The Flight of the Monarch: [Cu(L)(CH$_3$CN)(PPh$_3$)]ClO$_4$

(L = 2,5-Diphenyl-3,4-bis(2-pyridyl) Cyclopenta-2,4-dien-1-one)

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The mononuclear complex [Cu(L)(CH$_3$CN)(PPh$_3$)]ClO$_4$, (1), (L= 2,5-diphenyl-3,4-bis(2-pyridyl)cyclopenta-2,4-dien-1-one), has been synthesized and investigated by elemental analysis, IR, $^1$H NMR, UV-Vis spectroscopic methods and X-ray diffraction. The complex crystallizes in the non-centrosymmetric space group P2$_1$2$_1$2$_1$ in accord with the asymmetric (atropisomer) Cu centre. Its coordination polyhedron has four vertices and is devoid of any symmetry. The [Cu(L)(CH$_3$CN)(PPh$_3$)]ClO$_4$ is amongst the few MeL complexes crystallizing in a non-centrosymmetric space group. The bite-angle of the bidentate ligand L is 90.92(13)$^\circ$, indicating some strain in the structure; this entails an enhanced instability of the complex with respect to strongly coordinating solvents. The crystal of 1 owes its cohesion to a multitude of weak C-H...O and C-H...π interactions. The electrochemistry of the complex shows three reversible ligand-centred reduction processes and an irreversible metal-centred one. This indicates that the coordination of the Cu(I) moiety to the L leads to the delocalization of electron density from L to the Cu(I)(CH$_3$CN)(PPh$_3$) moiety. The electrocatalytic activity of Cu(I) complex in reduction of CO$_2$ was also investigated.

**Keywords:** Cu(I) complexes, Diene, Crystal structure, Electrochemistry, Electrocatalyst

**INTRODUCTION**

Copper(I) complexes have attracted attention in the past and continue to be an active area of research because of their diverse structural and photophysical properties [1]. Their potential applications lie in areas such as optoelectronics and catalysis [2] and as sensitizer in the field of dye-sensitized solar cells [3-5]. They are also essential for catalyses in many organic transformations like aryl guanidinylation [6], amination [7], photocycloaddition [8], oxidation of adrenaline [9], ferrocytrochrome c oxidation [10] and also olefin cyclopropanation [11].

Copper(I) complexes of heteroaromatic chelating bidentate ligands form an important class of coordination compounds and the coordination chemistry of these complexes has received considerable attention in recent years by Amirnasr and coworkers [12-18]. Copper(I) complexes with polypyridine ligands are featured by MLCT reactivity [19-20]. Formation of an exciplex (but non-emissive) via quenching of these excited states is also an essential reaction-pathway of these compounds. Differing from the CTTS character, however, they undergo photoinduced electron transfer only by means of direct redox quenching. They possess rich photophysical properties [21-29] and also play a large role in the field of asymmetric catalysis [30]. Copper(I) complexes prefer adopting a pseudo-tetrahedral geometry. They are often sensitive to oxidation and their stability is closely related to the nature of the ligands attached to the metal centre. In the absence of restricting steric effects from the ligands, these complexes are often oxidized to the stabler square planar Cu(II) species. For example, Cu$_2$ complexes of 2,2'-bipyridines (bpy) and 1,10-phenanthroline (phen) tend to be oxidized by O$_2$ [31].

We report here the synthesis and characterization of the original Cu(I) complex [Cu(L)(CH$_3$CN)(PPh$_3$)]ClO$_4$, 1,
where $L$ is 2,5-diphenyl-3,4(2-pyridyl)cyclopenta-2,4-dien-1-one.

**EXPERIMENTAL**

**Materials and Physical Measurements**

**Safety note.** Perchlorate salts of transition metal complexes with organic ligands are often explosive and should be handled with caution and using minimal quantities of substances.

$[\text{Cu(CH}_3\text{CN)}_4]\text{ClO}_4$ was prepared according to the method reported by Hemmerich and Srgwart [32]. Organic solvents were purified according to the literature methods [33]. Silica gel 60 (70-230 mesh, Fluka) was used for dehydration.

Elemental analyses were performed by using a Heraeus CHN-O-RAPID elemental analyzer. Electronic absorption spectra were obtained with a JASCO V-570 spectrophotometer. Infrared spectra were recorded on a FT-IR JASCO 680 PLUS instrument. $^1$H NMR spectra were measured by means of a Bruker ACP-500 spectrometer at 500 MHz in CDCl$_3$ with tetramethylsilane as internal standard. Cyclic voltammograms were recorded by using a SAMA 500 Research Analyzer.

**Synthesis of the Red Ligand**

The red ligand 2,5-diphenyl-3,4(2-pyridyl)cyclopenta-2,4-dien-1-one (L, monarch) was prepared by thermal dehydration of its white diol precursor, LH$_2$(OH)$_2$, over silica gel as reported elsewhere [34].

**Synthesis of $[\text{Cu(L)(CH}_3\text{CN)}(\text{PPh}_3)]\text{ClO}_4$**

52.2 mg (0.2 mmol) of PPh$_3$ was added to 32.8 mg (0.1 mmol) of $[\text{Cu(CH}_3\text{CN)}_4]\text{ClO}_4$ in CH$_3$CN (5 ml). The reaction mixture was stirred at room temperature for half an hour. After evaporating the solvent under vacuum at room temperature, the thus obtained white solid was added to 38.6 mg (0.1 mmol) of the red ligand L in CH$_3$CN (5 ml) and the reaction mixture was stirred for half an hour. The volume of the solution was then reduced to 2 ml under vacuum. Diethyl ether was allowed to diffuse, at room temperature, slowly into this concentrated solution. Purple-red crystals of 1 in good yield (~70%) suitable for X-ray studies crystallized in this manner.

**X-Ray Crystallography**

Bragg-intensities of 1 were collected on a Bruker SMART 1000 diffractometer with graphite-monochromatized MoKα ($\lambda = 0.71073$) radiation at 292(2) K. Cell refinement, data reduction and a numerical absorption correction were performed with the help of the program Bruker SAINT (1996) [35]. The structure was solved with direct methods using the program DIRDIF-2002 [36]. The structure refinement on $F^2$ was carried out with the program SHELXL-2014/7 [37]. All non-hydrogen atoms were refined anisotropically. The crystallographic and refinement data are summarized in Table 1. The habitus of 1, developing from this mother liquor (H$_3$CCN/Et$_2$O), may be idealized as a \{111\} disphenoid, a \{110\} c-prisms and a \{010\} pinacoid in D$_2$, but this would have to be checked with bigger crystal than those available at that time.

**RESULTS AND DISCUSSION**

**Crystal Structure of 1**

Compound 1 crystallizes in the non-centrosymmetric space group P2$_1$2$_1$2$_1$ in accord with the asymmetric Cu-centre. A summary of the crystallographic information is listed in Table 1. Selected bond distances [Å], bond and torsion angles (°) are listed in Table 2. The molecular structure of compound is illustrated in Figure 1. The length of the C=O bond indicates no electron transfer from the metal to L.
The average Cu-N [2.087(6) Å] and Cu-P [2.2205(12) Å] bond distances and the N18-Cu-N30 [101.48(14)°] and P-Cu-N17 [122.51(9)°] bond angles conform to those reported for the CoLCl and NiLBr complexes with the ligand L [38]. A highly puckered seven-membered chelation ring is formed with endocyclic torsion angles presented in Table S1. Relevant data are compiled in Table S1.

While a comparison of the bite-angles in 1, CoLCl and NiLBr (Table S1) with the van der Waals radii of the ancillary ligands is not entirely conclusive, it is the comparison of the P-Cu-N18 (Monarch) angle of [131.86(10)°] in 1 with the X-Me-N angles in CoLCl and NiLBr that furnish an explanation of the relative smallness of the bite-angle in 1: it is the replacement of the halogen with the bulky Ph3P ancillary ligand that causes enough steric hindrance to make the bite-angle in 1 small. Relevant data are compiled in Table S1.

In the free ligand the dihedral angles between the ring and the two pyridine rings are 44.82(8)° and 61.28(8)°, respectively. In the coordinated ligand (Monarch seated on the flower), the values of 57.28(15)° and 123.50(15)° show that the two pyridine rings had to rotate from a roughly antiparallel orientation to a spread-eagle one in order to obtain coordination to [Cu(CH3CN)_3](Ph3P) (the flower).

The structure of L consists of single-file Monarchs flying along [001]; they are weakly linked by a C16-H9···O1 (2.499 Å, 126.7°) interaction, and further stabilized by two intramolecular hydrogen bonds: C7-H11···O1 (2.732 Å, 104.25°) and C27-H18···O1 (2.631 Å, 106.98°). Neighbouring files fly in opposite directions, and are further linked by weak C-H···N1,N2 interactions (two per nitrogen), thus forming a 3D network. The Monarch’s hind wings are parallel (their nitrogen atoms being anti) and its fore wings are spread wide open and related by non-crystallographic reflection. This is an achiral molecule (atropisomer) crystallizing in the centrosymmetric space group P2_1/c.

A cousin of the Monarch’s, namely 2,3,4,5-tetakis(2-Pyridyl)cyclopenta-2,4-dien-1-one, C, provides a striking demonstration of the force of weak C-H···N interactions. Just two more nitrogen atoms succeed in breaking the elegant single-file of the Monarchs and in trussing them at the scary nodes of an ivy branch (i.e. offset by (½)c along the stem) by means of a multitude of weak interactions. This cobweb of interactions extends throughout the crystal. This stiffing network leads, accordingly, to an even higher packing coefficient of 0.695.

In accord with its ionic radius, Cu forms only a monomer with L, Ph3P and ACN. In the structure of 1, as in most, if not all of the other structures, the Monarch displays an approximate non-crystallographic mirror symmetry. In the structure there is one perchlorate sitting above each CPDO moiety. This anion links then three complexes by means of C-H···O interactions, forming a triangle. Above this triangle the CPDO-oxygen atoms links a fourth complex, again by C-H···O bonds, thus forming a tetrahedron (Fig. 2). This is the basic brick of the structure; these bricks are then further interconnected by C-H···O and C-H···π interactions, in particular those involving the methyl groups of the acetonitriles, to build-up a complex 3D network of weak interactions. The whole structure can be thought of as [001] stacks of corner-sharing, distorted tetrahedral, the inter-columnar space being filled with phenyl rings.

The packing of 1 with respect to that of L alone seems to be a little less compact (p.c. = 0.66) than that of the former (p.c. = 0.69) and that of the cousin (p.c. = 0.695). The crystal of 1 owes its cohesion to a multitude of weak C-H···O and C-H···π interactions (Table 3 and Fig. 2). These radiate from two centres, namely the CPDO oxygen and the perchlorate oxygen atoms and create a complicated 3D
Table 1. Crystal and Refinement Data of 1

<table>
<thead>
<tr>
<th>Complex</th>
<th>[Cu(L)(CH$_3$CN)(PPh$_3$)]ClO$_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C$<em>{47}$H$</em>{36}$ClCuN$_3$O$_5$P</td>
</tr>
<tr>
<td>Formula weight</td>
<td>852.75</td>
</tr>
<tr>
<td>Temperature (K)</td>
<td>292(2)</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Orthorhombic</td>
</tr>
<tr>
<td>Space group</td>
<td>P2$_1$2$_1$2$_1$</td>
</tr>
<tr>
<td>a (Å)</td>
<td>10.3372(6)</td>
</tr>
<tr>
<td>b (Å)</td>
<td>18.4118(10)</td>
</tr>
<tr>
<td>c (Å)</td>
<td>21.4227(11)</td>
</tr>
<tr>
<td>V (Å$^3$)</td>
<td>4077.3(4)</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
</tr>
<tr>
<td>$\rho_{calc}$, (g cm$^{-3}$)</td>
<td>1.389</td>
</tr>
<tr>
<td>Crystal dimensions (mm)</td>
<td>0.12 × 0.13 × 0.33</td>
</tr>
<tr>
<td>$\mu$ (mm$^{-1}$)</td>
<td>0.692</td>
</tr>
<tr>
<td>F(000)</td>
<td>1760</td>
</tr>
<tr>
<td>$\theta$ Range for data collection (°)</td>
<td>1.5-27.5</td>
</tr>
<tr>
<td>Index range</td>
<td>-13 $\leq$ h $\leq$ 13</td>
</tr>
<tr>
<td></td>
<td>-23 $\leq$ k $\leq$ 15</td>
</tr>
<tr>
<td></td>
<td>-27 $\leq$ l $\leq$ 26</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>28364</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>9359</td>
</tr>
<tr>
<td>$R_{int}$</td>
<td>0.0498</td>
</tr>
<tr>
<td>Maximum and minimum transmission</td>
<td>0.93189-0.84435</td>
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<tr>
<td>Number of parameters</td>
<td>560</td>
</tr>
<tr>
<td>Goodness-of-fit on $F^2$</td>
<td>1.050</td>
</tr>
<tr>
<td>Final R indices [I &gt; 2σ(I)]</td>
<td>R1 = 0.0450, $\omega$R2 = 0.0809</td>
</tr>
<tr>
<td>Final R indices (all data)</td>
<td>R1 = 0.0706, $\omega$R2 = 0.0898</td>
</tr>
<tr>
<td>Largest difference peak, hole (e Å$^{-3}$)</td>
<td>0.302, -0.271</td>
</tr>
</tbody>
</table>
Table 2. Selected Bond Distances (Å), Bond and Torsion Angles (°) for 1

<table>
<thead>
<tr>
<th>Bond lengths</th>
<th></th>
<th></th>
<th></th>
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<tbody>
<tr>
<td>Cu-P</td>
<td>2.2205(12)</td>
<td>Cl-O1A</td>
<td>1.39(3)</td>
</tr>
<tr>
<td>Cu-N17</td>
<td>2.108(3)</td>
<td>Cl-O2A</td>
<td>1.26(3)</td>
</tr>
<tr>
<td>Cu-N18</td>
<td>2.062(3)</td>
<td>Cl-O3A</td>
<td>1.48(3)</td>
</tr>
<tr>
<td>Cu-N30</td>
<td>2.093(4)</td>
<td>Cl-O4A</td>
<td>1.31(3)</td>
</tr>
<tr>
<td>N30-C31</td>
<td>1.115(7)</td>
<td>O-C1</td>
<td>1.203(5)</td>
</tr>
<tr>
<td>C31-C32</td>
<td>1.455(8)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Bond angles</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>P-Cu-N17</td>
<td>122.51(9)</td>
<td>N17-Cu-N30</td>
<td>97.59(14)</td>
</tr>
<tr>
<td>P-Cu-N18</td>
<td>131.86(10)</td>
<td>N18-Cu-N30</td>
<td>101.48(14)</td>
</tr>
<tr>
<td>P-Cu-N30</td>
<td>106.40(12)</td>
<td>N30-C31-C32</td>
<td>178.3(5)</td>
</tr>
<tr>
<td>N17-Cu-N18</td>
<td>90.92(13)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Torsion angles</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>N18-Cu-N17-C12</td>
<td>59.0(3)</td>
<td>Cu-N17-C12-C3</td>
<td>13.3(4)</td>
</tr>
<tr>
<td>N17-Cu-N18-C23</td>
<td>-67.0(3)</td>
<td>Cu-N18-C23-C4</td>
<td>-1.7(4)</td>
</tr>
<tr>
<td>C4-C3-C12-N17</td>
<td>-60.1(5)</td>
<td>C12-C3-C4-C23</td>
<td>-6.1(5)</td>
</tr>
</tbody>
</table>

Table 3. Selected Non-classical Hydrogen Bonds and C-H–π Interactions: Lengths (Å) and Angles (°) for 1

<table>
<thead>
<tr>
<th>No.</th>
<th>D-H...A</th>
<th>D-H</th>
<th>H--A</th>
<th>D--A</th>
<th>D-H--A</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>C19-H19A--O(1)</td>
<td>0.9300</td>
<td>2.6300</td>
<td>3.291(5)</td>
<td>128.1</td>
</tr>
<tr>
<td>2</td>
<td>C15-H15A--O4A(6)</td>
<td>0.9300</td>
<td>2.5500</td>
<td>3.16(2)</td>
<td>123.4</td>
</tr>
<tr>
<td>3</td>
<td>C22-H22A--O4A(3)</td>
<td>0.9300</td>
<td>2.5800</td>
<td>3.39(2)</td>
<td>145</td>
</tr>
<tr>
<td>4</td>
<td>C44-H44A--O3A(6)</td>
<td>0.9300</td>
<td>2.7100</td>
<td>3.38(3)</td>
<td>129.6</td>
</tr>
<tr>
<td>5</td>
<td>C32-H32A--O1A(6)</td>
<td>0.9600</td>
<td>2.5800</td>
<td>3.35(2)</td>
<td>137.6</td>
</tr>
<tr>
<td>6</td>
<td>C32-H32B--Cg1(0)</td>
<td>0.9600</td>
<td>3.1800</td>
<td>3.809(6)</td>
<td>124.9</td>
</tr>
<tr>
<td>7</td>
<td>C32-H32C--C62(0)</td>
<td>0.9600</td>
<td>3.0000</td>
<td>3.350(8)</td>
<td>102.7</td>
</tr>
<tr>
<td>8</td>
<td>C63-H63A--Cg2(0)</td>
<td>0.9300</td>
<td>2.7100</td>
<td>3.538(6)</td>
<td>148.9</td>
</tr>
</tbody>
</table>

Cg1 = CoG{C6,C7,C8,C9,C10,C11}; Cg2 = CoG{C40,C41,C42,C43,C44,C45}. Symmetry codes: (i) -1+x,y,z; (ii) 1/2-x,1-y,1/2+z; (iii) 1/2+x,1/2-y,1-z; (iv) 1-x,1/2+y,1/2-z; (v) 1/2+x,3/2-y,1-z.
network of weak interactions, quite opposite to that in the Monarch alone. The perchlorate is disordered between at least two orientations at room temperature. This is again an atropisomer of CPDO, but this time crystallizing in a non-centrosymmetric space group.

The packing of 1 in the crystal (Fig. 3) shows no significant bonding features (π-π stacking or strong hydrogen bonding); however there are weak H-bond interactions of the type C-H-π(C) and C-H-O (perchlorate anion) which are summarized in Table 3.

In summary, from a more structural vantage point, it will be revealing to see whether, and under what circumstances, one might obtain a tetradentate or polymer complex, if using the ligand C instead of L. Finally, in view of the disordered perchlorate counter-ion, a low temperature study will show how the various, weak interactions will order the structure of 1 further, and whether a phase transition is needed for a lock-in below room temperature. It would also be interesting to see whether the handedness of the copper centre translates into some important physical quantity, e.g. a polarization or a non-linear electric susceptibility. 1 is amongst the few MeL complexes crystallizing in a non-centrosymmetric space group. Providing an explanation for this observation is another, ambitious goal of our research.

**Spectral Studies**

The solid-state IR spectrum of the complex 1 was recorded in KBr pellets. The pyridine ring C-H stretching vibrations appearing at 3045 and 3015 cm⁻¹ for L are slightly shifted to higher frequencies in 1. The ketone C=O stretching mode observed at 1715 cm⁻¹ in L, is observed as a single sharp band at about 1717 cm⁻¹ in 1. This small shift is compatible with the weak C-H-O hydrogen bond. The pyridine C=N stretching mode appearing at 1580 cm⁻¹ for L is shifted to higher frequencies by 15-20 cm⁻¹ in 1. Additional shifts are expected for the ring breathing-mode occurring at 990 cm⁻¹ in L and at 1020-1025 cm⁻¹ in the IR spectra of 1. A new sharp band in the 2280 cm⁻¹ region is attributed to the acetonitrile C≡N stretching mode. The perchlorate stretching vibration appears at 1045 cm⁻¹ [38].

In the UV-Vis spectrum of L, three absorption bands at 492 nm (ε = 1167), 324 nm (ε = 5021), 258 nm (ε = 20010), respectively, were assigned to the ligand-centered n → π⁺ and π → π⁺ transitions. These transitions also appear in the spectra of 1 at 360 nm (ε = 4677) and 260 nm (ε = 38020). A new band at 518 nm (ε = 2188), which corresponds to an MLCT transition slightly overlapping with the LC (Ligand-centered) transition in this region. Deviating from the complexes of copper(I) with simple inorganic ligands, its coordination compounds with aromatic diimines (NN) such as bipyridine (bpy), phenanthroline (phen), biquinoline (biq) and their substituted derivatives also display strong absorption bands in the visible range which have been attributed to MLCT transitions wherein an electron is promoted from a 3d orbital of copper to a low-lying π⁺ orbital of the ligands [40-42]. The new band observed at 280 (ε = 26915) can be attributed to intraligand PPh₃ absorptions [43].

In the ¹H NMR spectrum of 1, taken in CDCl₃-d₅ at room temperature, the three protons of CH₂CN, coordinated to the Cu centre, appear as a singlet at 2.2 ppm, indicating free or 3-site rotation. The protons of the phenyl rings manifest as multiplet at 7.2-7.5 ppm, the protons belonging
Fig. 1. The molecular structure of 1 with its atom (50% probability level) labelling scheme. Hydrogen atoms were omitted for clarity. Note that only the major of the two orientations of the perchlorate anion is shown.

Fig. 2. Schematic representation of the structure of 1 showing the bricks. Starting from the grey one, the green one is generated by \( \{C_{2z}|1/2 3/2\} \) at \( 1/2 Y 3/4 \), the turquoise one by \( \{C_{2z}|3/2 1/2 1\} \) at \( 3/4 1/2 z \) and the mauve one by \( \{C_{2z}|1/2 1/2 1\} \) at \( x 1/4 1/2 \).
to the pyridine rings show a doublet at 6.8 ppm (2H₂) as well as a multiplet at 7.5 ppm (H₃, H₄), presenting some overlap with the phenyl protons, and a doublet at 9.4 ppm (2H₅).

The electrochemistry of 1 was investigated, at 25 °C, under an argon atmosphere in acetonitrile solutions containing 0.1 M of TBAH as supporting electrolyte. A three-electrode cell with a platinum auxiliary electrode, a glassy carbon-working electrode and a silver wire pseudo-reference electrode were used. Ferrocene (Fc) was used as internal standard and redox-potentials are expressed with reference to SCE [44].

As reported previously, L is reversibly reduced to its radical anion at -1.23 V in acetonitrile solution [39].

The cyclic voltammogram of 1 shows an electrochemically reversible reduction process at -0.61 V which we assign to the reduction of the coordinated L leading to the generation of its radical anion. The corresponding reduction wave of CPDO is shifted to less cathodic potentials with respect to the free, uncoordinated ligand; this shift occurs because the electron density is delocalized from the coordinated L ligand to the more electron withdrawing coordinated CH₃CN and PPh₃ ligands. The reversibility of the reduction process of the coordinated L is in agreement with similar reports showing that the redox behaviour of L is sensitive to the metal coordination at the pyridyl groups [39].

Two closely reversible processes observed at -1.17 V and -1.41 V are due to the reduction of pyridyl rings [45].
An electrochemically irreversible reduction wave at -0.44 V is metal-centred and attributed to the couple Cu(I)-Cu(0); this is in agreement with that reported for similar Cu(I) bipyridyl complexes [46,47].

The electro-catalytic activity of 1 in reduction of CO$_2$ was studied in acetonitrile solution under CO$_2$ atmosphere. Figure 5 shows a strong enhancement in the reduction wave current density at -1.92 V compared when no catalyst was used. A crossing of cathodic and anodic currents at around -1.48 and -1.81 V under CO$_2$ indicates the occurrence of a chain process during the anodic scan. Houman et al. had quantitatively interpreted this phenomenon in electrocatalytic reductions using cyclic voltammetry measurements [48]. They had concluded that the species, which is easier reduced than the initial compound, is continuously produced and reduced at the electrode until the trace crossing disappears [49].

CONCLUSIONS

When the Monarch meets the tri-acetonitrilo-triphenyl-phosphino copper adduct, he immediately falls for this beautiful flower. After brief courtship, she releases two petals (two acetonitrile molecules) and invites him for a rest. He gladly accepts and folds his wings. But the relationship remains shaky, since the Monarch is also attracted, strongly coordinating solvents.

The Cu(I) complex of the bidentate ligand L and two ancillary CH$_3$CN and PPh$_3$ ligand has been prepared. The coordination geometry around Cu(I) centre is fourfold, but devoid of any symmetry, with an N-Cu-N bite angle of 90.92(13)°. The strain imparted by the structurally rigid ligand L can lead to instability of the complex in strongly coordinating solvents. The cyclic voltammetry of the Cu(I) complex 1 in acetonitrile solution shows an electrochemically irreversible metal-centred reduction wave at -0.44 V and three L-centred redox processes at -0.61 V, -1.17 V and -1.41 V.

The redox-activity of L has also been confirmed for copper(I), but will be further complemented by a study of its complex-formation constants in various solvents. The strain in the chelation-ring will be further analysed theoretically.
and compared to those in similar complexes [39], finally related to their redox-activity. It might also be interesting to see whether the deposition of copper might be avoided by using different solvents or ligands. In general, it will be a challenging, but rewarding task to find out whether the redox-activity might be fine-tuned by putting into action differently substituted ligands, e.g. more polar ligands, such as trioxanephosphine or less polar ones such as triptylphosphine. The electocatalytic studies of 1 in the reduction of carbon dioxide was determined by cyclic voltammetry and the results shows a significant catalytic activity (about 220 mV at more positive potentials) compared to when no catalyst was used.

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Supplementary Material

Crystallographic data for 1 have been deposited, under the number CCDC-1039288, with the Cambridge Crystallographic Data Centre. Copies of this information may be obtained, free of charge, from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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