



Synthesis of organotin(IV) - mercury(II) heterobimetallic complexes using a hybrid ligand, 1, 2-bis(diphenylphosphino) ethane monoxide

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Abstract : The reaction of 1, 2-bis(diphenylphosphino)ethane monoxide, a hybrid ligand containing both soft (P) and hard (O) Lewis base centers in the same molecule, with organotin(IV) chloride and mercury(II) chloride has been carried out using dichloromethane as solvent. The products $[\text{HgCl}_2 \cdot (\text{dppeO}) \cdot \text{R}_2\text{SnCl}_2]_n$ [R = Me (1), Ph (2) and CH_2Ph (3)] have been obtained in excellent yields and are characterized using IR, ^1H and ^{31}P NMR spectroscopic methods. Based on the spectral data it is proposed that the structure may contain -Hg-P-O-Sn-O-P-Hg- polymeric array.

Keywords : hybrid ligands, organotin, mercury, phosphine, phosphine oxide

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1. Introduction

Hybrid ligands are polydentate ligands that contain at least two different types of chemical functionality capable of binding to metal centers. These functionalities are often chosen to be very different from each other to increase the difference between their resulting interactions with metal centers and thereby contribute to chemoselectivity. Combining hard and soft donors in the same ligand has marked the evolution of different and contrasting chemistries, thus leading to novel and unprecedented properties for the resulting metal complexes.¹ An important class of such hybrid ligands are bis-phosphine monoxides (BPMOs) of the general formula $R_1R_2P-Y-P(O)R_3R_4$, where Y is a divalent spacer. As both the *soft* (P) and *hard* (O) Lewis base centers are situated in the same molecule, these ligands are particularly suited for the stabilization of various transition metals in low and high oxidation states.² Furthermore, since these ligands provide labile metal chelates, the generation of coordinatively unsaturated species, which is an essential step in homogeneous catalytic cycle, is very facile.³ Thus, BPMOs by virtue of their unique properties have proven useful in important homogeneous catalytic processes such as methanol carbonylation⁴ (the Monsanto acetic acid process), olefin hydroformylation⁵ and hydrocarboxylation⁶ in addition to their utility as synthetic intermediates. Interestingly, these hybrid ligands have also been used in AIDS research.⁷

It was envisaged that BPMOs could offer excellent prospects for the generation of a novel class of heterobimetallic systems comprising of tin(IV) and mercury(II) centers. Organotin(IV) compounds have been used as catalyst for esterifications, transesterifications and in the synthesis of polyurethane.⁸ The utility of mercury compounds in organic transformations is widespread.⁹ Furthermore, the environmental toxicity of both organotin(IV) and mercury compounds imposes the need to develop efficient complexing agents.

This paper details the exploration of the reactions between a BP MO ligand, 1, 2-bis(diphenylphosphino)ethane monoxide (dppeO) with diorganotin(IV) dichlorides, R_2SnCl_2 ($R = Me, Ph, CH_2Ph$) and mercury(II) chloride.

2. Experimental

All synthetic manipulations were carried out under dinitrogen atmosphere. The solvents were dried and distilled using standard methods.¹⁰ Reactants and reagents were obtained from Aldrich Chemical Company and used without further purification. Dibenzyltin(IV) dichloride¹¹ and dppeO¹² were prepared following reported procedures. The 1H and $^{31}P\{-^1H\}$ NMR spectra were recorded on a Varian 200 MHz spectrometer, referenced relative to residual solvent and external 85% H_3PO_4 , respectively. The IR spectra in the interval of $4000-400\text{ cm}^{-1}$ were recorded on a Perkin-Elmer 1720X FT-IR spectrophotometer using KBr pellets.

2.1. Reaction of dppeO with Me_2SnCl_2 and $HgCl_2$ (1)

To a solution of dppeO (0.2 g, 0.48 mmol) in dichloromethane (10 ml), a solution of Me_2SnCl_2 (0.106 g, 0.48 mmol) also in dichloromethane (10 ml) was added and stirred overnight. To the resulting clear solution, solid $HgCl_2$ (0.131 g, 0.48 mmol) was added. The mixture was stirred additionally for 3 h, whereupon the entire solid went into the solution to give a clear solution. The solvent was reduced to 10 ml and *n*-pentane (10 ml) was added. The solution was cooled at $-5^\circ C$ for two days to yield colourless microcrystalline aggregates. Yield: 0.335 g. m.p. $>200^\circ C$ (decomposes). IR (KBr, cm^{-1}): 3052, 2913, 1588, 1483, 1436, 1406, 1332, 1155($\nu_{P=O}$), 1122, 1097, 1026, 997, 886, 775, 741, 727, 689, 575, 537, 505, 481.

2.2. Reaction of dppeO with Ph_2SnCl_2 and $HgCl_2$ (2)

To a solution of dppeO (0.2 g, 0.48 mmol) in dichloromethane (10 ml), a solution of Ph_2SnCl_2 (0.165 g, 0.48 mmol) also in dichloromethane (10 ml) was added and stirred

overnight. To the resulting turbid solution, solid HgCl_2 (0.131 g, 0.48 mmol) was added. The mixture was stirred additionally for 3 h, whereupon the entire solid went into the solution to give a clear solution. The solvent was reduced to 10 ml and addition of *n*-pentane (20 ml) caused the precipitation of a white solid which was filtered, washed with diethyl ether and vacuum dried. Yield: 0.32 g. m.p. $>200^\circ\text{C}$ (decomposes). IR (KBr, cm^{-1}): 3053, 1589, 1479, 1435, 1384, 1331, 1185, 1145($\nu_{\text{P=O}}$), 1122, 1092, 1023, 997, 882, 730, 692, 537, 514, 496.

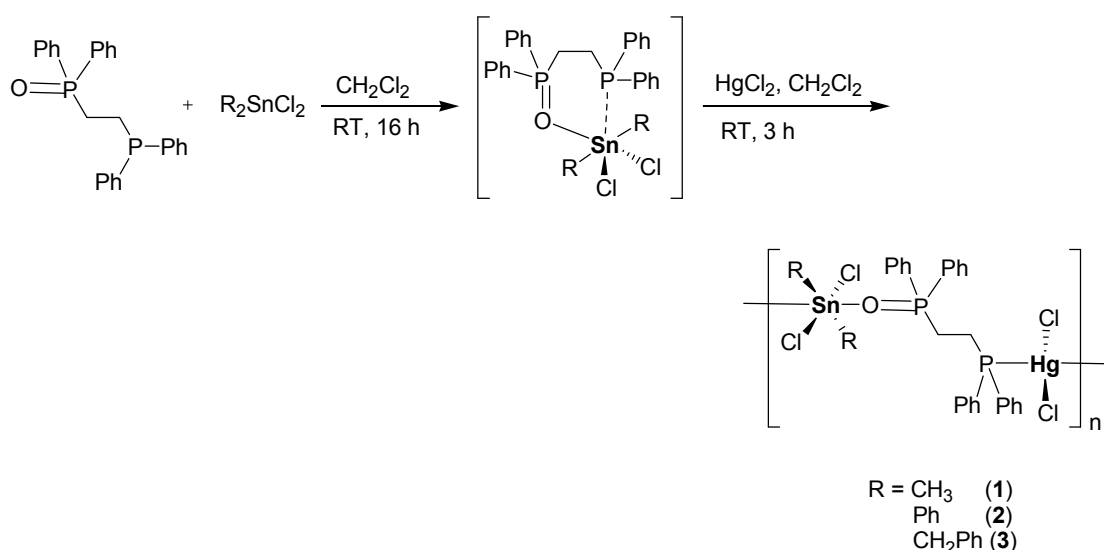
2.3. Reaction of dppeO with Bz_2SnCl_2 and HgCl_2 (3)

To a solution of dppeO (0.2 g, 0.48 mmol) in dichloromethane (10 ml), a solution of Bz_2SnCl_2 (0.178 g, 0.48 mmol) also in dichloromethane (10 ml) was added and stirred overnight. To the resulting clear solution, solid HgCl_2 (0.131 g, 0.48 mmol) was added. The mixture was stirred additionally for 3 h, whereupon the entire solid went into the solution to give a clear solution. The solvent was reduced to 10 ml and addition of *n*-pentane (20 ml) caused the precipitation of off-white solid which was filtered, washed with diethyl ether and vacuum dried. Yield: 0.35 g. IR (KBr, cm^{-1}): 3056, 2910, 1590, 1492, 1451, 1437, 1406, 1313, 1152($\nu_{\text{P=O}}$), 1123, 1088, 1027, 997, 739, 693, 550, 533, 500. ^1H NMR (200 MHz, CDCl_3): 2.94 (br, P- CH_2), 2.98 (t, Sn- CH_2); [$^2J(^{119}\text{Sn}-^1\text{H})$: 100.3], [$^2J(^{117}\text{Sn}-^1\text{H})$: 96.3], 6.87-7.87 (m, Ph). ^{31}P NMR (81 MHz, CDCl_3): 29.83 (br, PPh₂); [$^1J(^{199}\text{Hg}-^{31}\text{P})$: 4860], 37.01 (br, P(O)Ph₂).

3. Results and discussion

The reaction of dppeO with various organotin(IV) chlorides followed by treatment with mercury(II) chloride led to stable, colourless microcrystalline products. Compounds **1** and **2** are insoluble in common organic solvents, whereas compound **3** shows moderate solubility.

The IR spectra of the products **1**, **2** and **3** were recorded using KBr. The most important and strongest among the various IR spectral bands is the $\nu(\text{P}=\text{O})$ frequency, which occurs at 1155, 1145 and 1152 cm^{-1} , respectively for compounds **1**, **2** and **3**. The downward shift of this frequency by about $\sim 25 \text{ cm}^{-1}$ when compared to that of the free dppeO (1182 cm^{-1}) is a clear indicator of the phosphine oxide coordination. A comparison of P=O stretching frequencies in free dppeO as well as its mercuric chloride complexes is presented in Table 1. From the table, it can be inferred that the products are different from both 1:1 and 1:2 complexes of $\text{HgCl}_2 - \text{dppeO}$ in which the $\nu(\text{P}=\text{O})$ frequency occurs at 1161 and 1188 cm^{-1} , respectively.



Scheme 1. Synthetic pathway for the generation of heterobimetallic compounds

Due to the solubility of product **3** in CDCl_3 , both ^1H and ^{31}P NMR spectra were measured. The respective spectra are shown in Fig. 1 and 2. The presence of tin is indicated by the ^1H NMR spectrum. A signal at 2.98 ppm with the corresponding satellites due to coupling with ^{119}Sn and ^{117}Sn can be attributed to the benzylic CH_2 group attached to tin. The upfield shift of this signal when compared to the same signal in free dibenzyltin dichloride (3.15 ppm) indicates complexation. In addition, the increase in coupling constant [$^2J(^{119}\text{Sn}-^1\text{H})$: 100.3], [$^2J(^{117}\text{Sn}-^1\text{H})$: 96.3] when

compared to corresponding $^2J(^{119/117}\text{Sn-H})$ value of 78.2 Hz in free dibenzyltin dichloride confirms the increase of tin coordination number.¹³ The CH_2 protons of the ligand occur as a broad signal centred at 2.94 ppm.

The ^{31}P NMR spectrum shows two broad signals. The signal at 29.83 ppm with poorly resolved ^{199}Hg satellites [$^1J(\text{Hg-P}) = 4860$] indicates the Hg-P coordination. The similarity of the coupling constant with that for the $[\text{HgCl}_2(\text{dppeO})_2]$ complex [$^1J(\text{Hg-P}) = 4654$] is suggestive of 1:2 (Hg:P) coordination environment around mercury. It is to be noted that the 1:1 compound $[\text{HgCl}_2(\text{dppeO})]$ exhibits the $^1J(\text{Hg-P})$ coupling constant value 7449 Hz.¹⁴ The signal at 37.01 ppm can be attributed to Sn-O-P coordination. Based upon the above spectral properties it is proposed that the structure may contain -Hg-P---O-Sn-O---P-Hg- polymeric array as shown in Scheme 1. The solubility properties also support the polymeric nature of the resulting products.

4. Conclusions :

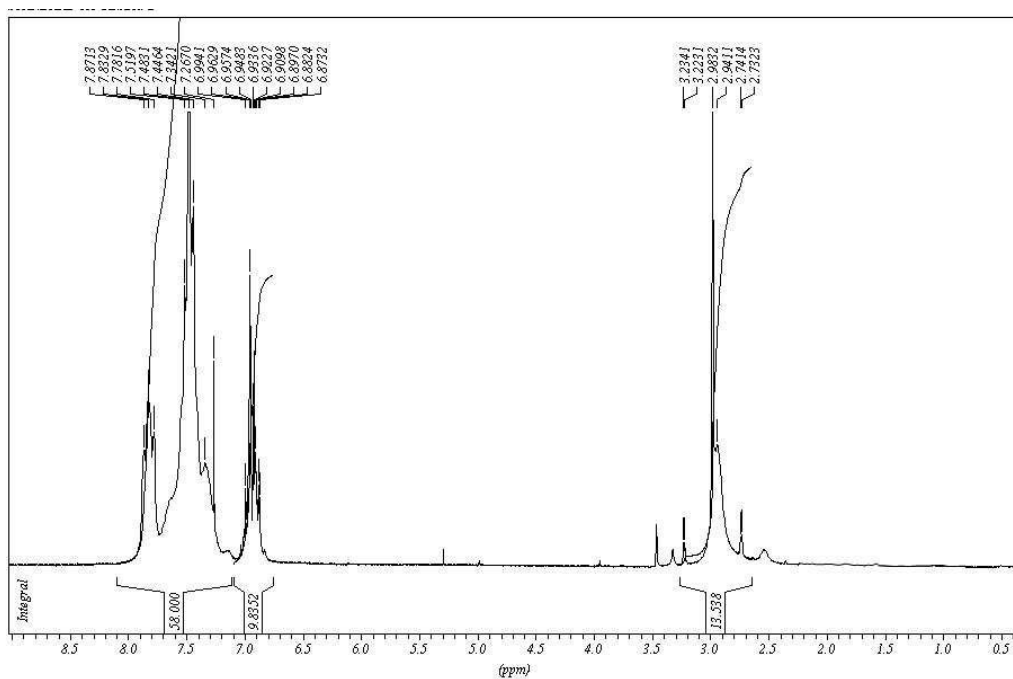
An exploration has been carried out to assess the ability of hybrid phosphine – phosphine oxide ligand, dppeO in the assembly of heterobimetallic complexes containing organotin(IV) and mercury(II) ions. The synthetic sequence has been optimized to avoid the formation of undesirable monomeric or polymeric HgCl_2 – dppeO complexes. The desired heterobimetallic compounds could be achieved by the sequential addition of organotin(IV) chloride followed by mercury(II) chloride to the ligand. Based on the IR, ^1H and ^{31}P NMR spectral studies a polymeric structure has been proposed in which the ligand binds to tin(IV) and Hg(II) in a bridging bidentate mode. The *hard* acid, tin(IV) coordinates to *hard* base, phosphine oxide and the *soft* acid, Hg(II) coordinates to *soft* base, phosphine in the hybrid ligand, dppeO.

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Table 1. Comparison of $\nu(\text{P}=\text{O})$ in selected dppeO complexes

Compound	$\nu(\text{P}=\text{O})$ (cm^{-1})
dppeO	1182
$\text{HgCl}_2 \cdot \text{dppeO}$	1161
$\text{HgCl}_2(\text{dppeO})_2$	1188
$\text{HgCl}_2 \cdot \text{dppeO} \cdot \text{Me}_2\text{SnCl}_2$	1155
$\text{HgCl}_2 \cdot \text{dppeO} \cdot \text{Ph}_2\text{SnCl}_2$	1148
$\text{HgCl}_2 \cdot \text{dppeO} \cdot \text{Bz}_2\text{SnCl}_2$	1150

**Figure 1. ^1H NMR (CDCl_3) spectrum of $\text{HgCl}_2 \cdot \text{dppeO} \cdot (\text{CH}_2\text{Ph})_2\text{SnCl}_2$ (3)**

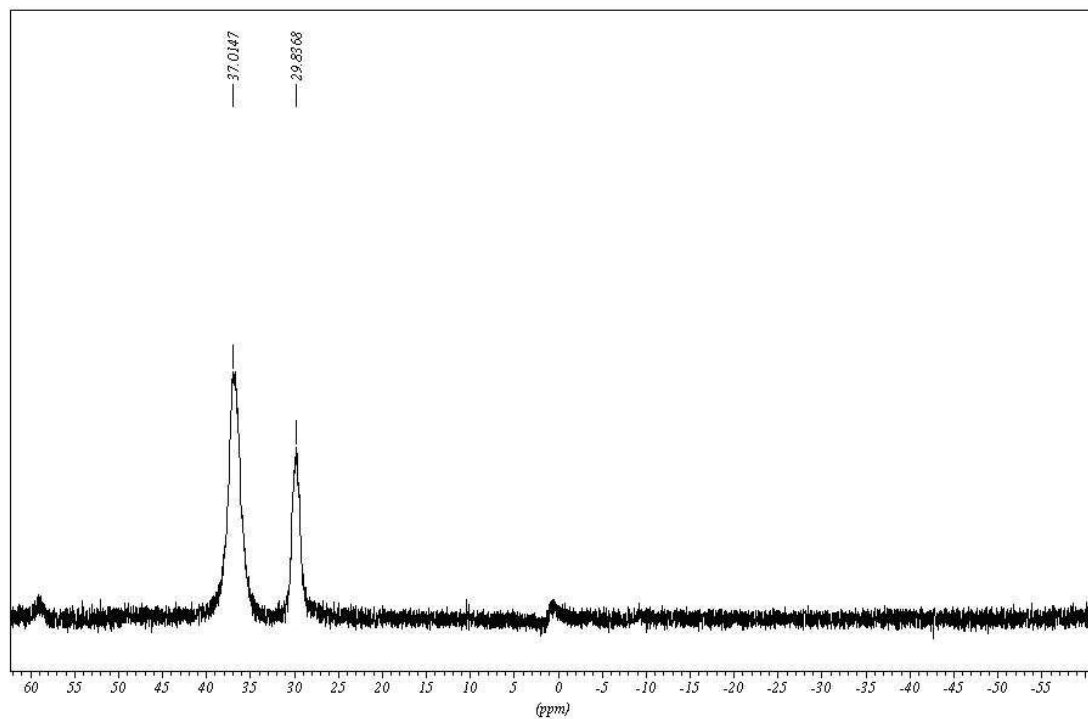


Figure 2. ^{31}P NMR (CDCl_3) spectrum of $\text{HgCl}_2 \cdot \text{dppeO} \cdot (\text{CH}_2\text{Ph})_2\text{SnCl}_2(3)$

