

The synthesis and structural characterisation of the mercury (II) halide complexes of the phosphorus ylide carbethoxymethylenetriphenylphosphorane

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Abstract

The reaction of the ylide carbethoxymethylenetriphenylphosphorane (EPPY), Ph₃PCHCOOEt, with mercury (II) halides has been investigated. The resulting dimeric mercury (II)-ylide complexes are isostructural and of the form [(EPPY)(HgX₂)₂] where X is either bromine (1), chlorine (2), or iodine (3). These complexes have been characterised by spectroscopic techniques and X-ray diffraction. The ylide ligands have been shown to be C-coordinated to the mercury (II) atom.

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1. Introduction

The utility of metalated phosphorus ylides in synthetic chemistry has been well documented [1,2]. Herein we report on the preparation and structural elucidation of the mercury halide complexes of the ylide EPPY.

The juxtaposition of the keto group and carbanion in phosphorus ylide EPPY allows for the resonance delocalisation of the ylidic electron density providing additional stabilisation to the ylide species (Scheme 1). This so-called α -stabilisation provides EPPY with the potential to act as an ambi-dentate ligand and thus bond to an Hg(II) centre through either the carbanion (ii) or the enolate oxygen (iii). The enolate form (iii) may assume either a *cis* or *trans* arrangement, the geometry of which will be retained upon bonding to Hg(II).

From consideration of the HSAB rules [3] it can be hypothesised that the EPPY ligand will coordinate to the ‘soft’ Hg(II) ion via the ‘soft’ ylidic carbon atom as opposed to the ‘hard’ carbonyl oxygen atom. Navarro and Urriolabeitia have published an excellent study of the bonding modes of α -stabilised phosphorus ligands [4], and the reader is directed to this article and the reference therein for a full appreciation of the flexible nature of the ligating properties of such ylides.

2. Experimental

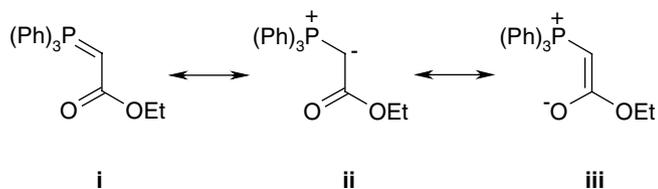
2.1. Sample preparation

2.1.1. EPPY [5]

The reaction of α -chloroethyl acetate with triphenylphosphine at 343–348 K gave the chloride salt of EPPY as a white crystalline solid; this was washed with diethyl ether and dried (m.p. 363 K, yield: 81.9%). To prepare the free ylide, a cold aqueous solution of KOH was added

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Scheme 1. The canonical forms of EPPY.

to an aqueous solution of the prepared phosphonium salt. A thick pasty solid separated out from this solution, which was subsequently refrigerated to give a white solid. This solid was then re-crystallised from benzene via the vapour diffusion method using petroleum ether as the diffusing solvent. m.p. 126–127 °C, yield: 89.5%.

2.1.2. Complexes **1**, **2** and **3**

A solution of the appropriate mercury (II) halide (0.05 mmol) in methanol was added to a methanolic solution of EPPY (0.20 g, 0.05 mmol) at room temperature and stirred overnight. The solvent was then removed in vacuo. White crystals were obtained by crystallisation of the crude product from chloroform using the vapour diffusion method using petroleum ether as the diffusing solvent.

1: m.p. 431–433 K, yield: 87.2%. Anal. Found: C, 35.48%; H, 2.84%. $C_{22}H_{21}O_2PHgBr_2$ Anal. Calc.: C, 37.29%; H, 2.99%.

2: m.p. 423–425 K, yield: 92.6%. Anal. Found: C, 41.42%; H, 3.34%. $C_{22}H_{21}O_2PHgCl_2$ Anal. Calc.: C, 42.63%; H, 3.42%.

3: m.p. 425–427 K, yield: 80.1%. Anal. Found: C, 33.10%; H, 2.63%. $C_{22}H_{21}O_2PHgI_2$ Anal. Calc.: C, 32.92%; H, 2.64%.

2.2. Instrumentation

Solution-state 1H , ^{31}P and ^{13}C NMR spectra at ambient probe temperature were obtained on solutions in CD_2Cl_2 using a Varian Mercury-400 spectrometer operating at 399.97 MHz for 1H , 161.91 MHz for ^{31}P and 100.57 MHz for ^{13}C . Solution-state 1H and ^{31}P spectra at 193 K were obtained in CD_2Cl_2 using a Varian Inova-500 spectrometer operating at 499.77 MHz for 1H , and 202.31 MHz for ^{31}P . All spectra were referenced to the relevant IUPAC standards via the frequency of the lock signal.

Solid-state ^{31}P NMR spectra at ambient probe temperature were obtained using a Varian Inova-300 spectrometer operating at 121.37 MHz for ^{31}P by cross-polarisation with a contact time of 3 ms and a recycle delay of 120 s.

2.3. X-ray crystallography

All data were collected at 120 K using graphite monochromated X-radiation ($\lambda = 0.71073 \text{ \AA}$) on a Bruker SMART 6 K diffractometer. Data processing was performed using standard Bruker software [6]. Structure

solutions were via Direct Methods. Refinement was on F^2 using full-matrix least-squares techniques. All data were corrected for absorption using SADABS [7]. All hydrogen atoms are placed at calculated positions, and have been refined with a riding model. The exception being the hydrogen atoms residing on the ylide carbon, these were located in the difference Fourier map and their positional parameters were refined (U_{iso} fixed at 120% of the parent atom). These were then fixed for the final round of least-squares refinement.

3. Results and discussion

3.1. X-ray crystallography

Table 1 provides crystallographic results and refinement information for all complexes. The molecular structures of **1**, **2**, and **3** are shown in Figs. 1–3, respectively. The dimeric complexes crystallise in the centrosymmetric space group $P\bar{1}$, and straddle the crystallographic inversion centre.

Monomeric material was found to be present as a minor component, approximately 5%, of the crystalline state of **2** (Fig. 2). The monomer is of the form $[(EPPY)(HgCl)]$ in which EPPY is C-coordinated to the Hg(II) centre. The chlorine atom of this second component could not be resolved from the disordered $CHCl_3$ solvent molecule. The crystallographic model for **3** also includes a disordered component. In this case, approximately 5% of un-reacted $(HgI_2)_2$ had crystallised with the complex. The positional and atomic displacement parameters for the disordered components in **2** and **3** were refined freely. The occupancy values were fixed at 0.05 for the final round of least-squares refinement. Further discussion of complexes **2** and **3** will be confined to consideration of the principal components only.

In all three complexes the mercury atom is sp^3 hybridised and resides in a distorted tetrahedral environment. The inter-nuclear distances between mercury atoms of the dimer units are greater than twice the ionic radii for 4-coordinate Hg(II) (2.20 Å) [8], indicating the absence of significant bonding interactions between the mercury atoms in these complexes.

The dimeric structure adopted by complexes **1**, **2** and **3** is in contrast to the C-coordinated trinuclear mercury (II) complex of the phosphorus ylide $Ph_3PCHCOPh$ [9], but are similar to the structure of *trans*-Di- μ -iodo-diiodobis(triphenylphosphoniumcyclopentadienylide)dimercury (II) reported by Baenziger et al. [10] and the C-coordinated dinuclear mercury (II) halide complexes of $Ph_3PCHCOPh$ (BPPY) [11].

Tables 2–4 list key bond lengths and angles for complexes **1**, **2** and **3**, respectively. The Hg–C, Hg–Cl bond lengths are notably shorter in **2** in comparison with the corresponding BPPY complex (Hg–C: 2.208(8) Å, Hg–Cl(μ): 2.710(2) Å, and Hg–Cl: 2.417(3) Å.). A similar scenario is found for complex **3** and the equivalent BPPY–Hg(II) dimer, with the exception being the terminal Hg–I bond

Table 1
Crystallographic data and refinement details for complexes 1–3

| | 1 | 2 | 3 |
|--|---|--|---|
| Crystal size (cm ³) | 0.19 × 0.17 × 0.16 | 0.17 × 0.15 × 0.14 | 0.19 × 0.17 × 0.16 |
| Crystal colour | Colourless | Colourless | Colourless |
| Crystal habit | Block | Block | Block |
| Chemical formula | C ₄₄ H ₄₂ Br ₄ Hg ₂ O ₄ P ₂ (CHCl ₃) ₂ | C ₄₄ H ₄₂ Cl ₄ Hg ₂ O ₄ P ₂ (CHCl ₃) ₂ ^a | C ₄₄ H ₄₂ I ₄ Hg ₂ O ₄ P ₂ ^a |
| Formula weight (g) | 1652.24 | 1715.15 | 1603.48 |
| Crystal system | Triclinic | Triclinic | Triclinic |
| Space group | <i>P</i> $\bar{1}$ | <i>P</i> $\bar{1}$ | <i>P</i> $\bar{1}$ |
| <i>Z</i> | 1 | 1 | 1 |
| <i>a</i> (Å) | 10.6974(4) | 11.2465(6) | 10.7970(5) |
| <i>b</i> (Å) | 11.1019(4) | 11.8297(7) | 11.0485(5) |
| <i>c</i> (Å) | 12.5683(4) | 12.0170(7) | 11.3649(5) |
| α (°) | 76.161(2) | 82.602(2) | 67.813(2) |
| β (°) | 68.698(2) | 80.642(2) | 81.098(2) |
| γ (°) | 81.658(2) | 78.368(2) | 69.550(2) |
| <i>V</i> (Å ³) | 1347.49(8) | 1537.5(2) | 1175.82(9) |
| μ (Mo K α) (mm ⁻¹) | 9.052 | 5.774 | 9.253 |
| Collected reflections | 8945 | 8546 | 6922 |
| Unique reflections | 5257 | 5361 | 4556 |
| Data completeness | 99% ($2\theta_{\max} = 26^\circ$) | 99% ($2\theta_{\max} = 25^\circ$) | 99% ($2\theta_{\max} = 26^\circ$) |
| No. parameters | 283 | 329 | 272 |
| <i>R</i> _{int} | 0.0204 | 0.0478 | 0.0240 |
| <i>R</i> ₁ [<i>I</i> > 2 σ (<i>I</i>)] | 0.0349 | 0.0538 | 0.0318 |
| <i>wR</i> ₂ [<i>I</i> > 2 σ (<i>I</i>)] | 0.0837 | 0.1239 | 0.0659 |

^a The exact formula units reported in the CIF for these structures do not have integer values for the number of atoms, this is because of the site disorder observed in these structures.

(Hg–C: 2.31(1) Å, Hg–I(μ): 3.010(1) Å, and Hg–I: 2.705(1) Å. These disparities can be attributed to the greater electron withdrawing properties of the EPPY ligand with respect to BPPY.

In all three complexes the ylide ligands are C-coordinated to the Hg(II) atoms in a *trans* arrangement within the dimer unit. The coordination of the EPPY molecules via the ylide carbon (C19) introduces chiral centre to the complexes, and as a centre of inversion is intrinsic to the molecules, the complexes are meso-isomers (achiral diastereoisomers).

The C-coordination of EPPY is in stark contrast to the O-coordination of the phosphorus ylide Ph₃PC(COMe) (COPh) (ABPPY) to the Hg(II) centre [12]. The difference in coordination mode between ABPPY and EPPY to Hg(II) can be rationalised in terms of the electronic properties and steric requirements of the ylides. The nucleophilicity of the carbanion in ABPPY is less than for EPPY, this is due to the additional delocalisation 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

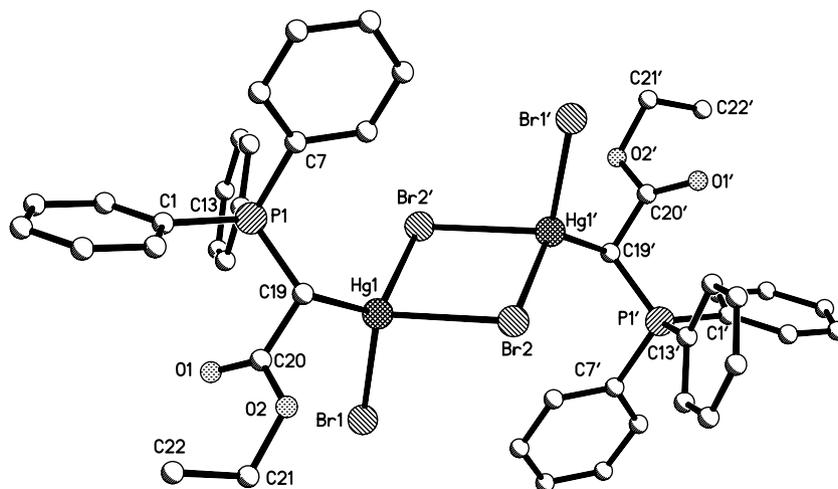


Fig. 1. The molecular structure of 1. The disordered CHCl₃ solvent molecule and hydrogen atoms have been excluded for clarity. Symmetry related atoms are shown for completeness.

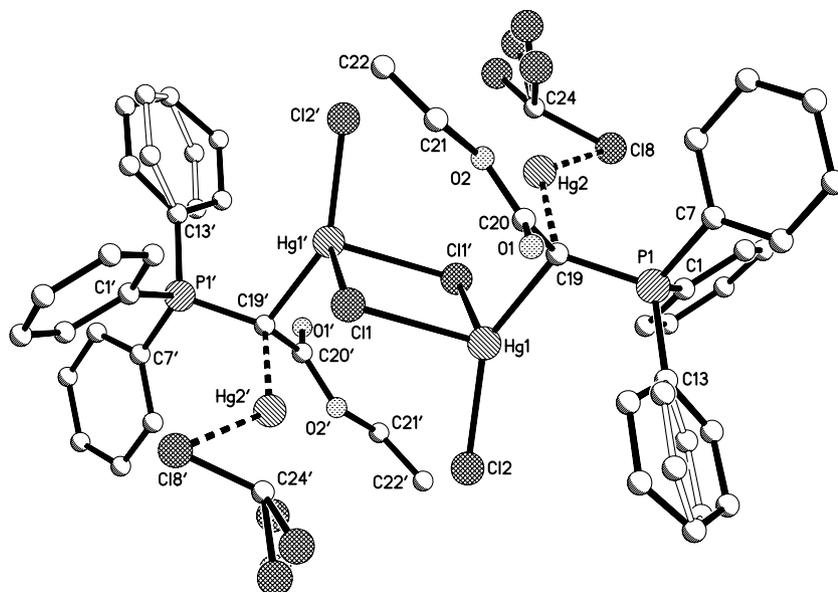


Fig. 2. Structure of complex **2**. Hydrogen atoms and the second solvent molecule are excluded for clarity. The minor monomer component is displayed using dashed bonds and disorder in the phenyl rings is shown using white bonds. Symmetry related atoms are shown for completeness.

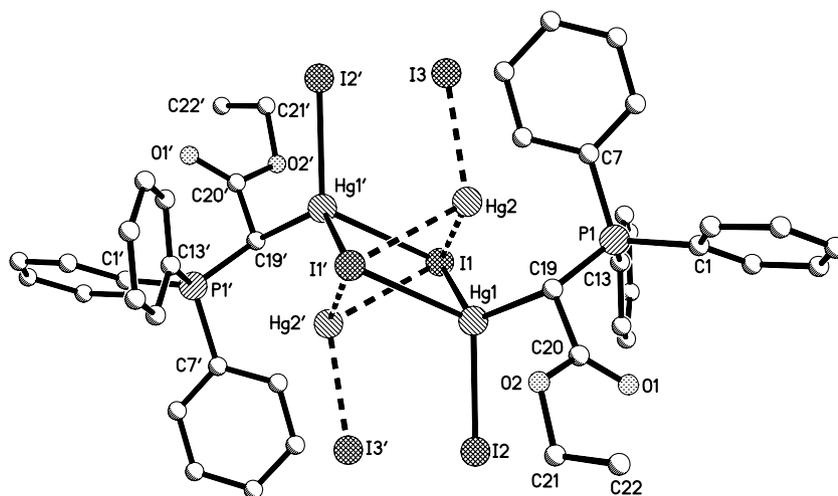


Fig. 3. Structure of complex **3**. Hydrogen atoms are omitted for clarity. The disordered component is represented with dashed bonds. Symmetry related atoms are shown for completeness.

Table 2
Selected molecular parameters for complex **1**

| Bond | Length (Å) | Atoms | Angle (°) |
|---------|------------|---------------|-----------|
| P1–C1 | 1.806(6) | P1–C19–C20 | 113.5(4) |
| P1–C7 | 1.796(5) | C19–C20–O1 | 124.5(5) |
| P1–C13 | 1.798(5) | C19–C20–O2 | 111.8(5) |
| P1–C19 | 1.788(5) | O1–C20–O2 | 123.8(5) |
| C19–C20 | 1.482(7) | O2–C21–C22 | 111.9(5) |
| O1–C20 | 1.207(7) | P1–C19–Hg1 | 111.2(2) |
| O2–C20 | 1.344(7) | Hg1–C19–C20 | 104.5(3) |
| O2–C21 | 1.455(7) | C19–Hg1–Br1 | 117.8(1) |
| C21–C22 | 1.52(1) | C19–Hg1–Br2 | 110(1) |
| Hg1–C19 | 2.224(5) | Br2–Hg1–Br2' | 87.85(2) |
| Hg1–Br1 | 2.5784(6) | P1–C19–C20–O1 | 35.3(7) |
| Hg1–Br2 | 2.8088(6) | | |

influences on the coordination modes of ylide molecules to Pt(II) systems [13]. 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, both BPPY and EPPY are slightly less sterically demanding than ABPPY, and are both C-coordinated to Hg(II).

The significant elongation of the P1–C19 and C19–C20 bonds in complexes **1**, **2** and **3** with respect to the free ylide [14] (1.706(2) Å and 1.408(2) Å, respectively) is consistent with the loss of resonance delocalisation within the ylide ligands upon complexation. The non-bonding distance between the phosphorus and oxygen atoms of the ylide molecules are 3.048(4) Å (**1**), 3.155(8) Å (**2**), and

Table 3
Selected molecular parameters for complex **2**

| Bond | Length (Å) | Atoms | Angle (°) |
|---------|------------|---------------|-----------|
| P1–C1 | 1.787(9) | P1–C19–C20 | 115.7(7) |
| P1–C7 | 1.79(1) | C19–C20–O1 | 124.6(9) |
| P1–C13 | 1.796(9) | C19–C20–O2 | 111.2(8) |
| P1–C19 | 1.78(1) | O1–C20–O2 | 124.1(9) |
| C19–C20 | 1.49(1) | O2–C21–C22 | 111(1) |
| O1–C20 | 1.22(1) | P1–C19–Hg1 | 111.2(5) |
| O2–C20 | 1.32(1) | Hg1–C19–C20 | 107.2(6) |
| O2–C21 | 1.47(1) | C19–Hg1–Cl1 | 104.4(3) |
| C21–C22 | 1.38(2) | C19–Hg1–Cl2 | 148.2(3) |
| Hg1–C19 | 2.159(9) | Cl1–Hg1–Cl1' | 90.08(7) |
| Hg1–Cl1 | 2.648(2) | P1–C19–C20–O1 | –44(1) |
| Hg1–Cl2 | 2.352(3) | | |
| | | P1–C19–Hg2 | 113.5(5) |
| Hg2–C19 | 2.25(1) | C19–Hg2–Cl8 | 130.8(4) |
| Hg2–Cl8 | 2.569(9) | C20–C19–Hg2 | 105.5(7) |

Table 4
Selected molecular parameters for complex **3**

| Bond | Length (Å) | Atoms | Angle (°) |
|---------|------------|---------------|-----------|
| P1–C1 | 1.805(7) | P1–C19–C20 | 114.0(5) |
| P1–C7 | 1.811(6) | C19–C20–O1 | 125.0(6) |
| P1–C13 | 1.799(6) | C19–C20–O2 | 111.4(6) |
| P1–C19 | 1.786(6) | O1–C20–O2 | 123.6(6) |
| C19–C20 | 1.472(9) | O2–C21–C22 | 114.1(7) |
| O1–C20 | 1.216(8) | P1–C19–Hg1 | 111.3(3) |
| O2–C20 | 1.348(7) | Hg1–C19–C20 | 102.3(4) |
| O2–C21 | 1.460(8) | C19–Hg1–I1 | 128.8(2) |
| C21–C22 | 1.45(1) | C19–Hg1–I2 | 110.8(2) |
| Hg1–C19 | 2.275(7) | I1–Hg1–I1' | 90.46(1) |
| Hg1–I1 | 2.8030(5) | P1–C19–C20–O1 | –24.0(8) |
| Hg1–I2 | 2.7349(5) | | |
| | | I1–Hg2–I3 | 110.3(3) |
| Hg2–I1 | 2.820(7) | I1–Hg2–I1' | 91.2(2) |
| Hg2–I3 | 2.70(1) | | |

3.013(5) Å (**3**). These values are considerably less than the sum of the van der Waals radii for these atoms (3.3 Å) [15] and imply the presence of significant interactions between these two atoms in all three complexes. This type of short contact is a well-known feature of ylide chemistry [16,17].

3.2. Spectroscopy

Solution-state spectra of the free ylide were obtained for reference purposes. The ^{31}P spectrum of the free ylide indicated that the *trans*-ylide was the major species [18].

^1H , ^{31}P , and ^{13}C NMR spectra of the three complexes (provided as electronic supplementary information) were consistent with the determined crystal structure being the major component present in each sample, but also indicated that the major component was present as part of a dynamic mixture. This can be most easily seen in the ^{31}P spectrum of compound **2** at 193 K (Fig. S1), where exchange between the species present has been substantially slowed. In this spectrum it is possible to distinguish peaks which we believe correspond to free *cis*-ylide

(21.0 ppm), free *trans*-ylide (21.2 ppm), *cis*-ylide in a complex containing two mercury atoms (34.3 ppm) and a peak at 26.5 ppm which we believe corresponds to both the *trans* ylide in the complex containing two mercury atoms, and *trans* ylide in a complex containing only one mercury atom, a possible monomer complex. At low temperature (193 K) the peak at 26.5 ppm exhibits satellites due to coupling to ^{199}Hg (8% intensity each, $^2J_{\text{P-Hg}} \sim 210$ Hz). These mercury satellites are also apparent in the corresponding solid-state ^{31}P spectra at ambient temperature, but cannot be resolved in the solution-state ^{31}P spectra at ambient temperature, presumably because the faster exchange at ambient temperature causes exchange decoupling. The presence of peaks due to free ylide and of peaks corresponding to a complex containing only one mercury atom in the spectrum of compound **2** suggests an excess of ylide and this is supported by the results of elemental analysis.

Comparison of the above with solution-state ^{31}P spectra of the three complexes at ambient temperature (Fig. S2) and solid-state ^{31}P spectra of the three complexes at ambient temperature (Fig. S3) shows the same basic pattern, but indicates that the amount of excess ylide present decreases in the order **2** > **1** > **3**. This is again in agreement with the results from elemental analysis. The apparent rates of exchange between the various species also changes across the series. In particular, the relatively sharp peak due to *cis*-ylide in a complex containing two mercury atoms at 33.6 ppm in the ambient temperature spectrum of compound **2** shows considerable broadening and shifts to lower frequency (32.4 ppm) in the spectrum of **1**, and is absent from the spectrum of compound **3** but an additional sharp peak is apparent in the region of the main peak (25.4 ppm) possibly the result of complete exchange averaging between free *cis*-ylide and *cis*-ylide in a complex containing two mercury atoms. However, it must be remembered that the observed effects may also depend on the relative proportions of the components so it is not possible to make firm conclusions about relative rates of exchange from the limited data available.

The dynamic nature of the mixture was further confirmed in a solution-state ^{31}P NMR experiment where a small amount of free ylide was added to a sample of **2** (CD_2Cl_2 , ambient temperature) in an attempt to confirm the assignment for free *trans*-ylide. Instead of an increase in the signal assigned to free *trans*-ylide, an increase in the relative intensity of the peak around 27 ppm was observed, together with a broadening of the signal assigned to *cis*-ylide in complex containing two mercury atoms. Our interpretation of this observation is that the presence of additional free ylide shifts the equilibrium in favour of the formation of complexes containing only one mercury atom.

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Appendix A. Supplementary material

CCDC 263302, 263303 and 263304 contain the supplementary crystallographic data for **1**, **2** and **3**. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. CIFs for complexes **1**, **2** and **3** are deposited with the Cambridge Structural Database. Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorganchem.2006.11.002](https://doi.org/10.1016/j.jorganchem.2006.11.002).

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