CHEMCOMM
Communication
www.rsc.org/chemcomm

Subtlety in the reactivity of a diketo phosphorus ylide towards mercuric halides: the unprecedented O-coordination of α-acetyl-α-benzoylmethylenetriphenylphosphorane to Hg(II)†

Parthasarathi Laavanya,[a] Ulaganathan Venkatasubramanian,[a] Krishnaswamy Panchanatheswaran*[a] and Jeanette A. Krause Bauer[b]

[a] *Department of Chemistry, Bharathidasan University, Tiruchirappalli 620 024, India.*
E-mail: pan@bdu.ernet.in
[b] *Department of Chemistry, University of Cincinnati, OH 45221-0172, USA.*
E-mail: Jeanette.Krause@UC.edu

Received (in Cambridge, UK) 9th May 2001, Accepted 20th July 2001
First published as an Advance Article on the web 6th August 2001

The reactions of the title ylide with HgX_2 (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, $Ph_3PCHCOPh$ coordinates through carbon and oxygen to Hg(II)[1,2] and U(VI),[3] respectively. The diketo ylide, α-acetyl-α-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.[3] 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 $Ph_3PCHCOPh$ and spectrally characterized as published.[4] The action of HgX_2 on an equimolar methanolic solution of the ylide afforded the complexes $HgCl_2(ABPPY)_2$ (**1**), $[HgBr_2(ABPPY)]_2$ (**2**) and $[HgI_2(ABPPY)]_2$ (**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 ν_{CO} for the COMe group observed at 1537 cm^{-1} for ABPPY is shifted to 1526, 1573 and 1575 cm^{-1} in **1**, **2** and **3**, respectively. The corresponding frequencies for the COPh group occur at 1566, 1568, 1600 and 1596 cm^{-1} in the above molecules. It is significant that the ν_{CO} values are very similar in **2** and **3** as expected for the identical environment of their two carbonyl groups. In the $^{13}C\{^1H\}$ NMR spectra of the products in $CDCl_3$, the resonance due to the ylidic carbon at δ 86.35 as well as the $^1J_{PC}$ of 101.8 Hz observed for the free ylide is not very much shifted in the products. The ^{31}P NMR spectra contain a single signal around δ 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 ^{13}C chemical shifts[5] and also by the downfield shifts of ^{31}P NMR signals.[1] 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 ^1H NMR spectra in which the methyl group resonances appear at δ 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‡ 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.[6] The Hg–O bond lengths are distinctly longer in the chloro complex and denoted[7] 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.[8] Semiempirical calculations at the PM3 level[9] 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[10] on the title ylide shows that the oxygen of the COMe group possesses a higher negative charge (−0.47) than the oxygen of the COPh 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[11]/LANL2DZ[12] calculations for the identical Hg–O bonds in $HgCl_2(HCHO)_2$[13] and likely to be present in the crystal structure of $HgCl_2$(chd) (chd = cyclohexane-1,4-dione) complex[14] 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

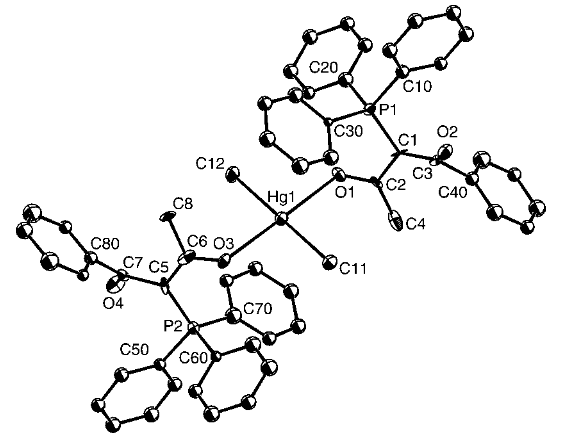

Fig. 1 ZORTEP view of **1** with 50% probability thermal ellipsoids and selected atom labelling scheme. The hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Hg1–O1 2.707(2), Hg1–O3 2.735(2), Hg1–Cl1 2.283(4), Hg1–Cl2 2.297(3); O1–C2 1.275(11), O2–C3 1.227(11), O3–C6 1.249(12), 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).

---

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

DOI: 10.1039/b104082k

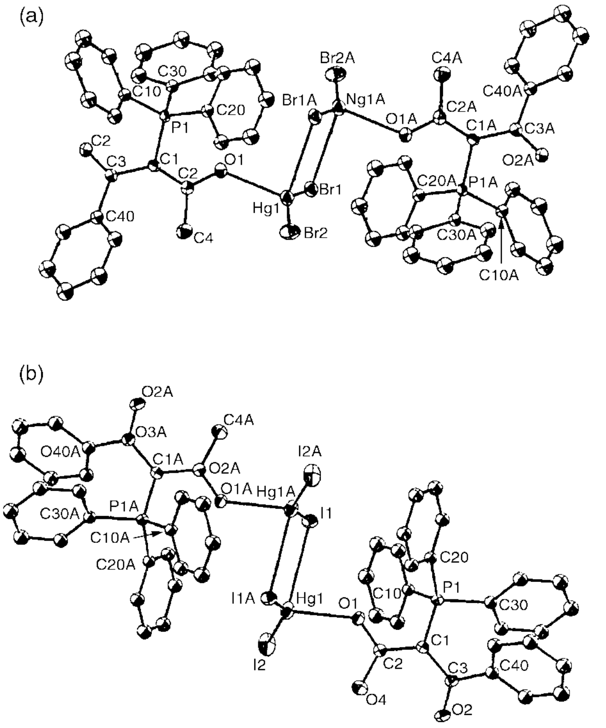

Fig. 2 ZORTEP view of **2** and **3** with 50% probability thermal ellipsoids and selected atom labelling scheme. The hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): for **2**: Hg1–O1 2.397(3), Hg1–Br1 2.4693(5), Hg1–Br2 2.4420(5), Hg1–Br1A 2.9997(5), O1–C2 1.270(5), 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–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 $HgCl_2$ 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 ν_{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 $Ph_3PCHCOMe$.[15] We ascribe this keto-coordination of the ylide found in both **2** and **3** to the symbiotic effects of the softer halogens.

P. L. thanks the Council of Scientific and Industrial Research, Government of India for the award of Senior Research Fellowship [9/475(92)/99-EMRI]. The authors thank the Ohio Crystallographic Consortium, funded by the Ohio Board of Regents 1995 Investment Fund [(CA)-075] located at the University of Toledo, Instrumentation Center in A&S, Toledo, OH 43606, USA for X-ray data collection, the Sophisticated Instruments Facility, Indian Institute of Science, Bangalore, India, for recording ^{13}C NMR spectra for the samples and Dr Mariappan Manoharan, Post-Doctoral Fellow, Centre for Computational Quantum Chemistry, University of Georgia, Athens, GA 30602-2525, USA for DFT calculations.

Notes and references

‡ *Crystal data*: for **1**: $C_{56}H_{46}Cl_2HgO_4P_2$, a = 13.4399(2), b = 10.0105(3), c = 17.9576(4) Å, β = 100.525(2)°, V = 2375.37(10) Å^3, space group $P2_1$, Z = 2, D_c = 1.561 Mg m^{-3}, μ(Mo-Kα) = 3.467 mm^{-1}, 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**: $C_{28}H_{23}Br_2HgO_2P$, a = 9.5287(6), b = 11.6425(8), c = 12.3992(8) Å, α = 94.835(2)°, β = 98.281(2), γ = 102.172(2)°, V = 1321.22(15) Å^3, space group $P1$, Z = 2, D_c = 1.968 Mg m^{-3}, μ(Mo-Kα) = 8.933 mm^{-1}, 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**: $C_{28}H_{23}I_2HgO_2P$, a = 8.9528(2), b = 11.7157(3), c = 13.8223(2) Å, α = 107.6152(12), β = 91.6914(4), γ = 99.4180(4)°, V = 1358.37(5) Å^3, space group $P1$, Z = 2, D_c = 2.144 Mg m^{-3}, μ(Mo-Kα) = 8.020 mm^{-1}, 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[16] (X-ray data processing), SADABS[17] (absorption correction), MOPAC6.0[18] (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.

1 M. Kalyanasundari, K. Panchanatheswaran, W. T. Robinson and Huo Wen, *J. Organomet. Chem.*, 1995, **491**, 103.
2 B. Kalyanasundari, K. Panchanatheswaran, V. Parthasarathi and W. T. Robinson, *Bull. Chem. Soc. Jpn.*, 1999, **72**, 33.
3 M. Kalyanasundari, Ph.D. Thesis, Bharathidasan University, Tiruchirapalli, India, 1998.
4 P. A. Chopard, R. J. G. Searle and F. H. Devitt, *J. Org. Chem.*, 1965, **30**, 1015.
5 G. Facchin, R. Bertani, M. Calligaris, G. Nardin and M. Mari, *J. Chem. Soc., Dalton Trans.*, 1987, 1381.
6 M. Kaupp and H. G. von Schnering, *Inorg. Chem.*, 1994, **33**, 2555.
7 N. W. Alcock, *Adv. Inorg. Chem. Radiochem.*, 1972, **15**, 1.
8 W. Clegg, M. R. J. Elsegood and N. C. Norman, *J. Mater. Chem.*, 1994, **4**, 891; G. M. Whitesides, J. P. Mathias and C. T. Seto, *Science*, 1991, **254**, 1312; J. J. Golding, D. R. MacFarlane, L. Spiccia, M. Forsyth, B. W. Skelton and A. H. White, *Chem. Commun.*, 1998, 1593; D. H. Williams and M. S. Westwell, *Chem. Soc. Rev.*, 1998, **27**, 57.
9 J. J. P. Stewart, *J. Comput. Chem.*, 1989, **10**, 221.
10 R. S. Mulliken, *J. Chem. Phys.*, 1955, **23**, 1833.
11 A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648.
12 M. J. Frish, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Alhaham, V. G. Zakrewski, J. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Matin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. J. P. Stewart, M. H. Gordon, C. Gonzalez and J. A. Pople, GAUSSIAN94, revision B.3, Gaussian, Pittsburgh, PA, 1995.
13 Calculated parameters for $HgCl_2(HCHO)_2$: Hg–O 2.571 Å, C–O 1.248 Å, Hg–Cl 2.472, 2.542 Å; O–Hg–O 96.8, Cl–Hg–Cl 156.9°.
14 P. Groth and O. Hassel, *Acta Chem. Scand.*, 1964, **18**, 1327.
15 L. R. Falvello, S. Fernandez, R. Navarro and E. P. Urriolabeitia, *Inorg. Chem.*, 1996, **35**, 3064.
16 Siemens, SMART V5.051 and SAINT V5.A06, Area Detector Control and Integration Software, BRUKER-AXS Inc., Madison, WI, USA, 1994.
17 G. M. Sheldrick, SADABS, University of Göttingen, Germany, 1996.
18 J. J. P. Stewart, MOPAC6.0, QCPE No. 455, Indiana University, Bloomington, IN, 1990.