</sup> in the above molecules. It is significant that the  $\nu_{\text{CO}}$  values are very similar in **2** and **3** as expected for the identical environment of their two carbonyl groups. In the <sup>13</sup>C{<sup>1</sup>H} NMR spectra of the products in CDCl<sub>3</sub>, the resonance due to the ylidic carbon at  $\delta$  86.35 as well as the <sup>1</sup>J<sub>PC</sub> of 101.8 Hz observed for the free ylide is not very much shifted in the products. The <sup>31</sup>P NMR spectra contain a single signal around  $\delta$  17 for the ylide and each of the complexes. This suggests the presence of a single isomer in all the complexes, with the oxygen being bonded to the metal. In contrast, the C-coordination which implies a change in the hybridization for the ylidic carbon is characterized by its upfield <sup>13</sup>C chemical shifts<sup>5</sup> and also by the downfield shifts of <sup>31</sup>P NMR signals.<sup>1</sup> That the bonding of the ylide to Hg(II) in the chloro complex is much weaker than in the bromo and the iodo complexes is indicative in the <sup>1</sup>H NMR spectra in which the methyl group resonances appear at  $\delta$  1.80, 1.81, 1.70 and 1.71 for the free ylide and complexes **1**, **2** and **3**, respectively.

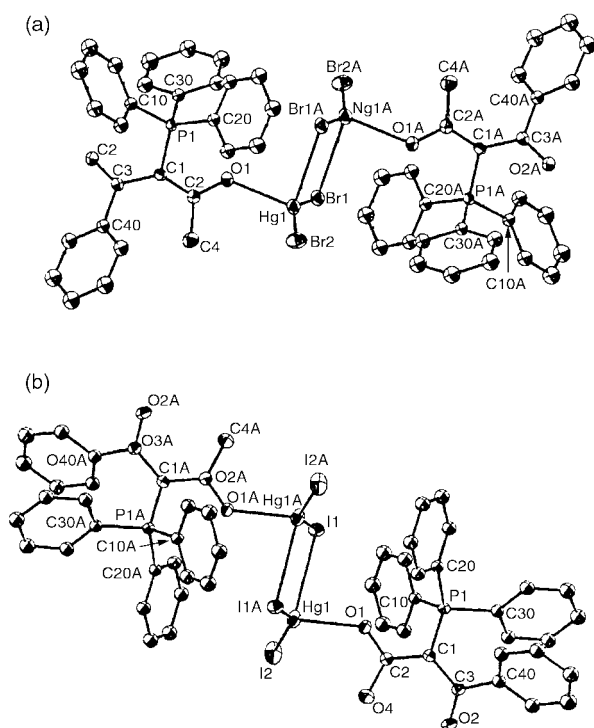
In order to establish the region and mode of coordination, single crystal X-ray analysis<sup>‡</sup> of the complexes has been

undertaken. The solid state structure of **1** shows that it adopts a square planar geometry with two collinear strong covalent Hg–Cl bonds referred to as ‘characteristic coordination.’ The preference for a characteristic coordination number of two for mercury in its complexes with electronegative ligands, as observed in **1** has been attributed to relativistic effects.<sup>6</sup> The Hg–O bond lengths are distinctly longer in the chloro complex and denoted<sup>7</sup> as ‘secondary bonds.’ The importance of such inter-species interactions has been realized in solid state architecture, molecular recognition, prototype ‘ionic liquids’ and biological chemistry.<sup>8</sup> Semiempirical calculations at the PM3 level<sup>9</sup> corroborate the geometry and bond parameters of **1**, discerned from X-ray crystallography. In particular, the calculated values, 173.9 and 179.2°, for O–Hg–O and Cl–Hg–Cl angles, respectively, are comparable to the experimental values (Fig. 1). Mulliken population analysis<sup>10</sup> on the title ylide shows that the oxygen of the COMe group possesses a higher negative charge (–0.47) than the oxygen of the CPh group (–0.38). The linear disposition of secondary bonds in **1** is traceable to the electrostatic interactions caused by the bulky ylide ligands precluding any weak covalent interactions involving p orbitals. The latter type of interactions is indicated by B3LYP<sup>11</sup>/LANL2DZ<sup>12</sup> calculations for the identical Hg–O bonds in HgCl<sub>2</sub>(HCHO)<sub>2</sub><sup>13</sup> and likely to be present in the crystal structure of HgCl<sub>2</sub>(chd) (chd = cyclohexane-1,4-dione) complex<sup>14</sup> with an observed O–Hg–O angle of 86°. The Hg(II) in each of the molecules **2** and **3** has a tetrahedral coordination environment with two unsymmetrically bridging Hg–X bonds. The oxygen of the acetyl group is oriented *cis* to the phosphorus



**Fig. 1** ORTEP view of **1** with 50% probability thermal ellipsoids and selected atom labelling scheme. The hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Hg1–O1 2.707(2), Hg1–O3 2.735(2), Hg1–Cl1 2.283(4), Hg1–Cl2 2.297(3); O1–C2 1.275(11), O2–C3 1.227(11), O3–C6 1.249(12), O4–C7 1.247(11), P1–C1 1.788(8), P2–C5 1.731(10), Cl1–Hg1–Cl2 179.8(2), O1–Hg1–O3 179.0(2), Hg1–O1–C2 118.4(7), Hg1–O3–C6 123.5(7).

<sup>†</sup> Electronic supplementary information (ESI) available: analytical and spectroscopic data for **1–3**. See <http://www.rsc.org/suppdata/cc/b1/b104082k/>



**Fig. 2** ZORTEP view of **2** and **3** with 50% probability thermal ellipsoids and selected atom labelling scheme. The hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): for **2**: Hg1–O1 2.397(3), Hg1–Br1 2.4693(5), Hg1–Br2 2.4420(5), Hg1–Br1A 2.9997(5), O1–C2 1.270(5), O2–C3 1.239(5), P1–C1 1.770(4); O1–Hg1–Br1 100.86(7), O1–Hg1–Br2 105.87(7); O1–Hg1–Br1A 87.67(7), Br1–Hg1–Br1A 90.76(2), Hg1–O1–C2 128.9(3). For **3**: Hg1–O1 2.370(3), Hg1–I1 3.120(1), Hg1–I2 2.615(1), Hg1–I1A 2.676(1), O1–C2 1.269(5), O2–C3 1.223(5), P1–C1 1.766(4); O1–Hg1–I1 81.37(8), O1–Hg1–I2 104.05(8), O1–Hg1–I1A 102.80(8), I1–Hg1–I1A 92.49(1), Hg1–O1–C2 129.6(3).

in all the three complexes as is evident from the P–C–O torsion angles of 0.0 and 6.1° in **1**, 0.8° in **2** and 8.31° in **3**.

We conclude that novel bonding modes to Hg(II) could be mediated by the flexidentate ylide, ABPPY. It is significant that HgCl<sub>2</sub> prefers to form the 1:2 complex, *albeit* with secondary Hg...O interactions. The coordination of the ylide to mercury in **2** and **3** through the lone pair on the unpolarized acetyl oxygen is shown by the C2–O1 and C1–C2 bond lengths, by the bond angles around the trigonal acetyl oxygen (Fig. 2) and also by the upward shifts for the  $\nu_{\text{CO}}$  of COMe group in the IR spectra of the products. This type of bonding that involves the canonical keto form of the ylide contrasts with the enolate bonding of Ph<sub>3</sub>PCHCOMe.<sup>15</sup> We ascribe this keto-coordination of the ylide found in both **2** and **3** to the symbiotic effects of the softer halogens.

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## Notes and references

† Crystal data: for **1**: C<sub>56</sub>H<sub>46</sub>Cl<sub>2</sub>HgO<sub>4</sub>P<sub>2</sub>,  $a = 13.4399(2)$ ,  $b = 10.0105(3)$ ,  $c = 17.9576(4)$  Å,  $\beta = 100.525(2)^\circ$ ,  $V = 2375.37(10)$  Å<sup>3</sup>, space group  $P2_1$ ,  $Z = 2$ ,  $D_c = 1.561$  Mg m<sup>-3</sup>,  $\mu(\text{Mo-K}\alpha) = 3.467$  mm<sup>-1</sup>, reflections collected/unique 25177/11404, refinement method: full-matrix least-squares on  $F^2$ ; data/restraints/parameters 11403/1/254, goodness-of-fit on  $F^2$  1.025. Final  $R$  indices [ $I > 2\sigma(I)$ ]  $R_1 = 0.0267$ ,  $wR_2 = 0.0587$ ;  $R$  indices (all data)  $R_1 = 0.0430$ ,  $wR_2 = 0.0645$ .

For **2**: C<sub>28</sub>H<sub>23</sub>Br<sub>2</sub>HgO<sub>2</sub>P,  $a = 9.5287(6)$ ,  $b = 11.6425(8)$ ,  $c = 12.3992(8)$  Å,  $\alpha = 94.835(2)^\circ$ ,  $\beta = 98.281(2)^\circ$ ,  $\gamma = 102.172(2)^\circ$ ,  $V = 1321.22(15)$  Å<sup>3</sup>, space group  $P\bar{1}$ ,  $Z = 2$ ,  $D_c = 1.968$  Mg m<sup>-3</sup>,  $\mu(\text{Mo-K}\alpha) = 8.933$  mm<sup>-1</sup>, reflections collected/unique 13906/6329, refinement method: full-matrix least-squares on  $F^2$ , data/restraints/parameters 6329/0/142, goodness-of-fit on  $F^2$  1.041. Final  $R$  indices [ $I > 2\sigma(I)$ ]  $R_1 = 0.0310$ ,  $wR_2 = 0.0743$ ;  $R$  indices (all data)  $R_1 = 0.0371$ ,  $wR_2 = 0.0766$ .

For **3**: C<sub>28</sub>H<sub>23</sub>I<sub>2</sub>HgO<sub>2</sub>P,  $a = 8.9528(2)$ ,  $b = 11.7157(3)$ ,  $c = 13.8223(2)$  Å,  $\alpha = 107.6152(12)^\circ$ ,  $\beta = 91.6914(4)^\circ$ ,  $\gamma = 99.4180(4)^\circ$ ,  $V = 1358.37(5)$  Å<sup>3</sup>, space group  $P\bar{1}$ ,  $Z = 2$ ,  $D_c = 2.144$  Mg m<sup>-3</sup>,  $\mu(\text{Mo-K}\alpha) = 8.020$  mm<sup>-1</sup>, reflections collected/unique 14475/6554, refinement method: full-matrix least-squares on  $F^2$ , data/restraints/parameters 6554/0/142, goodness-of-fit on  $F^2$  1.019. Final  $R$  indices [ $I > 2\sigma(I)$ ]  $R_1 = 0.0313$ ,  $wR_2 = 0.0637$ ;  $R$  indices (all data)  $R_1 = 0.0401$ ,  $wR_2 = 0.0669$ .

The intensity data, collected at 150 K on a standard Siemens SMART 1K CCD diffractometer were corrected for decay, Lorentz and polarization effects. Non-hydrogen atoms anisotropic; hydrogen atoms in idealized positions. Programs used: SAINT<sup>16</sup> (X-ray data processing), SADABS<sup>17</sup> (absorption correction), MOPAC6.0<sup>18</sup> (semiempirical PM3 calculations) SIR-97, (structure solution) SHELX-97 (structure refinement), PARST96 (geometrical calculations) and ZORTEP (molecular Graphics).

CCDC reference numbers 167767–167769. See <http://www.rsc.org/suppdata/cc/b1/b104082k/> for crystallographic data in CIF or other electronic format.

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