Investigation of structural changes of metal complexes (Cu(I) and Ag(I)) utilizing a flexible, yet sterically demanding multidentate phosphine oxide ligand

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multidentate phosphine oxide – flexible ligand - structural dynamic – variable-temperature NMR – reversable redox-activity.

ABSTRACT: The syntheses of a sterically demanding, multidentate bis(quinaldinyl)phenylphosphine oxide ligand and some Cu(I) and Ag(I) complexes thereof are described. By introducing a methylene group between the quinaldinyl unit and the phosphorus atom, the phosphine oxide ligand gains in additional flexibility. This specific ligand design induces not only a versatile coordination chemistry but also a rarely observed and investigated behavior in solution. The flexibility of the bird-like ligand offers the unexpected opportunity of open-wing and closed-wing coordination to the metal. In fact, the determined crystal structures of these complexes show both orientations. Investigations of the ligand in solution show a strong dependency of the chemical shift of the CH_2 protons on the solvent used. Variable-temperature, multinuclear NMR spectroscopy was carried out and an interesting dynamic behavior of the complexes is observed. Due to the introduced flexibility, the quinaldinyl substituents change their arrangements from open-wing to closed-wing upon cooling, while still staying coordinated to the metal. This change in conformation is completely reversible when warming up the sample. Based on 2D NMR spectra measured at −80°C, an assignment of the signals corresponding to the different arrangements was possible. Additionally, the copper(I) complex shows reversable redox activity in solution. The combination of structural flexibility of a multidentate ligand and the positive redox properties of the resulting complexes are key factors for an application of such compounds in transition-metal catalysis. *Via* a reorganization of the ligand, occurring transition states can be stabilized and selectivity is enhanced.

INTRODUCTION

The versatile coordinating behavior of hemilabile P-N-compounds is a widely used property, not only for coordination chemistry but also in the fields of catalysis, bioinorganic chemistry or material science.[1–13] The comprehensive design of such multidentate phosphine ligands is beneficial when trying to provoke or improve specific properties of the resulting metal complex, e.g. luminescence or catalytic activity. A broad variety of phosphine and phosphine oxide ligands with nitrogen containing aromatic substituents directly bonded to phosphorus have been published.[14–21] Despite the fact that these compounds do not allow for any flexibility of the ligand, they show impressive material properties, such as luminescence or catalytic activity and in general a rich coordination chemistry.[22–24] For the application in transition metal catalysis, a certain flexibility in conformation of the ligand can be beneficial, as possible transition states can be stabilized more easily.[25–29] The benefit of flexibility in catalysis is an already proven concept in the case for enzymatic systems, and has recently been discussed for a variety of other catalyst classes by Sigman *et al.*[30–33]

The steric demand of the phosphine ligand when coordinating to a metal, can be varied by changing the substituents on the phosphorus accordingly. The increased steric demand can lead to a bridging of the ligand across two metal centers, which has been demonstrated before for some transition metals and shows promise for an application in catalysis.[5,34–36] The ligands can even support metallophilic interactions, which lead to interesting photophysical properties.[37,38]

With the introduction of a CH_2-group between phosphorus and the coordinating aromatic substituents, our goal was to create a new class of flexible ligands. These types of ligands should be able to adapt their geometry to the present circumstances and promise a versatile coordination chemistry. However, the flexibility of the ligand can cause different structural conformations of the complexes in solid-state and solution, which can make the design and investigation of such metal complexes challenging. Understanding the functional ability and performance of such type of complexes is of great importance. Studies observing different solution and solid-state structures of metal complexes utilizing phosphorus containing ligands have been published mostly in the 1990s.[39–49] Most of these studies show a dynamic equilibrium in solution between the complex and the dissociated free ligand. A different dynamics in solution has been reported by Klausmeyer *et al.* for silver(I) and copper(I) complexes of bis(pyrid-2-ylmethyl)phenyl-phosphine.[39] Here, the observed dynamic is probably based on the flexibility of the ligand, which remains coordinated to the metal. The precise knowledge of the constitution and conformation is essential for application of a material/compound in solution (e.g. solution processed functional materials or catalysis).[50–52]

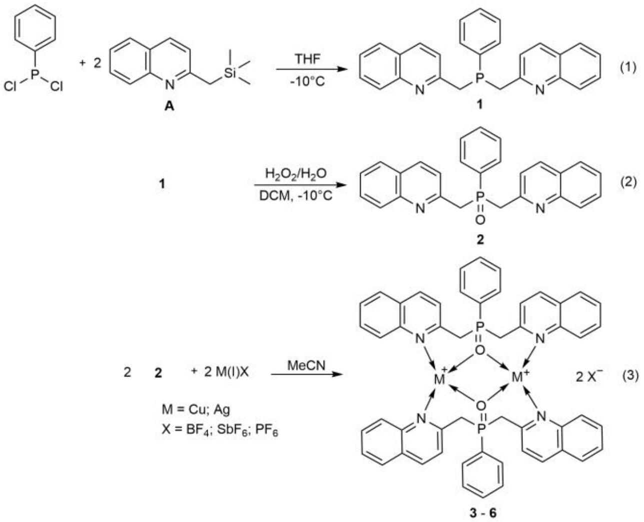
In the present work, we adapted the ligand design in two ways: with the introduction of an additional aromatic ring in the π-system, the ligand becomes sterically more demanding. The additional usage of the phosphine oxide instead of the phosphine is intended to slow down any possible movements and should give a first insight into the type of dynamics in complexes utilizing such flexible ligands.

We describe unexpected properties of a novel, flexible though sterically demanding phosphine oxide ligand and its coordination compounds with selected Cu(I) and Ag(I) salts. These compounds show interesting and reversable conformational changes in solution depending on the temperature, non-coordinating counter ion and also on the solvent used, in addition to an electrochemical activity. A thorough investigation of the solutions is done by VT-NMR and electrochemical experiments. With the help of solid-state NMR and single crystal X-ray crystallography, supported by Hirshfeld analysis, solid state structures could be identified. The presented results reveal a first, in-depth analysis of the dynamic of flexible quinaldinyl-based ligands. Utilizing the so gained knowledge, a variety of options for application in catalysis could be created by refinement and expansion of this interesting ligand system to various use cases.

RESULTS AND DISCUSSION

Synthesis and structural characterization of phosphine oxide metal complexes.

The precursor 2-((trimethylsilyl)methyl)quinoline **A** was synthesized according to the literature.[53] For the bis(quinaldinyl)phenylphosphine (**1**) as well as for the corresponding phosphine oxide (**2**), the synthesis was adapted according to a similar compound previously published by Braunstein *et al.* and is shown in Scheme 1 (see SI for details).[54] This reaction allows for a convenient synthesis of large quantities of the phosphine (quantitative yield) in one batch (> 5 g). Practically no side reactions take place, allowing for an easy work-up. For the synthesis of **2**, bis(quinaldinyl)phenylphosphine **1** is dissolved in DCM, oxidized utilizing a H_2O_2/water mixture and later isolated in 82 % yield. For the synthesis of the coinage metal complexes, bis(quinaldinyl)phenylphosphine oxide (**2**) was dissolved in dry, degassed acetonitrile and the resulting mixture transferred *via* a cannula to the respective amount of Cu(I)BF_4, Cu(I)PF_6, Ag(I)BF_4 or Ag(I)SbF_6 under inert gas (see Scheme 1). All complexes can be isolated in high yields (>80 %).



Scheme 1. Synthesis of bis(quinaldinyl)phenylphosphine (**1**), bis(quinaldinyl)phenylphosphine oxide (**2**) and copper(I) tetrafluoroborate complex (**3**), copper(I) hexafluorophosphate complex (**4**), silver(I) tetrafluoroborate complex (**5**) and silver(I) hexafluoroantimonate complex (**6**) of the phosphine oxide (**2**) showing the coordination mode of the ligand to the respective metal ions.

The molecular structures of compounds **2–6b** of the asymmetric unit in the crystal are shown in Figure 1 and Figure S1 of the SI. The geometry of the ligand **2** in the solid state is reminiscent of a bird, with both quinaldinyl substituents being the wings, with one open wing (containing N1) and the other being closed. Through movement of these wings, the ligand can adapt its coordination geometry to a given metal center, which is impressively shown in the structures of the complexes (see also Scheme 2).

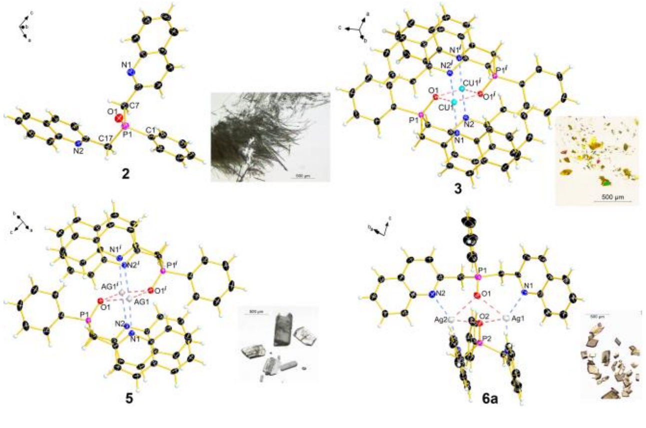
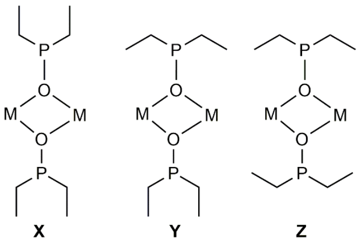


Figure 1. Molecular structures of compounds **2**, **3**, **5** and **6a** of the asymmetric unit in the crystal. Thermal ellipsoids are drawn at 50% probability level. Solvent molecules and anions are omitted.

In all complexes, the binuclear metal (Cu(I), Ag(I)) unit is bridged by two phosphine oxide ligands. The copper(I) ions in **3** and **4** as well as the silver ions in **5**, **6a** and **6b** are coordinated in a distorted disphenoidal geometry (see-saw geometry) by both oxygen (equatorial) and nitrogen (axial) atoms of the ligands. This see-saw coordination is very rare for copper(I) complexes, less so for silver(I).[55–59] There are no hydrogen atoms in proximity suitable to complete a possible trigonal bipyramidal or even octahedral geometry around the metal, either *via* agostic or conventional H-bonding to the metal(I) center. This type of coordination leaves one side of the metal ion free for further coordination. This is an interesting feature, which might be of special interest for a possible application in catalysis.

Earlier, we compared the ligand to a flexible bird-like structure. And we indeed see the different types of double closed wing (**X**, Scheme 2) and mixed open wing/closed wing arrangements (**Y**, Scheme 3) using the same anion (structures **6a** vs. **6b**). If both wings are closed, like in complexes **3–5** and **6b**, a distortion in the ring system occurs due to the close proximity of the rings to each other (Figure S2 of SI). If the wings are mixed open wing/closed wing as in complex **6a**, no distortion appears in any of the quinaldinyl substituents, as the phenyl ring is facing far away from the other aromatic systems.



Scheme 2. Visualization of the double closed wing (**X**), open wing/closed wing (**Y**) and double open wing (**Z**) arrangement of the ligand in the complexes.

NMR characterization of structure and dynamics of phosphine oxide metal complexes in solution.

The NMR signal of the methylene group is substantial for investigating and validating the structure of the complexes in solution. In the ligand, both methylene groups are equivalent, the protons of one methylene group are diastereotopic and should show the typical splitting pattern of an AB part of an ABX spin system (Figure 2, left). The positions of the signals show an impressive dependency of the solvent used, which generates situations ranging from a clear ABX case to a clear A_2X case ($\Delta A = \Delta B$). As described by Braunstein *et al.*[54] for the similar bis(2-picolyl)phenylphosphine, the ABX pattern is also visible for the phosphine **1** (Figure 2, right), as also expected from earlier research from our group.[53,60] These hydrogen atoms are also the most acidic protons of this molecule. They readily form non-classical hydrogen bonds with neighboring molecules in the solid state (see **Fehler! Verweisquelle konnte nicht gefunden werden.** S3 of SI).

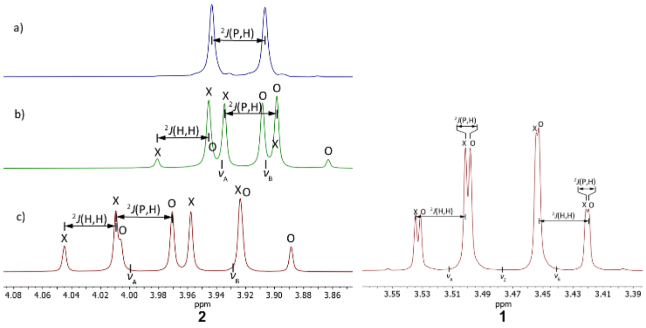


Figure 2. ^1H NMR spectra (left) of **2** in a) $CDCl_3$ (blue), b) CD_2Cl_2 (green) and c) CD_3CN (red) showing the signals of the CH_2-group. ^1H NMR spectrum of **1** in $CDCl_3$ (right) highlighting the diastereotopy of the CH_2-protons. X and O highlight the different AB sub spectra.

Due to the different coordination of the quinaldinyl substituents of one ligand in the complexes, two different methylene groups should be visible in the ^1H NMR. However, the proton spectra at RT show the presence of only one set of methylene protons. Consequently, NMR measurements done at varying temperatures were recorded to observe possible dynamics in solution more closely. Dichloromethane was chosen as the deuterated solvent for the variable temperature measurements. This solvent is known to be non-coordinating and allows for measurement temperatures of as low as −80°C. Selected NMR details of all compounds are shown in Table 1.

The ^{31}P NMR spectrum for **3** at RT shows a relatively sharp single resonance and upon cooling to −80°C, the signal for **3** is symmetrically split into two singlets, both with an integral of one. This indicates the presence of two different phosphorus environments with the same probability at low temperature (Figure S10 of SI). However, none of these signals corresponds to the free ligand. Additionally, in the ^1H NMR of compound **3**, the presence of signals for two different methylene groups and additional signals in the aromatic region are visible at low temperature. As the signals in the ^1H NMR of compound **3** get very broad upon cooling, additional 2D NMR could not be conducted. However, in case of the silver complexes, the situation seems to be much clearer, as the signals show a higher resolution at low temperature. Both silver complexes **5** and **6** were investigated under the same conditions and show a similar behavior to copper complex **3** (Figure 3).

Table 1. Selected NMR details of the synthesized phosphorus containing compounds **1–6b**. Chemical shifts δ in ppm and in reference to CD_2Cl_2, if not otherwise stated.

	1	2	3	4	5	6
$^{31}P\{H\}$ at RT	−13.9 ($CDCl_3$)	33.9	44.0	36.2, −141.8 (sept, $^1J_{P-F}$ = 710.0 Hz)	43.6	42.3

				(CD_3CN)		
$^{31}P\{H\}$ at −80°C			46.4, 40.8		41.7, 42.6	41.4, 42.3

Additional 2D NMR spectra were recorded, to further characterize the situation at −80°C.

The observations are the following: At RT, compound **5** shows only one broad phosphorus signal, one single set of diastereotopic methylene groups and very broad signals for the phenyl ring, whereas the signals for the quinaldinyl ring are sharp. When lowering the temperature to −80°C, the ^{31}P NMR signal is split into two sharp signals with a coalescent temperature between 0 and −20°C. Both phosphorus signals have an intensity ratio of 1:1.

In the ^{1}H NMR at −80°C, the signals for the methylene group and in general for the quinaldinyl rings are split into two different sets in accordance with the two phosphorus signals. The corresponding $^{1}H^{1}H$-NOESY and $^{1}H^{13}C$-HSQC NMR of the CH_2 group of **5** at −80°C further confirms the presence of two different sets of quinaldinyl rings (Figure 4). The diastereotopy of one methylene group is significantly larger than of the other methylene group. The dynamic of the phenyl ring is slowed down at −80°C and the three different signals of the protons in *o*-, *m*- and *p*-position can be observed. The two sets of signals for the quinaldinyl rings differ mostly in the chemical shift of the proton closest to the CH_2 group. For one set, it is close to the chemical shift at RT and in the other set, a shift to lower frequencies ($\Delta\delta$ = 0.4 ppm) is observed. When thawing the sample, the observations in the ^{1}H and ^{31}P NMR are completely reversed back to the initial state at RT. The variable temperature NMR spectra of **6** show a similar behavior in CD_2Cl_2 and are shown in Figure 3. The ^{31}P NMR shifts of complexes **5** and **6** at RT are very similar and thus seem to be independent of the non-coordinating counter ion, indicating the presence of distinct cations and anions in solution. No coupling to $^{107,109}Ag$ is observed in any of the spectra of the silver complexes.

Our general interpretation of this behavior in solution is the following: The differences arise from the different orientation of the quinaldinyl rings with respect to the phenyl ring in the complex. As we know from the different polymorphs of **6** in the solid state, the phosphine oxide ligand **2** is very flexible and can adapt different orientations. At RT, both ligands are coordinating to the metal in the open wing arrangement **Z** shown in Scheme 2. This way, the mentioned proton of the quinaldinyl ring gets in close proximity to the phenyl ring and its shielding cone and this signal is observed shifted to lower frequencies at 7.22 ppm. When cooling, one of the quinaldinyl substituents rearranges to a closed wing conformation (**Y**, Scheme 2), in which the mentioned proton moves away from the phenyl ring. Consequently, the proton moves out of the shielding cone and its signal is shifted to higher frequencies in the ^{1}H NMR ($\Delta\delta$ = 0.4 ppm). This interpretation is supported by the comparison of the chemical shift of this proton in methylquinaldine (7.30 ppm) and 2-((trimethylsilyl)methyl)quinoline (7.12 ppm), where the influence of a phenyl substituent is missing completely. This is further confirmed by the ^{1}H NMR of the phosphine ligand **1** at RT (7.15 ppm), where a similar open-wing conformation is anticipated. The both possible arrangements of the quinaldinyl substituents and the different proximities of the proton to the phenyl ring are visualized in the solid-state by the crystal structure of **6a**. The arrangement with two closed wings (**X**, Scheme 2) would reflect the situation at even lower temperatures. This observed conformational flexibility of this type of ligand in solution can be of special interest for a possible catalytic application. This ligand type has the ability to reorganize to stabilize any possible transition state for e.g. enhanced selectivity in transition-metal catalysis.

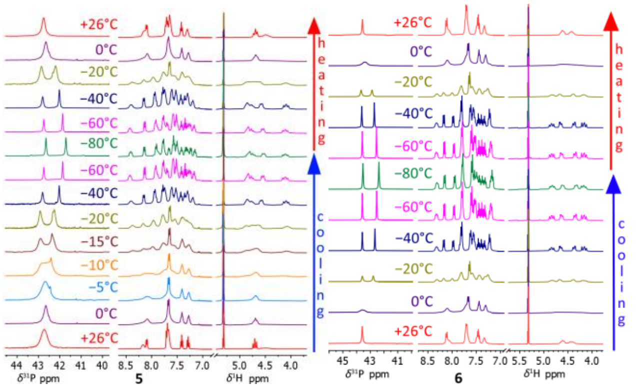


Figure 3. ^{31}P NMR (left) and ^{1}H NMR (right) of compound **5** and **6** in CD_2Cl_2 at different temperatures.

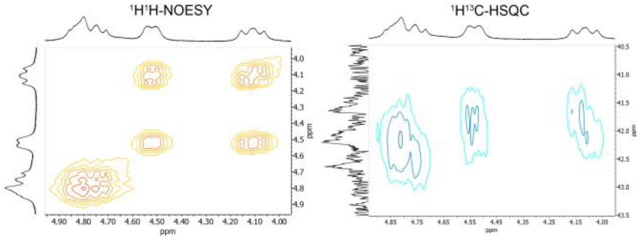


Figure 4. $^{1}H^{1}H$-NOESY and $^{1}H^{13}C$-HSQC NMR of the CH_2 group of **5** at −80°C.

Solid-state NMR characterization of the phosphine oxide metal complexes.

With the aid of solid-state NMR, the chemical shifts of the solid or even crystalline compounds can be compared to the chemical shifts in solution at varying temperatures. The solid-state NMR of the free ligand **2** is in good agreement with solution NMR. The chemical shift in both ^{31}P NMRs is very similar ($\delta^{31}P$ (CD_2Cl_2) = 33.9 ppm; ^{31}P MAS [20 kHz] δ = 33.5 ppm, Figure 5). However, the results of the ^{31}P MAS NMR of the complexes are different than those achieved from solution NMR (Figure 5). Differences in the chemical shift comparing solution NMR and SS NMR of the complexes might be due to a distortion and differences in the geometry surrounding the phosphorus in the solid state.[61] Additionally, Hirshfeld analysis indicates an interaction of the counterion with the rest of the complex in the crystal (see Figure S11 in SI), which might also have an effect on the chemical shifts observed in the solid-state NMR of the complexes.

The chemical shift visible in the ^{63}Cu MAS NMR fits to the unusual coordination of the copper(I) in the crystal of complex **3** (Figure 5). In a publication by Tang et al.[62] the solid-state NMR results of different Cu(I) phosphine complexes with different geometries are discussed. The signal with the lowest frequency was reported with −150 ppm for $CpCuPEt_3$. To the best of our knowledge, solid-state NMR results of similar copper(I) phosphine oxide complexes have not been reported in the literature so far.

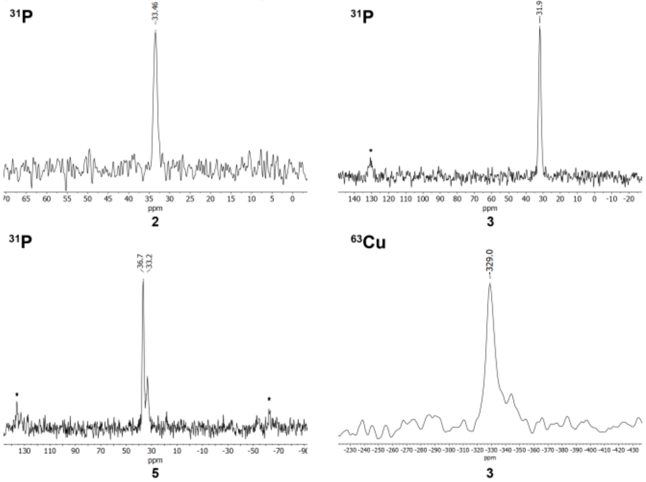


Figure 5. Solid-state ^{31}P MAS NMR [20 kHz] of **2**, **3** and **5** and ^{63}Cu MAS NMR [20 kHz] of **3**. Spinning side bands are marked with an asterisk.

Electrochemical characterization of complex 3.

To study the redox activity of complex **3** in solution and to determine the application as a possible catalyst, complex **3** was dissolved in acetonitrile and studied by cyclic voltammetry. The measurements were performed in a three-electrode cell using a Pt coil as working electrode, a glassy carbon counter electrode and an $Ag/AgNO_3$ (0.01 M) reference electrode (Figure 6 and Figure S11 of SI). Complex **3** and the respective ligand were studied in cathodic and anodic scans, respectively, which were performed at potential ranges from 0.5 V to −1.2 V (Figure 6, left) and from 0 V to 2 V (Figure 6, right) at a scan rate of 50 mV s^{-1}.

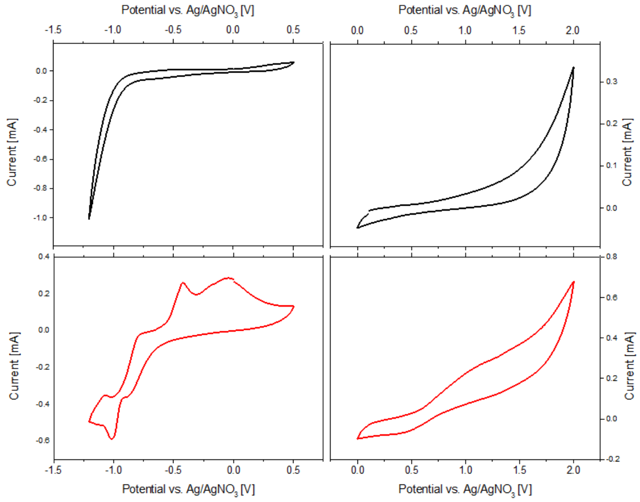


Figure 6. Cyclic voltammograms of complex **3** (red curves) and ligand **2** (black curves) recorded between 0.5– (−1.2) V (left) and 0–2 V (right). The measurements were performed in a three-electrode cell using a Pt coil as working electrode, a glassy carbon counter electrode and a Ag/AgNO3 (0.01 M) reference electrode at a scan rate of 50 mV s^{-1}.

Complex **3** shows several reduction peaks with corresponding re-oxidation peaks in the reverse scan in contrast to the ligand alone, which is electrochemically inactive (Figure 6). During the initial cathodic scan, a broad reduction peak at −0.97 V vs $Ag/AgNO_3$ composed of two overlapping redox peaks is detected, which become more distinct and better separated in the subsequent scans (Figure S11 of SI). In the second and the following scans, two pairs of quasi-reversible redox peaks are observed. The first redox couple shows a reduction peak at −1.02 V vs $Ag/AgNO_3$ and a corresponding re-oxidation peak at −0.42 V vs $Ag/AgNO_3$. A large separation between the cathodic and anodic peak of 600 mV point to a very slow kinetics of charge transfer. The second redox couple shows a reduction peak at −0.90 V with a corresponding oxidation peak at −0.79 vs $Ag/AgNO_3$, which are followed by a much smaller redox couple with peak reduction and oxidation potentials at 1.14 V and −1.07 V vs $Ag/AgNO_3$, respectively. The electrochemical activity of complex **3** in cathodic direction is most probably related to the ligand-assisted redox transformation of Cu(I)/Cu(0) couple according to the information in the literature,[63] although the reduction products cannot be identified yet. This transformation is however electrochemically irreversible for the complex dissolved in acetonitrile resulting in a deposition of reduction product on the Pt electrode, whose re-oxidation is observed in the reverse scan at potential of −0.50 V vs $Ag/AgNO_3$.

Oxidation behavior of Complex **3** is electrochemically slow (quasi-reversible) but chemically stable. In the anodic scan a broad redox couple superimposed on the electrolyte oxidation curve can be observed, with an oxidation and reduction peaks at 1.10 and 0.51 V vs $Ag/AgNO_3$, respectively. The oxidation activity of complex **3** is most probably related to the Cu(I)/Cu(II) redox transformation.

These measurements reveal, that complex **3** is redox active and oxidation and reduction are reversable. The ligand stays connected to the metal during the stressful electrochemical measurements, which is an important property for its potential use as a metal complex in catalytic reactions.

Conclusion

It was shown, that the special type of bis(quinaldinyl)phenylphosphine oxide ligand exhibits a reversable dynamic in solution at different temperatures in its copper(I) and silver(I) complexes, which has not been discussed in this extend before. An explanation for this surprising phenomenon could be given *via* the synergy of a broad variety of complementary analytical methods (VT-NMR, SS NMR, single crystal structures, Hirshfeld analysis, cyclovoltammetry). We found, that both quinaldinyl substituents, which are referred to as wings in a figurative sense, are involved in this interesting behavior of the complexes. Their individual flexibility enables different conformations (open wing, closed wing and mixed) when coordinating to the metal and are found in the crystal structures of the complexes. The careful examination of the VT-NMR spectra in CD_2Cl_2 point at the transition from an open wing arrangement at RT to an open wing-closed wing arrangement at low temperature and exclude a dissociation and reassociation of the complex. The solid-state ^{63}Cu NMR spectrum shows a signal with an unusual chemical shift, which fits to the unusual see-saw geometry of copper(I) observed in the crystal. In addition to the conformational flexibility, a first series of electrochemical measurements clearly show a reversible redox activity for Cu(I) complex **3** in solution. This indicates a potential application for catalysis, since the complex is stable and does not dissociate under these stressful electrochemical conditions. The combination of the advantageous conformational flexibility and electrochemical stability make this new type of bird-like ligand a promising candidate in future transition-metal catalysis. The ability to reorganize to stabilize any possible transition states is crucial to enhance selectivity. However, further mechanistic studies utilizing these types of ligands in catalysis would be necessary to prove the suitability.

ASSOCIATED CONTENT

Supporting Information. Experimental, crystallographic and spectroscopic data is available free of charge via the Internet at http://pubs.acs.org.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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Notes

There are no conflicts of interest to declare.

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