

The First *Bis* Phosphine monoxide (BPMO) Complexes of Copper(I)

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Abstract

Copper(I) complexes of *bis* phosphine monoxide ligands, diphenylphosphinoethane monoxide (dppeo) and diphenylphosphinomethane monoxide (dppmo) have been prepared and characterized. One of the complexes with dppeo was characterized by X-ray crystal structure analysis confirming Cu(I) coordination to hard and soft donors. The stability of these complexes in solution was probed via spectroscopic and electrochemical studies. Copper(I) is more readily oxidized in the presence of the hard O donor ligands. In solution, they readily exchange the hard donor O, for soft ligands. Although copper(I) prefers soft ligands and is more stable towards oxidation in their presence, it coordinates to hard donors when there is electrostatic or an entropy driven advantage.

Keywords: *bis* phosphine monoxides, Cu(I), chelates, NMR, Electrochemistry, Hard-soft acids and bases.

1. Introduction

Coordination complexes of copper(I) with tertiary phosphine ligands are ubiquitous. The soft phosphine ligand stabilizes the +1 oxidation state effectively and hence appears as a major class of ligands in the chemistry of copper(I) [1]. In the absence of soft ligands to stabilize it, copper(I) disproportionates quite readily [2]. Phosphine oxides on the contrary, are hard donors [3], and known to complex with hard Lewis acids [4]. In the case of copper, phosphine oxides prefer to complex with hard Cu(II) centers rather than Cu(I). Several structurally characterized complexes illustrate that phosphine oxides are suitable ligands for copper(II) chemistry [1,5,6]. Understandably, phosphine oxide chemistry of Cu(I) remains largely unexplored. However, coordination complexes of copper(I) with Cu-O bonds are known, though rare. In several structurally characterized complexes, oxo anions such as NO_3^- , ClO_4^- , RCOO^- , or O_2^{2-} are present in the coordination sphere [7]. In these cases, soft ligands are present in addition to the hard donors. A rare copper(I) complex $[\text{Cu}(\text{dppf})(\text{Odppf})] \text{BF}_4$, (where dppf = diphenyl phosphino ferrocene, and Oddpf = diphenyl phosphino ferrocene oxide) with phosphine oxide and phosphine in its coordination sphere has been characterized by Pilloni *et. al* [8]. It was shown by them that both soft and hard ligands coordinate to the metal center in the solid state. And quite interestingly, in solution it is the P=O group which remains coordinated to the metal atom, while the phosphine group dissociates. It was pointed out, that the ligand set $\{\text{P}_2\text{O}_2\}$ is well suited for stabilizing Cu(I) against disproportionation reactions.

Mixed Phosphine -Phosphine oxide ligands known as Bis phosphine monoxides (BPMO) can offer both hard and soft donors to the metal center (Fig. 1). An efficient method for the selective oxidation of several bidentate phosphine ligands was recently reported [9]. BPMOs are being used as valuable ligands in inorganic or organometallic synthesis [10]. Several transition metal complexes have been studied due to their relevance in catalysis, and their versatile coordination behavior [11]. However to our knowledge, complexes of BPMO ligands with copper(I) are unknown. Owing to the presence of a mixed donor environment in these ligands, they can be explored for their coordination behavior towards Cu(I), particularly in the context of phosphine oxide coordination. In this work, two such ligands, diphenylphosphinoethane monoxide (dppeo), and diphenylphosphinomethane monoxide (dppmo) have been studied. We report spectroscopic and electrochemical studies on the complexes with phosphine and

phosphine oxide coordination, along with structural characterization of the dppeo complex. The solvent and anion dependent lability of P=O coordination in solution has also been studied.

2. Experimental

All the reactions were carried out under an atmosphere of purified nitrogen, and the solvent chloroform was dried with P₂O₅ and distilled prior to the reaction. Diethyl ether and petroleum ether were distilled before use. The ligands were synthesized according to the reported procedure [9].

Physical measurements

¹H NMR spectra were recorded on a Bruker ACF 200 MHz spectrometer with tetramethylsilane as the internal reference. ³¹P {¹H} NMR spectra were recorded on a Bruker AMX 400 MHz spectrometer operating at 162 MHz. IR spectra were recorded in the solid state dispersed in KBr pellets on a Bruker spectrometer. The MALDI mass spectra were recorded on a Kratos PCKompact spectrometer using an α -cyanocinnamic acid matrix. A CH Instruments 600A potentiostat was used for the electrochemical measurements.

Preparation of the complexes

Cu (dppeo)₂ ClO₄ (1)

About 0.02 g of [Cu(CH₃CN)₄]ClO₄ was mixed with 0.05 g (2 eq) of the ligand in chloroform (5 mL) and stirred for 20 minutes. Completion of reaction was ascertained by the absence of free ligand using TLC (eluant: diethyl ether: chloroform, 50:50). During this time, a white turbidity appeared in the reaction mixture. Addition of excess of diethyl ether precipitated complex **1** as a white powder in 83% yield. Anal. calc. for C₅₂H₄₈P₄O₆ClCu·CHCl₃ C 57.22, H 4.41; found C 57.8, H 4.62 %. ¹H-NMR (δ , CDCl₃): 7.26-7.72 (40H, m), 2.50 (8H, br).

Cu (dppmo)₂ ClO₄ (2)

Synthesis of complex **2** was carried out following the procedure used for complex **1**. After 2 h. of stirring, the reaction was complete and the complex was precipitated with diethyl ether in 69% yield. Anal. calc. for C₅₀H₄₄P₄O₆ClCu·0.5CHCl₃: C 59.24, H 4.35; found C 58.44, H 4.41%. ¹H-NMR (δ , CDCl₃): 7.20-7.75 (40H, m), 3.52 (4H, d, $J_{\text{HH}}=6$).

Crystallographic structure determinations

Single crystals were grown from a dichloromethane solution of complex **1** by layering with diethyl ether. Although most of them were opaque, a moderately formed single crystal (0.3×0.2×0.3 mm) was sealed in a Lindemann capillary along with the mother liquor and used for data collection. The intensity data were collected on an Enraf-Nonius CAD4 single crystal diffractometer equipped with graphite-monochromatized Mo K α radiation. The lattice parameters and standard deviations were obtained by least squares refinements of 25 well orientated reflections in the range $12^\circ \leq 2\theta \leq 24^\circ$. Three reflections were used to monitor the stability and orientation of the crystal during the time of data collection. All computations were performed using the WINGX [12a] package. Data collected at 25°C were corrected for Lorentz, polarization and absorption effects using DIFABS [12b]. The positions of the heavy atoms were determined by SHELX86 [12c]. The remaining atoms were located from difference Fourier analysis using SHELXL-97 [12c]. Hydrogen atoms were included in the final stage of the refinement on calculated positions bonded on their carrier atoms.

3. Results and Discussion

Copper(I) complexes were made by mixing the BPMO ligand with [Cu(CH₃CN)₄]ClO₄ in the appropriate ratio. Since this source of copper(I) has labile acetonitrile ligands, it has been used effectively for the preparation of several complexes with less volatile ligands [1]. In this case, completion of reaction could be confirmed by the absence of free ligand. Once complexation of the ligand was complete, the reaction mixture was treated with a solvent in which the complex was less soluble such as diethyl ether or petroleum ether. MALDI mass spectral analysis of the complexes in a α -cyanocinnamic acid matrix revealed the presence of the molecular ion Cu(BPMO)₂⁺. In the case of complex **1**, single crystals suitable for X-ray diffraction studies could be obtained. A brief summary of the crystal structure determination is given in Table 1.

Molecular structure of **1**

The molecular structure of Cu(dppeo)₂ClO₄ consists of a cation containing Cu(I) coordinated to the ligand and a non coordinating perchlorate anion. Fig. 2 shows the cationic part of the molecular structure, and the selected bond distances and angles are given in Table 2. Two

dppeo ligands are in chelating mode. The central copper atom adopts a severely distorted tetrahedral geometry with two P atoms and two O atoms coordinating to it, thus confirming phosphine oxide coordination. The Cu-P distances (2.225 Å) and Cu-O distances (2.117 Å) are in the usual ranges expected for Cu(I) complexes. Chelation produces two six-membered rings which are present in a chair conformation very similar to the reported six-membered chelate structure found in Cu(dppp)₂ClO₄, where dppp is bis diphenylphosphino propane [13]. The molecule possesses a two-fold axis passing through the central metal ion. The angles involving O-Cu-P atoms are symmetry related. The chelate angles O-Cu-P are each 99.0° and the non-chelating O-Cu-P angles are 120.3°. The other angles comprising of O-Cu-O and P-Cu-P are 98.3° and 119.2° respectively. In the case of copper(II) complexes with PPh₃O, the P=O-Cu (II) [6] unit has an angle of 180° whereas in the present case an angle of 119.9° is observed.

A perchlorate anion, and a solvent molecule were also located in the structure. The perchlorate group remains non-coordinating. As observed in other systems [14], the non-bonded anion is disordered with the chloride atom in a special position, and oxygen atoms exhibiting positional disorder with huge thermal parameters. Modeling the perchlorate ion as two intermeshed tetrahedra with partial occupancies did not improve the fit. The error observed in bond lengths, and angles might be due to the poor quality of the crystal examined.

IR Spectroscopy

In the absence of a crystal structure for complex **2**, IR spectroscopy appears suitable for characterization of the compound. The coordination of aromatic phosphine oxides to metal complexes is identified by a shift in the $\nu_{(P=O)}$ stretch. This characteristic band is moderately intense and occurs around 1180 cm⁻¹, and 1183 cm⁻¹ in the free ligands, dppeo and dppmo respectively. IR spectroscopy thus offers the quickest means of proving oxygen atom coordination to Cu. Bonding to Cu(I) results in a significant shift of the PO stretching frequency to lower values in complexes **1**, and **2**. Structurally characterized phosphine oxide complexes show broadening of the $\nu_{P=O}$ vibration in some cases. Cotton *et. al* [15], have explained the line broadening to the coupling of two P-O vibrations via the metal atom. In complex **1** no broadening of the PO stretching frequency could be observed, although, complex **2** exhibited a slight broadening. The bands due to perchlorate anions present in complex **1** and **2** are similar and occur at 1090 cm⁻¹ as expected for a non-coordinating perchlorate anion [16].

³¹P NMR studies

The lability of copper(I) complexes in solution is well known [17]. In order to examine the solution behavior of these complexes, the ³¹P NMR spectra were recorded for the complexes and the free ligand. The free dppeo ligand is soluble in chloroform and slightly soluble in acetone, whereas the complex is sparingly soluble in chloroform and freely soluble in acetone. As a result spectroscopic studies on the free ligand were carried out in acetone-d₆ or when greater concentrations were required, as in ³¹P NMR, in a mixture of acetone-d₆ and CDCl₃. No significant solvent effect was found for the ³¹P NMR chemical shifts on increasing CDCl₃ content. The spectrum exhibits a signal at -12 ppm for the P(III) center, and another peak at +33 ppm for the phosphine oxide group (Fig. 3). Similarly, for dppmo, the signals are at -28 ppm for the P(III) center and at +28 ppm for the phosphine oxide center. These signals also exhibit a doublet pattern with a coupling of 55 Hz [9].

An acetone-d₆ solution of complex **1** displays a broad peak at -9 ppm, δ complex- δ ligand ($\Delta\delta$) = 3 ppm, attributable to coordinated phosphine and a relatively more intense peak at 42 ppm ($\Delta\delta$ = 9 ppm) for the phosphine oxide group. A noteworthy feature of the ³¹P NMR of complex **1** is the disappearance of the doublet pattern observable in the free ligand (Fig 3). The solution ³¹P NMR of complex **1** illustrates that the solid state structure is predominantly retained in solution. However, an exchange process involving breaking of Cu-P and Cu-O bonds leads to broad signals at room temperature. The peaks are significantly narrower at low temperature. The solution NMR of Cu(dppmo)₂ClO₄ obtained in CDCl₃ and in acetone-d₆, is similar to that of **1** in terms of upfield shifts of the signals ($\Delta\delta_{\text{P=O}}$ = 10 ppm, $\Delta\delta_{\text{P}}$ = 8 ppm) and the line broadening due to an exchange process involving an equilibria where chelation is lost.

The two different methylene protons of the dppeo framework are degenerate in ¹H NMR and appear as a broad singlet in the free ligand. The accidental degeneracy is almost removed in the ¹H NMR of **1** and a slight upfield shift (0.31 ppm) of the peaks is observed. Hence it is certain that **1** and **2** possess the expected phosphine oxide coordination in non-coordinating solvents like acetone-d₆ and CDCl₃. Based on these evidences we suggest similar solution and solid state structures for **1** and **2** in which only equilibria with non-chelated forms is occurring.

Since rapid equilibria with the non-coordinated forms are involved, it is of interest to examine the relative strengths of the Cu-O / Cu-P bonds through challenge experiments.

Coordinating power of the P=O group to copper(I) relative to acetonitrile, which is a moderate π acceptor was examined by recording the NMR spectrum of complex **1** in CD₃CN as the solvent. The influence of solvent is quite pronounced on the signal for the phosphine oxide group. The P=O group now resonates at +33 ppm very close to that of free phosphine oxide group. Interestingly, the signal appears as a doublet and resembles the signal for free P=O present in the ligand. On the contrary, the signal due to phosphine group shows little difference in CD₃CN and retains the position (8.8 ppm) and line shape observed in acetone-d₆. The spectrum of complex **2** in CD₃CN produces similar results as well. The phosphine moiety shows binding ($\Delta\delta_{\text{P}} = 8$ ppm), while the phosphine oxide signal occurs close to the free ligand with a doublet pattern. ($\Delta\delta_{\text{P=O}} = 1$ ppm). These results are in accord with the preference of copper(I) for acetonitrile, a moderate π acceptor rather than the oxygen of P=O when the former is present in excess.

In another experiment, four equivalents of the ligand were added to the *tetrakis* acetonitrile complex of copper(I) in CDCl₃. The presence of 4 equivalents of the dppeo ligand with respect to the copper(I) source, leads to a competition between the chelated structure (CuP₂O₂) and a complex with all four phosphine centers coordinated to Cu(I), with uncoordinated PO centers. The spectrum indicates the presence of free PO group and bound phosphine moiety with signals at +33 ppm and at -9 ppm respectively. The reappearance of the doublet near the free ligand value for the P(V) center is clearly due to loss of Cu-O bonding. The NMR results indicate that the intermolecular P(III) center is more acceptable to the Cu(I) center than intramolecular interaction from P(V) (see scheme). Thus the CuP₂O₂ unit is stable only in the absence of competitive interactions from soft donors.

In a separate experiment, tetra butyl ammonium bromide was added to the complex **1** in 1:1 ratio. Addition of bromide increases the solubility of **1** in CDCl₃, the phosphine signal in ³¹P NMR is shifted downfield, where as the PO signal is close to the free ligand value. The shifts in the ³¹P NMR spectrum illustrate that the bromide ion retards the coordination of PO moiety. The accidental degeneracy of the ¹H NMR signal in the free ligand is lifted on coordination. Two sets of broad peaks are observed in the ¹H NMR spectrum (2.34 and 2.58 ppm) and thus different from what is observed for complex **1**. The $\nu_{\text{P=O}}$ stretch of the product in this reaction, also occurs close to the free ligand and the IR studies are consistent with what is expected on the basis of NMR studies. When two equivalents of the ligand dppeo are mixed with CuBr in CDCl₃, similar observations were made in ³¹P NMR and ¹H NMR spectra.

An attempt was made to isolate the complex $(\text{CuBr})(\text{dppeo})_2$ formed in the reaction of CuBr with dppeo following the procedure used for making **1** and **2**. The IR spectral changes for the complex generated in this fashion closely resembles the free ligand spectrum in the $\nu(\text{P}=\text{O})$ region. It is to be noted that the ^{31}P resonance of the P=O moiety occurs close to the δ value for free P=O and is different from that in the perchlorate complex, and the resulting NMR matches that observed in the in situ generation of the complex. In addition, the doublet pattern reappears for the P=O signal as in the case of non-coordinating phosphine oxides. However, the white complex isolated in this reaction was relatively unstable and became colored precluding complete characterization.

Electrochemical studies

Electrochemical studies were performed in chloroform solution using Pt as working electrode and Ag/AgCl as the reference electrode. Tetra butyl ammonium perchlorate was used as the supporting electrolyte (0.08 M). All the complexes examined had an electrochemical event in the potential window of 1.4 to 0 V where the Cu(I)/Cu(II) redox couple is usually observed for copper(I) phosphine complexes [18]. A clean background was ascertained in each experiment prior to the addition of the complex. The results from cyclic voltammograms at 50 mV S^{-1} are reproduced in Fig. 4 and the details of cyclic voltammograms at other scan speeds are summarized in Table 3.

The cyclic voltammogram of $\text{Cu}(\text{dppeo})_2\text{ClO}_4$ (0.1 mM solution in chloroform) displays well-defined anodic and cathodic peaks (Fig. 4a). However, the process is only quasi reversible, as indicated by ΔE_p values and I_{pa}/I_{pc} , at different scan rates. The electrochemical behavior of complex **2**, $\text{Cu}(\text{dppmo})_2\text{ClO}_4$ was also examined under identical conditions. Although the $E_{1/2}$ values at different scan rates are comparable to that of **1**, the cathodic process in complex **2** is suppressed and I_{pa}/I_{pc} values at different scan rates are quite large (Fig. 4b). The electrochemical behavior of the BPMO derived complexes are dependent on the chain length. The influence of chain length on electrochemical processes in chelate complexes has been noted quite often [19]. The I_{pa}/I_{pc} values indicate that complex **1** with dppeo shuttles between two oxidation states more readily than complex **2**.

The complex $\text{Cu}(\text{dppe})_2\text{ClO}_4$ with all soft phosphorous centers in the coordination sphere was also studied for comparison. Unlike complexes **1** and **2**, the $\text{Cu}(\text{dppe})_2\text{ClO}_4$ shows a broad

oxidation wave, while the reduction wave is well defined and occurs at more positive potentials than for BPMO complexes. The broad anodic peak precludes accurate measurement of an E_{pa} value, and E_{pa} was calculated from the derivative of the cyclic voltammogram. The electrochemical behavior of the relevant ligands was also probed in order to confirm the origin of electrochemical processes. In the potential window studied, the ligands are inactive and the complexes are clearly distinguishable from the ligands due to the presence of the Cu(I)/Cu(II) couple.

The results of the electrochemical studies on BPMO complexes with a mixed coordination sphere are compared with the results from studies on the dppe complex which possesses only soft ligands in the coordination sphere. The reduction potential values are well defined in all three complexes, and indicate that the phosphine complex is more easy to reduce (more positive potential), than complex **1** and **2**. Similarly the broad anodic wave of the dppe complex illustrates a less favorable, slower oxidation processes than the BPMO analogues. This trend is also supported by the observation that the addition of excess dppeo (2 eq) to the complex **1** shifts the redox processes anodically by 50 mV and approaches the behavior of the CuP_4 complex. The addition of bromide to the complex to generate the bromide complex, complicates the oxidation event with multiple processes presumably due to the presence of an equilibrium in solution as illustrated in the Scheme. However, at least one of the processes requires a more positive potential than the CuP_2O_2 system. This can be reasonably attributed to the dimeric species, while the other wave might originate from the three-coordinated monomer. As expected, the reduction potential of the bromide complex is more positive than the BPMO complexes.

Hence the electrochemical results are suggestive of the fact that the CuP_2O_2 system is relatively easier to oxidize to the copper(II) complex. Whereas, a complex with an all-soft coordination environment, is more difficult to oxidize. Complexes with the P_2O_2 ligand set are readily synthesized and stable enough for isolation when copper(I) is not given a choice to coordinate to soft ligands.

4. Summary

The present study indicates that BPMO ligands form stable copper(I) complexes. It is also clear that the Cu-O bond and Cu-P bonds are quite labile. Unlike the Cu-P bond the Cu-O bond requires a non-coordinating counter anion or solvent to remain in the coordination sphere

of copper(I). Spectroscopic studies show that copper(I) would favor soft donors to O, a hard donor in its coordination sphere. In a situation where four equivalents of the BPMO ligand are made available for copper(I), the coordination of four P atoms to Cu is favored. Even entropy driven stabilization of the CuP_2O_2 coordination fails to win over the CuP_4 coordination. The electrochemical behavior of the complexes illustrates that the mismatched coordination environment leads to a copper(I) center that is more easily oxidized. Thus the four phosphine-coordinated complex is more difficult to oxidize than the complex with two O and two P atoms. The greater stability Cu(I) complexes with a complement of soft ligands is evident from these competition experiments.

5. Supplementary material

Crystallographic data for the crystal structure of **1** has been deposited at the Cambridge Crystallographic Data center as CCDC-175552. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Director, Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk.

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Table 1 Brief Summary of the Crystal Structure Determination.

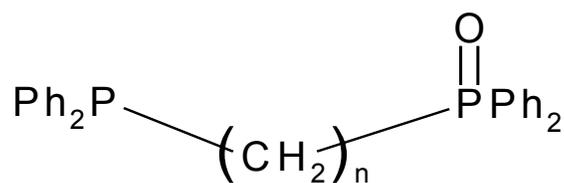
Crystal data	Compound 1
Empirical Formula	C ₅₂ H ₄₈ Cl Cu O ₆ P ₄ .CH ₂ Cl ₂
Formula weight	1076.4
Crystal system	Monoclinic
Space group	C 2/c
a (Å)	23.041(11)
b (Å)	10.047(3)
c (Å)	24.683(11)
α (deg)	90
β (deg)	105.66(4)
δ (deg)	90
V (Å ³)	5502(4)
Z, ρ _{calcd.} (Mg/M ³)	4, 1.178
Abs coeff (mm ⁻¹)	0.603
θ	1.71 to 24.97
F(000)	2024
Independent reflections	4984
Data/restraints/parameters	4827 / 0 / 312
Final R ₁ ^a , wR ₂ ^b [I>2σ(I)]	0.0950, 0.1981
Final R ₁ ^a , wR ₂ ^b (all data)	0.2420, 0.2571
Goof	0.933
Largest diff. peak and hole (e Å ⁻³).	0.669 and -0.601

Table 2Selected bond lengths (Å) and angles (°) for compound **1**

Cu(1)-O(1)	2.117(6)	O(1)-Cu(1)-P(2)	120.32(19)
Cu(1)-P(2)	2.225(3)	O(1)#1-Cu(1)-O(1)	98.3(4)
P(1)-O(1)	1.495(6)	O(1)-Cu(1)-P(2)#1	99.03(18)
		P(2)#1-Cu(1)-P(2)	119.19(16)

Table 3 Cyclic Voltammetry Data.

Complex	Scan rate mV S^{-1}	E_{pa}	E_{pc}	$E_{1/2}$	$I_{\text{A}}/I_{\text{C}}$
$\text{Cu}(\text{dppeo})_2 \text{ClO}_4$	20	1.19	0.70	0.94	0.6
	50	1.17	0.67	0.92	0.6
	100	1.30	0.48	0.89	-
$\text{Cu}(\text{dppmo})_2 \text{ClO}_4$	20	1.06	0.68	0.87	4
	50	1.14	0.65	0.89	3.8
	100	1.20	0.56	0.88	-
$\text{Cu}(\text{dppe})_2 \text{ClO}_4$	50	1.25	0.80	1.02	
$\text{Cu}(\text{dppeO})_2 \text{ClO}_4 + 2 \text{ eq of dppeo}$	50	1.24	0.73	0.98	
$\text{CuBr}(\text{dppeo})_2$	50	1.25, 1.08	0.78		

**Fig. 1** Bis Phosphine monoxide

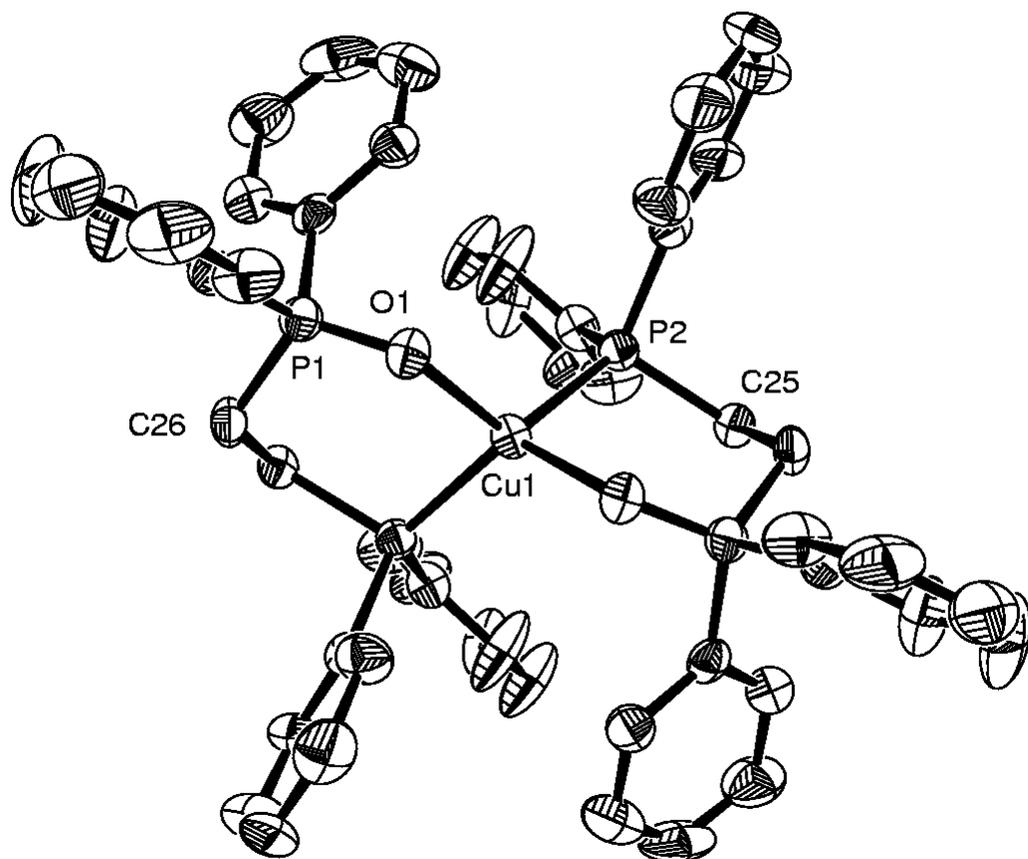


Fig. 2 ORTEP diagram of complex **1** at the 30% probability level. The hydrogen atoms and the disordered counter anion are omitted for clarity.

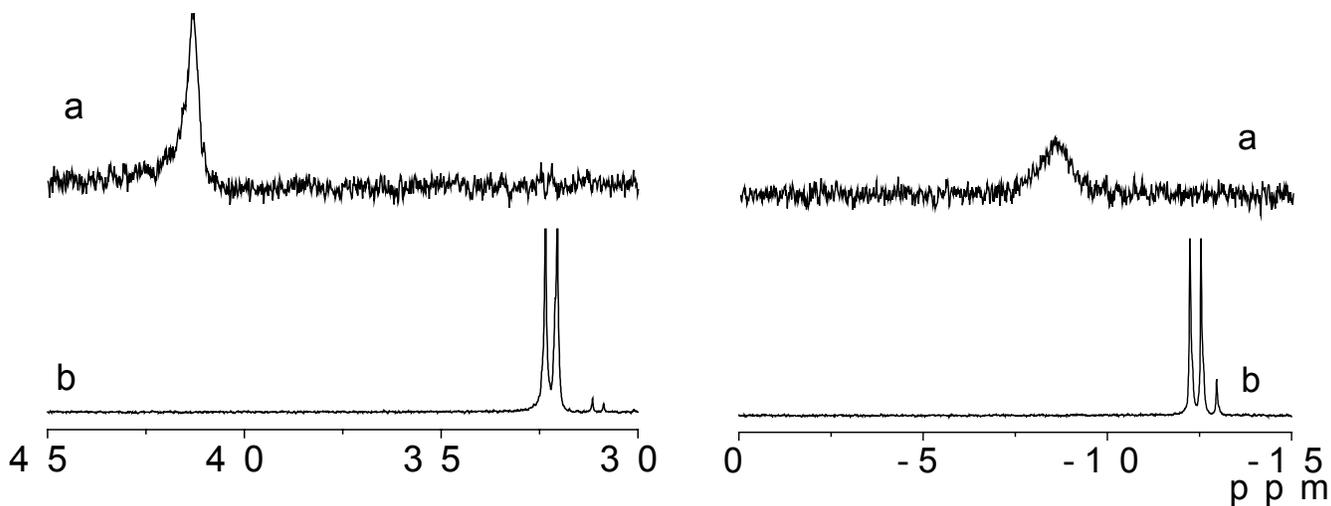


Fig. 3 The ^{31}P NMR of (a) complex 1, and (b) dppeo.

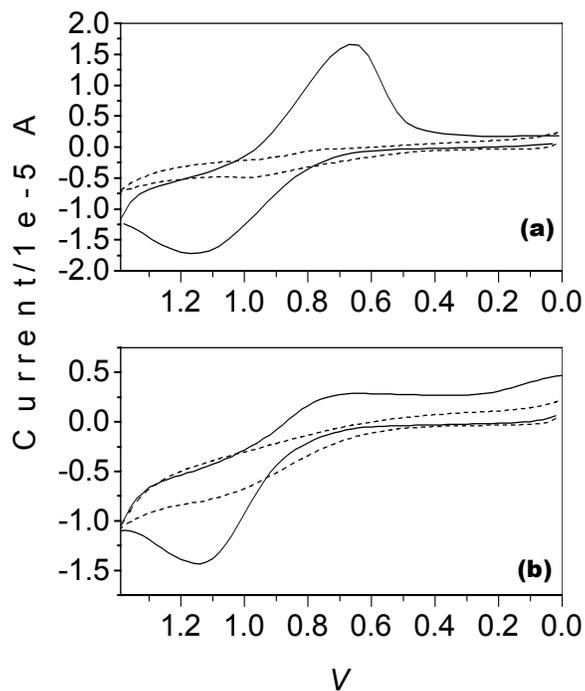
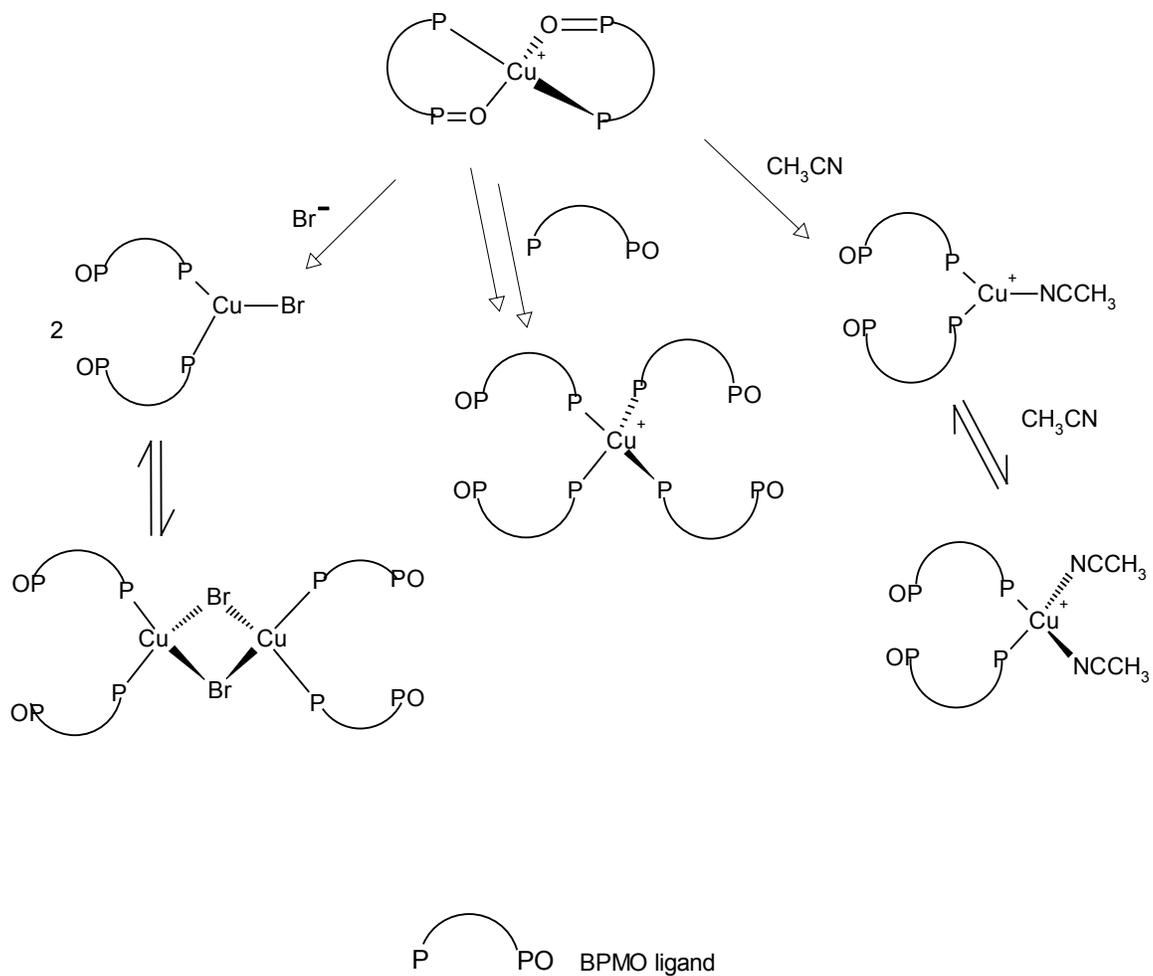


Fig. 4 Cyclic voltammogram of complex 1(a), and complex 2(b). The broken line traces are for the respective free ligands. (Scan rate: 50 mV S^{-1})

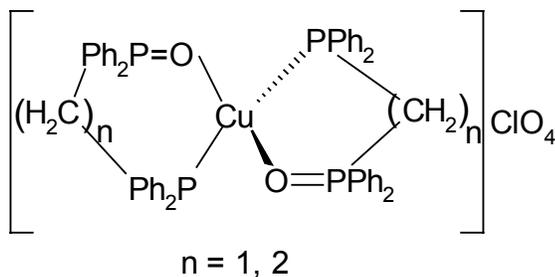
Scheme



**The First *Bis* Phosphine
monoxide (BPMP)**

Complexes of Copper(I)

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Copper(I) complexes of *bis* phosphine monoxide ligands, have been prepared and characterized, confirming Cu(I) coordination to hard and soft donors. Spectroscopic and electrochemical challenge experiments demonstrate the delicate balance between the preference of copper(I) for softer bases and entropy driven P=O coordination.