

Research paper

Preparation, photo- and electrochemical studies of a homoleptic imine-phosphaalkene Cu(I) complex

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A B S T R A C T

A 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) functionalized phosphaalkene was used as a bidentate ligand towards a $[\text{Cu}(\text{I})\text{L}_2]^+$ complex. The spectroscopic, electrochemical and photophysical properties of the compound were studied revealing a rich redox chemistry indicative of ligand non-innocence. The compound is weakly emissive with excited state lifetimes of up to 9 ns. NMR and electrochemical analysis indicate a complex dynamic behavior of this photosensitizer in solution.

1. Introduction

The synthesis of main group molecular compounds in low coordinate and atypical bonding states allows for the design of systems possessing useful optical and electronic properties which can be further fine-tuned using various strategies depending on the heteroelement incorporated and the desired application in mind [1–4]. Derivatization of the heteroelement, e.g. oxidation is widely used to tailor the optical properties of group 15 containing heterocyclic compounds [5–9]. On the other hand, Lewis acid base chemistry is extremely versatile for optoelectronic materials containing group 13 and 15 elements to trigger rapid and very specific optical responses [10–14]. Transition metal coordination to organopnictogen compounds in unusual bonding situations has been studied extensively for optoelectronic and catalytic applications [15,16]. Phosphaalkenes and phosphinines as well as their heavier analogs are explored as ligands for their weakly σ -donating, but strongly π -accepting properties, which has proven beneficial by stabilizing low oxidation states of catalytically active species (Fig. 1, I to III) [17–20]. Chelating ligands combining a heavy (phosphorus and heavier) and a light (nitrogen) pnictogen center emerged as an excellent class of ligands over the past decade combining the soft and hard Lewis base properties with different degrees of σ -donation and π -acceptor capabilities [21–24] (Fig. 1, I–III, V, VII).

Copper (I) complexes of phosphaalkenes are relatively rare, spanning coordination numbers from two to four depending on the employed Cu(I) salt and the ligand framework [25,26]. A linear $[\text{CuL}_2]^+$ complex was described by Weber and coworkers using non-coordinating tetrafluoroborate counter ions [27], while mono and bidentate phosphaalkene ligands with coordinating counter ions resulted in tricoordinate neutral copper complexes $[\text{CuX}(\text{P}_\text{P})]$ (IV) or $[\text{CuX}(\text{L})_2]$

[28–30]. Tetragonal(ly distorted) complexes are also found for some bidentate phosphaalkene ligand frameworks in a variety of chloride bridged and solvent assisted coordination [31]. Interestingly, highly restricted tridentate PNP-ligand frameworks often result in highly distorted tetragonal or planar T-shaped geometries (V) [24,32–34].

Recently, large efforts are made to develop systems capable of converting solar energy into chemical fuels. Common photosensitizers for the light harvesting process use rare metals (e.g. Ru or Ir) [35], so alternatives are needed for large scale sustainable applications. Recent efforts shifted towards using cheap and abundant copper metal cations allowing also for facile Cu(I/II) single electron transfer processes. Bipyridine, phenanthroline and phosphine based Cu(I) complexes are studied extensively in light harvesting and as opto-electronic materials [36,37]. These π -acceptor type ligands often allow for pronounced metal–ligand-charge transfer excited states [38]. Recently, they have found applications as photosensitizers for hydrogen generation and carbon dioxide reduction [39–41]. However, both stability and excited state lifetimes of copper complexes are often limited due to the fact that upon excitation, the preferred coordination sphere of the Cu(I) metal center changes from a tetrahedral configuration via Pseudo-Jahn-Teller distortion towards a more flattened tetragonal or square planar configuration [42], additionally opening up a fifth or sixth coordination site [43]. These effects often compromise excited state life-times and emission quantum yields [44]. Many studies especially on homoleptic copper complexes with phenanthroline-based ligands have been done to determine the influence of ligand makeup on the photophysical properties of the complex [45]. A promising strategy to increase life-times and quantum yields is to include steric and geometric constraints introduced by the ligand framework, in order to hinder the flattening effect [46]. In recent years, mixed-ligand Cu complexes have gained

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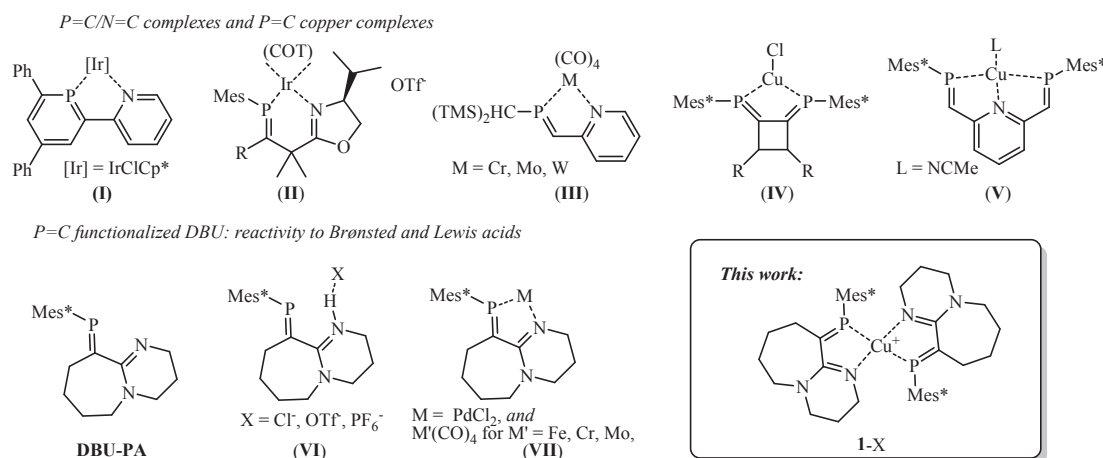


Fig. 1. Literature known complexes of ligands with unsaturated P and N centers; selected phosphalkene copper complexes; Reactivity and coordination behavior of DBU-PA. (Mes* = 2,4,6-*tert*-butyl phenyl).

attention, as this strategy increases the flexibility of ligand modification [43]. This includes homoleptic and heteroleptic complexes with e.g. one phenanthroline and one xantphos ligand [47,48].

As opposed to phosphinines [25] and phospholes [49], phosphalkenes and their coordination compounds rarely exhibit strong luminescence [50]. Recently, we have studied the Lewis acid base interactions of the 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU)-functionalized phosphalkene DBU-PA illustrating the protonation of the imine using Brønsted acids and stabilization of the phosphalkene hydrochloride adduct by a hydrogen bonded water dimer (VI) [51]. Metal coordination of this ligand was limited to the formation of metal (0) carbonyl complexes (where M = Fe, Mo, Cr), increasing the kinetic stabilization by the steric bulk of the metal carbonyl fragments [52], and a *cis*-PdCl₂ complex (VII) [51]. In view of the possibility to use the phosphalkene and imine center in a concerted fashion, the electron accepting nature, and the steric overcrowding of this framework we were intrigued to probe its reactivity as a ligand towards Cu(I) centers. The reaction occurs rapidly as evidenced by ³¹P NMR spectroscopy, yielding a sensitive, intense pink-red, emissive species. The optical and electronic properties are studied using electro-chemical analysis and optical spectroscopy.

2. Results and discussion

The synthesis of the copper(I) complexes occurred straightforwardly using suitable copper sources with BF₄[−] and PF₆[−] counterions, i.e. [Cu(MeCN)₄]⁺X[−]. Based on the non-coordinating nature and redox innocence of the counter ions we expect almost identical photophysical and electrochemical properties in solution, in line with numerous other examples [53,54]. In order to ensure good solubility of both starting materials and the complex, the reaction is performed in a 1:1 DCM/MeCN mixture. The onset of the reaction occurs immediately as observed by an intense color change from pale yellow to dark red. The complex can be isolated in 65% yield after filtration through Celite® and evaporation of all volatiles. Despite numerous efforts we were unable to grow single crystals of this complex, however high resolution mass spectrometry allowed us to confirm formation of the expected [Cu(DBU-PA)₂]⁺ molecular fragment (Fig. 2).

With these findings we have optimized the structure of this complex in the gas phase using a density functional theory (DFT) approach (BPE86/Def2TZV). Due to the semi-rigid ligand backbone and the steric demand of the Mes* substituent we identified two distinctively different conformations as local minima on the relative shallow PES (Fig. 3, and Table 1). The two presented models **M1**⁺ and **M2**⁺ differ only by ca. 3.6 kcal/mol, supporting the idea that this complex may exist in a

number of different conformations in solution. The core of **M1**⁺ shows a highly distorted tetragonal arrangement with P-Cu distances significantly longer (> 2.5 Å) compared to the previously reported structures of mono- bi- and tri-dentate ligand frameworks [24,31]. The distortion from an ideal tetrahedral arrangement is most evident from the significantly widened P-Cu-P and N-Cu-N angles, as well as from the small P-Cu-N angle (ca. 80°) imposed by the ligand backbone. The angle between planes of the ligands P,N atoms and the copper center is reduced to ca. 52.8°. The structure of **M2**⁺ is slightly less distorted, also showing shorter P-Cu and longer N-Cu distances of 2.4 and 2.0 Å, respectively. Most notably the N-Cu-N and P-Cu-P angles are significantly reduced (113.1 and 124.1°), while the angle between the two P,N,Cu planes is closer to a right angle (79.8°).

The ³¹P NMR resonance of the complex **1**-BF₄ displayed a slight shift to lower frequencies (δ³¹P = 241 ppm) compared to the free ligand (254 ppm). This small coordination shift of Δδ = 13 ppm is indicative of weak bonding to the transition-metal fragment to this non-polarized phosphalkene. The obtained ³¹P NMR signals were also significantly broadened (FWHM = 116 Hz, See SI Fig. 3). Similarly, proton and carbon resonance are broadened, which complicates a detailed assignment of these resonances. This behavior can be rationalized by an intermittent de-coordination of the phosphorus atoms due to the weak binding of the ligand as well as a dynamic behavior of energetically quite similar conformers in solution.

In order to study the photophysical properties of the Cu(I)-complex we have studied the electronic absorption and emission properties of **1**-BF₄. Further support of the assignments was corroborated by means of (TD)-DFT studies (Fig. 3, right). Solvation - using single point calculations in a continuum solvation model - has a minor impact on transition probabilities and energies, but does not alter the nature of the states significantly. Notably, both solvents (DCM and MeCN) show very similar results and in the following only results in DCM are discussed. The experimental UV-Vis absorption spectrum in DCM consists of two discernible bands. The strong transition with an absorption maximum at 277 nm (ε_{277nm} = 13,160 M^{−1}cm^{−1}) was assigned to ligand-centered (LC) π → π* and metal-ligand charge transfer (MLCT) transitions [55]. The low-energy absorption contributions are observed as a broad shoulder with an inflection point in the UV region at ~380 nm and extending well into the visible region of the spectrum (λ_{onset} ~ 600 nm). Interestingly the two studied model compounds **M1**⁺ and **M2**⁺ show a large difference of the low energy transitions. The calculated isomer **M1**⁺ has a prominent MLCT band around 515 nm (f = 0.0753) and a weaker MLCT transition at 460 nm (f = 0.0057); in contrast **M2**⁺ shows a MLCT band composed of a weak transition at 495 nm (f = 0.0015) and a prominent transition at 458 nm

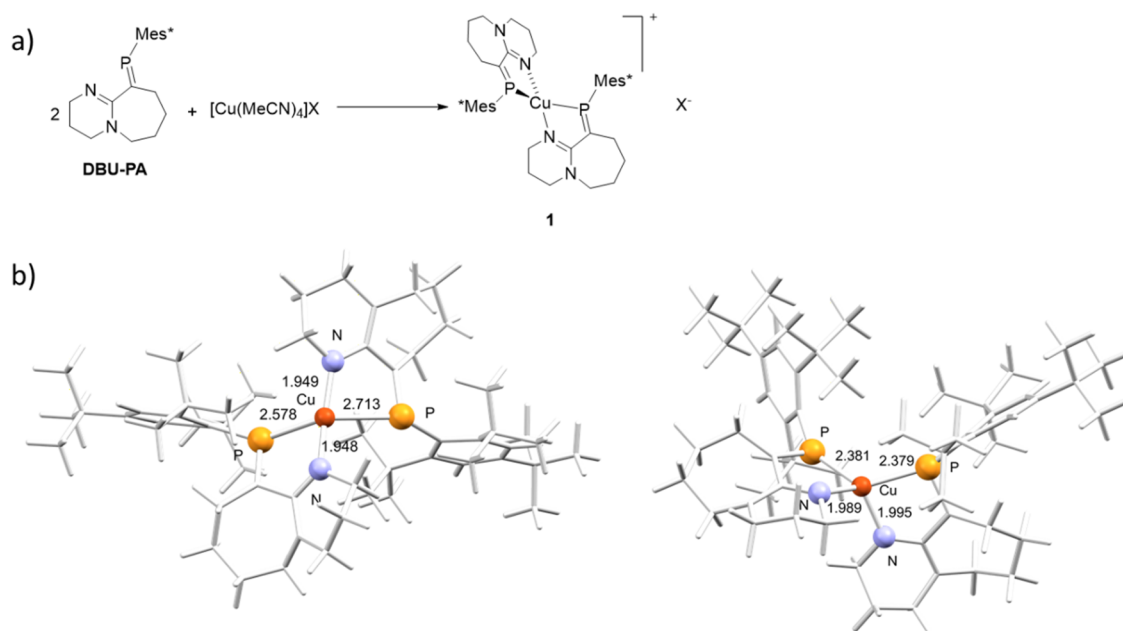


Fig. 2. a) Synthesis of homoleptic complex **1**. i) MeCN:DCM 1:1, r.t. 1 h. for $X = \text{BF}_4^-$ or PF_6^- b) calculated models **M1**⁺ and **M2**⁺ of the synthesized complex.

($f = 0.0585$). These theoretical calculations allow us to assign the experimentally absorption tailing into the visible region to different MLCT states typical of these copper complexes [38,56]. These findings also support the dynamic equilibrium and presence of different isomeric forms.

The emission spectrum of **1-BF₄** was measured in DCM and resulted in an emission wavelength maximum at 555 nm. In view of the mostly non-emissive nature of phosphalkene (complexes) we were quite intrigued to further study this phenomenon. The emission of **1-BF₄** was probed by irradiating the low-lying MLCT electronic transitions (λ_{ex} of 470 nm), so as to avoid overlap with LC events which would complicate the analyses. The emissive behavior of **1-BF₄** changes with concentration; while the absorption has the expected linear dependency following Lambert-Beer's law, increasing the concentration tenfold severely reduced the emission intensity (See SI Fig. 6). This behavior has been previously observed in copper(I) diimine complexes and was related to flattening distortions in the excited state and opening of non-radiative decay pathways [55]. The observed quenching of the emission in **1-BF₄** on the other hand, could have additional contributions from solution dynamics and other complex phenomena as evidenced by the

Table 1

Selected distances [Å] and angles [°] of optimized structures of **1**. DFT PBE86/def2TZV gas phase. ^a Relative free Energy differences at room temperature (kcal mol⁻¹). ^b Relative difference of electronic energies (kcal mol⁻¹). ^c Angle between the planes spanned by the P,N-atoms of one ligand and the copper center.

	M1 ⁺	M2 ⁺
ΔG^a	+3.6	0.0
ΔE^b	+3.5	0.0
P1-Cu	2.578	2.381
P2-Cu	2.713	2.379
N1-Cu	1.948	1.989
N2-Cu	1.949	1.995
P1-Cu-P2	135.1	124.1
N1-Cu-N2	159.8	113.1
P1-Cu-N1	81.2	83.1
P2-Cu-N2	79.9	82.9
P2-Cu-N1	101.8	134.4
P2-Cu-N2	112.0	124.4
(PCuN) vs. (PCuN) ^c	52.8	79.8

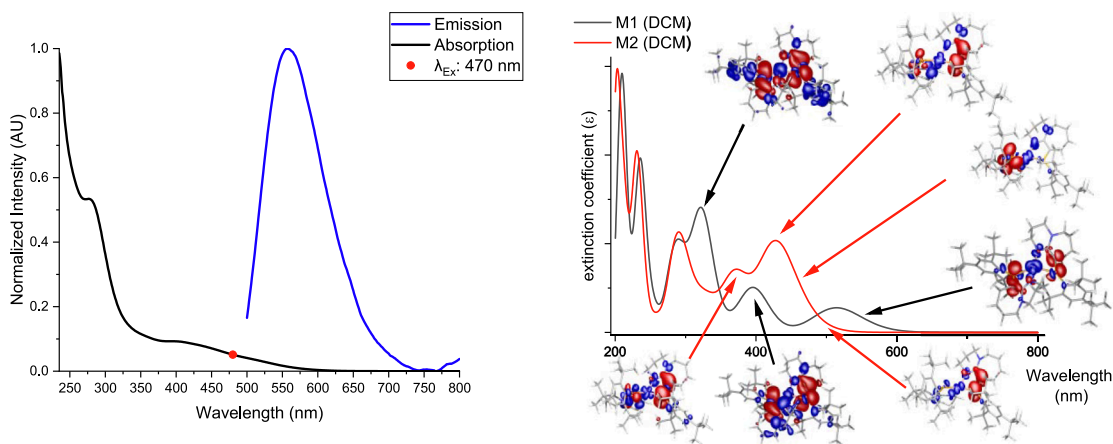


Fig. 3. Left: Absorption and emission spectra of **1-BF₄** in DCM at r.t. $\lambda_{\text{ex}} = 470$ nm. Right: Calculated absorption spectrum of **M1**⁺ and **M2**⁺ including selected Electron Density Difference Map (EDDM) plots of the major transitions (blue surfaces and red surfaces indicate a decrease and increase in electron density respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

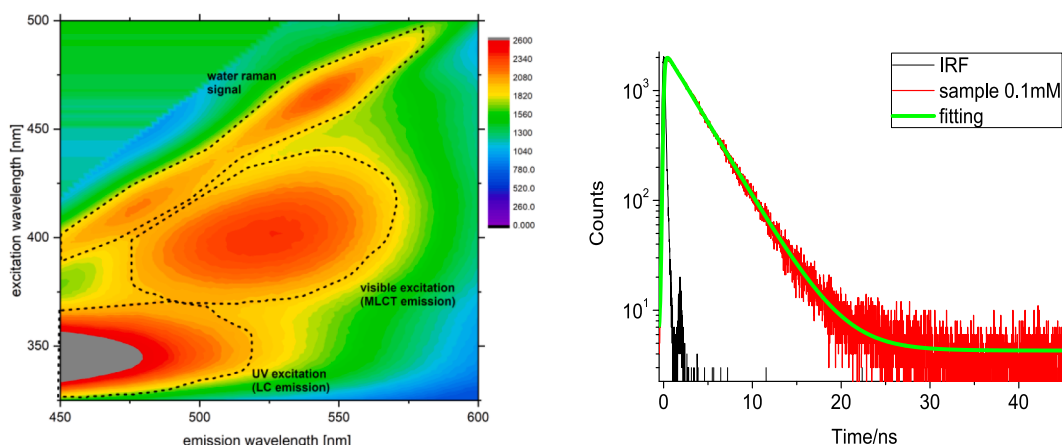


Fig. 4. 3D Emission/Excitation plot of a 0.43 mM solution of 1-PF₆ in frozen MeCN at 77 K. b) Emission decay measurement of 1-BF₄ (DCM, 0.1 mM); excitation wavelength: 470 nm.

signal broadening of the complex's NMR spectra (*vide infra*).

A more complete overview of the emission properties in 1-PF₆ was acquired by a combined extinction-emission spectrum in a frozen MeCN matrix at 77 K; as can be seen in Fig. 4 (left), separate LC and MLCT absorption and emission events occur. Two “islands” of emission belonging to LC and MLCT states respectively are visible, as well as a Raman line stemming from water. Clearly shown is the separation between a ligand-based “island” and the MLCT one in the visible. It is interesting to mention the disappearance of the emission band at 570 nm at an excitation wavelength of 470 nm.

In order to increase our understanding of the excited state dynamics in phosphalkene-containing 1-BF₄, time resolved fluorescence spectroscopy was used to investigate the decay of the excited states arising from the low-lying MLCT transitions. The observed results varied from 3 to 9 ns (Fig. 4, right), which are at best only moderate for state-of-the-art copper sensitizers [47,57]. The longest but still rather modest lifetime of ~9 ns was observed with the use of a 10^{−4} M solution of 1-BF₄ in DCM, whereas higher concentrations gave the lower lifetimes, in line with the observed concentration dependent self-quenching effects.

The electrochemical properties of the copper complexes were probed via cyclic voltammetry and compared to that of the ligand framework. The DBU-PA ligand shows a fully reversible one electron reduction at a mid-potential of −1.853 V vs. Fc/Fc⁺. The facile reduction substantiates the low lying LUMO levels based on the antibonding phosphalkene orbitals in conjunction with the imine moiety. The oxidative processes are irreversible with anodic peaks at +0.876 and +1.148 V, typical of phosphalkene containing compounds [58].

Electrochemical studies of 1-BF₄ show ambipolar behavior in the studied window. The complex shows on the reductive side three electrochemical events; two at −1.883 and −2.286 V are clearly visible, as well as a third one close to the solvent window (−2.467 V, Fig. 5). These events are all almost completely chemically irreversible, even at scan rates (SR) up to 1 V s^{−1}. Based on our DFT calculations, the LUMO is mainly located on the ligand backbone, specifically at the phosphalkene-imine antibonding orbitals with minor contributions from the metal, potentially promoting ligand dissociation and irreversible reductions. The further reductive events are tentatively assigned to both ligand and metal-based reductions. On the oxidative cycle, i.e. anodic sweep, the phosphalkene copper(I) complex is equally complex. The presence of two oxidation events as shoulders and peaks with anodic peak potentials occurring at approximately +0.111 V and +0.393 V vs. Fc/Fc⁺ at significant milder potentials compared to the oxidation of the free ligand indicate metal centered oxidation to play a major role of this Cu(I) complex. Based on the DFT calculations the first event potentially corresponds to a metal-centered Cu^I/Cu^{II} oxidation with minor antibonding metal–ligand contributions. At higher scan rates, this process

becomes quasi-reversible. Further oxidation events could be assigned to ligand-based oxidations. The nature of the process at ~0.9 V vs. Fc/Fc⁺ is less conclusive because the signal coincides with the oxidation potential of uncoordinated ligand. This could correspond to free ligand (from dynamic equilibria or scrambling processes) but also be a consequence of ligand de-coordination as a result of the metal centered oxidation.

3. Conclusion

An interesting aspect of this ligand framework is the presence of two very distinct nitrogen centers, i.e. the imine and the amine nitrogens. While the former is in conjugation with the phosphalkene moiety and leads to the stabilization of the π -symmetric LUMO levels, and thus gives the ligand framework a distinct acceptor character, the latter acts as an internal electron donor moiety via a different delocalization pathway (see orbital depictions SI). In contrast to other pyridine substituted phosphine ligand systems, this framework does not easily allow to reduce the steric demand at the phosphorus center without compromising its ambient stability. However, replacing the DBU fragment with other commercially available diazabicyclic systems with different ring sizes, e.g. DBN, 1,5-diazabicyclo-[4.3.0]-non-5-ene, could give easy access to electronically very similar imine-phosphalkene systems that differ only in their *P,N*-bite angle. This could as well impact the steric interactions of the Mes^{*} substituents favoring stronger ligand binding. Further studies on the impact of this geometric parameter are currently studied in our lab. In summary, we have synthesized a new type of homoleptic copper complex using an imine-phosphalkene based bidentate ligand framework. Theoretical and spectroscopic studies illustrate the acceptor character of the ligand and excited state lifetimes of up to 9 ns upon irradiating into the MLCT band. This represents a rare example of an emissive phosphalkene complex opening new possibilities for the design of luminescent materials.

4. Experimental section

4.1. Materials and methods

All non-deuterated solvents were dried and distilled under argon using standard methods; THF, acetonitrile (MeCN) were dried over sodium / benzophenone and DCM over CaCl₂. Deuterated chloroform (CDCl₃) and DCM (CD₂Cl₂) were purchased from Sigma Aldrich, dried over molecular sieves and distilled. DBU was bought from Sigma Aldrich, dried from calcium hydride and distilled under reduced pressure. [Cu(MeCN)₄]BF₄ and [Cu(MeCN)₄]PF₆ were purchased from Sigma Aldrich and used as received. All synthetic reactions were

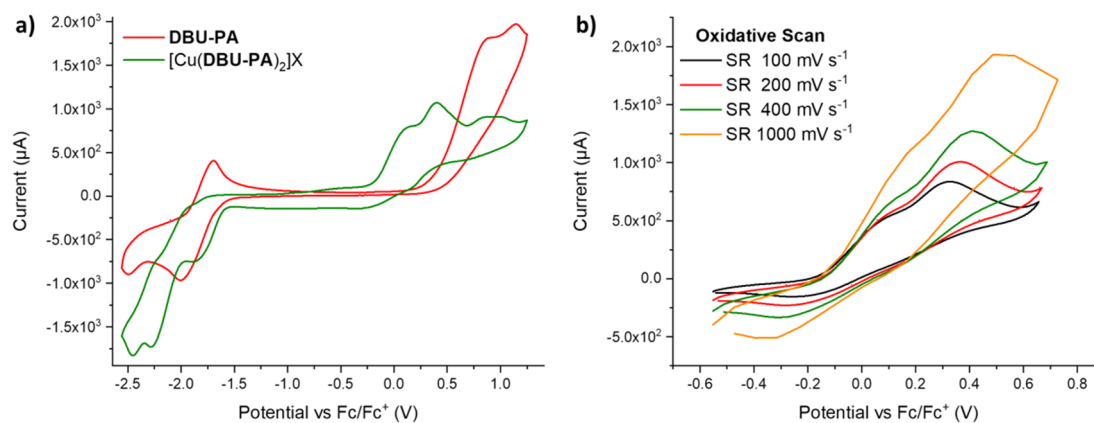


Fig. 5. Electrochemical analysis of complex **1-BF₄** ($X = BF_4^-$) and the free ligand **DBU-PA**. a) Full scan: DCM, Fc/Fc^+ ; WE: GC electrode, CE: Pt electrode, RE: $Ag/AgNO_3$; scan rate (SR) 100 mV s^{-1} b) Oxidative scans and scan rate dependence*, DCM, Fc/Fc^+ ; WE: GC electrode, CE: Pt electrode, RE: $Ag/AgNO_3$. *at a scan rate of 1 V s^{-1} low sampling density leads to slight distortions of the signal.

performed under argon using Schlenk techniques or in the glovebox. NMR measurements (1H , ^{13}C , ^{31}P) were performed on a JNM-ECZ400S/L1 JEOL 400 MHz spectrometer and analyzed with a licensed version of Mestrenova 12.01. Chemical shifts are reported as δ values (ppm) relative to residual solvent signals or referenced externally. High-resolution mass spectra were measured using ESI in the positive mode in a Bruker spectrometer. DFT analyses were performed using Gaussian 09 revision D.01 software. The cyclic voltammetry experiments were carried out in the glovebox, using a standard three-electrode electrochemical cell set-up: Working electrode (WE): glassy carbon (GC), 3 mm; Counter electrode (CE): platinum; Reference electrode (RE): $Ag/AgNO_3$ (silver wire in a 0.1 M $AgNO_3$ acetonitrile solution). The electrolyte was a 0.1 M solution of TBAPF₆ in MeCN, with a cell volume of 6 mL, containing a 0.01 M solution of **1-BF₄**. The signals were referenced to the ferrocene redox couple (Fc/Fc^+). Electrochemical measurements were performed using an Autolab PGSTAT302 potentiostat with a GPES electrochemical interface. UV/vis, steady state, and excited-state lifetime spectroscopy measurements were made in 1 cm path-length cuvettes from 3 mL of solution using Varian Cary 50 Bio UV-Vis spectrophotometer and FluoroMax-3 (JOBIN YVON, HORIBA), and Horiba Scientific FluoroMax 4 spectrofluorophotometer.

Synthesis of 1-X: The phosphalkene ligand (**DBU-PA**) was synthesized according to our previously reported procedure [59], $[Cu(DBU-PA)_2]^+$ (**1-X**) was synthesized with either a BF_4^- (**1-BF₄**) or a PF_6^- (**1-PF₆**) counterion using identical procedures. Because of the instability of the complexes, the spectroscopic and electrochemical measurements were measured using freshly prepared complex species. The electrochemical experiments were done using **1-BF₄** unless otherwise stated and the complex was synthesized directly and used without purification. In a glovebox, 46 mg (0.11 mmol, 2 eq.) of **DBU-PA** and 17 (or 20) mg of $[Cu(MeCN)_4]BF_4$ (or $[Cu(MeCN)_4]PF_6$) (0.05 mmol) were dissolved in 10 mL of a 1:1 MeCN:DCM mixture. The resulting red solution was stirred at room temperature for 1 h and used without further purification. For spectroscopic characterization the sample is filtered through Celite® and all volatiles are removed under reduced pressure. The product can be isolated as dark red solid (**1-BF₄** in 65% isolated yield (35 mg). 1H NMR (400 MHz, $CDCl_3$) δ 7.43 (br, 4H, Ar-H), 3.67–3.21 (m, 18H, DBU-CH₂), 2.00 (br, residual MeCN), 1.76 (br, 10H, DBU-CH₂), 1.51 (m, 36H), 1.32 (m, 18H). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) δ 242.4 ppm. $^{13}C\{^1H\}$ -NMR (101 MHz, $CDCl_3$) 166.5, 163.8, 154.6, 152.3, 122.9, 119.6, 54.8, 50.9, 48.8, 47.9 (d), 40.0, 38.4, 35.2, 33.7, 32.5, 31.7, 31.3, 26.7, 25.1, 24.3, 23.9, 22.8, 19.5. HRMS (ESI, CH_3CN , positive mode): m/z = calcd. for $[Cu(DBU-PA)_2]^+$ ($C_{54}H_{86}N_4P_2Cu$): 915.56237; found 915.56106.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Dedication

This manuscript is dedicated to Maurizio Peruzzini, who enriched the phosphorus community with his fascinating chemistry and amiable personality.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.ica.2020.119958>.

References

- [1] M. Hirai, N. Tanaka, M. Sakai, S. Yamaguchi, *Chem. Rev.* 119 (2019) 8291–8331.
- [2] S.M. Parke, M.P. Boone, E. Rivard, *Chem. Commun.* 52 (2016) 9485–9505.
- [3] J.P. Green, J.A.L. Wells, A. Orthaber, *Dalton Trans.* 48 (2019) 4460–4466.
- [4] M.P. Duffy, W. Delaunay, P.A. Bouit, M. Hissler, *Chem. Soc. Rev.* 45 (2016) 5296–5310.
- [5] E. Regulski, C. Romero-Nieto, *Dalton Trans.* 47 (2018) 10344–10359.
- [6] D. Joly, P.A. Bouit, M. Hissler, *J. Mat. Chem. C* 4 (2016) 3686–3698.
- [7] M.A. Shameem, A. Orthaber, *Chem. Eur. J.* 22 (2016) 10718–10735.
- [8] H. Imoto, K. Naka, *Chem. Eur. J.* 25 (2019) 1883–1894.
- [9] G. Pfeifer, F. Chahdoura, M. Papke, M. Weber, R. Szücs, B. Geffroy, D. Tondelier, L. Nyulászi, M. Hissler, C. Müller, *Chem. Eur. J.* 26 (2020) 10534–10543, <https://doi.org/10.1002/chem.202000932>.
- [10] M. Yang, D. Tofan, C.-H. Chen, K.M. Jack, F.P. Gabbaï, *Angew. Chem. Int. Ed.* 57 (2018) 13868–13872.
- [11] C.J. Berger, G. He, C. Merten, R. McDonald, M.J. Ferguson, E. Rivard, *Inorg. Chem.* 53 (2014) 1475–1486.
- [12] I.A. Adams, P.A. Rupar, *Macromol. Rapid Commun.* 36 (2015) 1336–1340.
- [13] W. Zhang, G. Li, L. Xu, Y. Zhuo, W. Wan, N. Yan, G. He, *Chem. Sci.* 9 (2018) 4444–4450.
- [14] L. Ji, S. Griesbeck, T.B. Marder, *Chem. Sci.* 8 (2017) 846–863.
- [15] P.L. Floch, *Coord. Chem. Rev.* 250 (2006) 627–681.
- [16] C. Müller, L.E.E. Broeckx, I. de Krom, J.J.M. Weemers, *Eur. J. Inorg. Chem.* 2013 (2013) 187–202.
- [17] O. Diebolt, C. Cruzeuil, C. Müller, D. Vogt, *Adv. Synth. Catal.* 354 (2012) 670–677.

- [18] L.E.E. Broeckx, A. Bucci, C. Zuccaccia, M. Lutz, A. Macchioni, C. Müller, *Organometallics* 34 (2015) 2943–2952.
- [19] M. Freytag, S. Ito, M. Yoshifuji, *Chem. Asian J.* 1 (2006) 693–700.
- [20] I. de Krom, E.A. Pidko, M. Lutz, C. Müller, *Chem. – A Eur. J.* 19 (2013) 7523–7531.
- [21] J. Dugal-Tessier, G.R. Dake, D.P. Gates, *Organometallics* 26 (2007) 6481–6486.
- [22] J. Dugal-Tessier, G.R. Dake, D.P. Gates, *Angew. Chem., Int. Ed.* 47 (2008) 8064–8067.
- [23] A. Hayashi, T. Ishiyama, M. Okazaki, F. Ozawa, *Organometallics* 26 (2007) 3708–3712.
- [24] A. Hayashi, M. Okazaki, F. Ozawa, R. Tanaka, *Organometallics* 26 (2007) 5246–5249.
- [25] C. Müller, Chapter 1 - Copper(I) complexes of low-coordinate phosphorus(III) compounds, in: M.S. Balakrishna (Ed.), *Copper(I) Chemistry of Phosphines, Functionalized Phosphines and Phosphorus Heterocycles*, Elsevier, 2019, pp. 1–19.
- [26] J.F. Nixon, *Chem. Rev.* 88 (1988) 1327–1362.
- [27] L. Weber, J. Krümlberg, H.-G. Stämmler, B. Neumann, *Z. Anorg. Allg. Chem.* 632 (2006) 879–884.
- [28] G. Märkl, R. Hennig, *Liebigs Annalen* 1996 (1996) 2059–2064.
- [29] L. Weber, J. Krümlberg, H.G. Stämmler, B. Neumann, *Z. Anorg. Allg. Chem.* 630 (2004) 2478–2482.
- [30] D. Gudat, M. Nieger, K. Schmitz, L. Szarvas, *Chem. Commun.* (2002) 1820–1821.
- [31] A. Jouaiti, M. Geoffroy, G. Bernardinelli, *J. Chem. Soc., Dalton Trans.* (1994) 1685–1688.
- [32] Y. Nakajima, T. Tsuchimoto, Y.-H. Chang, K. Takeuchi, F. Ozawa, *Dalton Trans.* 45 (2016) 2079–2084.
- [33] A. Orthaber, F. Belaj, R. Pietschnig, *Inorg. Chim. Acta* 374 (2011) 211–215.
- [34] S.C. Serin, F.S. Pick, G.R. Dake, D.P. Gates, *Inorg. Chem.* 55 (2016) 6670–6678.
- [35] J.-H. Shon, T.S. Teets, *ACS Energy Lett.* 4 (2019) 558–566.
- [36] I. Andrés-Tomé, J. Fyson, F. Baião Dias, A.P. Monkman, G. Iacobellis, P. Coppo, *Dalton Trans.* 41 (2012) 8669–8674.
- [37] Y. Cao, Y. Saygili, A. Ummadisingu, J. Teuscher, J. Luo, N. Pellet, F. Giordano, S.M. Zakeeruddin, J.E. Moser, M. Freitag, A. Hagfeldt, M. Grätzel, *Nat. Commun.* 8 (2017) 15390.
- [38] D.V. Scaltrito, D.W. Thompson, J.A. O'Callaghan, G.J. Meyer, *Coord. Chem. Rev.* 208 (2000) 243–266.
- [39] S.P. Luo, E. Mejia, A. Friedrich, A. Pazidis, H. Junge, A.E. Surkus, R. Jackstell, S. Denurra, S. Gladiali, S. Lochbrunner, M. Beller, *Angew. Chem. Int. Ed.* 52 (2013) 419–423.
- [40] B.J. McCullough, B.J. Neyhouse, B.R. Schrage, D.T. Reed, A.J. Osinski, C.J. Ziegler, T.A. White, *Inorg. Chem.* 57 (2018) 2865–2875.
- [41] K.E. Dalle, J. Warnan, J.J. Leung, B. Reuillard, I.S. Karmel, E. Reisner, *Chem. Rev.* 119 (2019) 2752–2875.
- [42] M. Iwamura, S. Takeuchi, T. Tahara, *Acc. Chem. Res.* 48 (2015) 782–791.
- [43] Y. Zhang, M. Schulz, M. Wächter, M. Karnahl, B. Dietzek, *Coord. Chem. Rev.* 356 (2018) 127–146.
- [44] R. Giereth, A.K. Mengele, W. Frey, M. Kloß, A. Steffen, M. Karnahl, S. Tschierlei, *Chem. Eur. J.* 26 (2020) 2675–2684.
- [45] A.K. Ichinaga, J.R. Kirchhoff, D.R. McMillin, C.O. Dietrich-Buchecker, P.A. Marnot, J.P. Sauvage, *Inorg. Chem.* 26 (1987) 4290–4292.
- [46] G. Mani, V. Subramanian, Chapter 8 - Homoleptic and heteroleptic copper(I) complexes bearing diimine-diphosphine ligands, in: M.S. Balakrishna (Ed.), *Copper (I) Chemistry of Phosphines, Functionalized Phosphines and Phosphorus Heterocycles*, Elsevier, 2019, pp. 237–258.
- [47] A. Friedrich, O.S. Bokareva, S.-P. Luo, H. Junge, M. Beller, O. Kühn, S. Lochbrunner, *Chem. Phys.* 515 (2018) 557–563.
- [48] A.R. Cabrera, I.A. Gonzalez, D. Cortés-Arriagada, M. Natali, H. Berke, C.G. Daniliuc, M.B. Camarada, A. Toro-Labbé, R.S. Rojas, C.O. Salas, *RSC Adv.* 6 (2016) 5141–5153.
- [49] M. Hissler, C. Lescop, R. Réau, *CR Chim.* 11 (2008) 628–640.
- [50] S. Sarkar, J.D. Protasiewicz, B.D. Dunietz, *J. Phys. Chem. Lett.* 9 (2018) 3567–3572.
- [51] D. Morales Salazar, A.K. Gupta, A. Orthaber, *Dalton Trans.* 47 (2018) 10404–10409.
- [52] R. Appel, L. Krieger, *J. Organomet. Chem.* 354 (1988) 309–312.
- [53] C.E.A. Palmer, D.R. McMillin, *Inorg. Chem.* 26 (1987) 3837–3840.
- [54] T. Gneuß, M.J. Leitl, L.H. Finger, H. Yersin, J. Sundermeyer, *Dalton Trans.* 44 (2015) 20045–20055.
- [55] T.J. Penfold, S. Karlsson, G. Capano, F.A. Lima, J. Rittmann, M. Reinhard, M.H. Rittmann-Frank, O. Braem, E. Baranoff, R. Abela, I. Tavernelli, U. Rothlisberger, C.J. Milne, M. Chergui, *J. Phys. Chem. A* 117 (2013) 4591–4601.
- [56] M.Z. Zgierski, *J. Chem. Phys.* 118 (2003) 4045–4051.
- [57] M. Heberle, S. Tschierlei, N. Rockstroh, M. Ringenberg, W. Frey, H. Junge, M. Beller, S. Lochbrunner, M. Karnahl, *Chem. Eur. J.* 23 (2017) 312–319.
- [58] Y.V. Svyaschenko, A. Orthaber, S. Ott, *Chem. Eur. J.* 22 (2016) 4247–4255.
- [59] D. Morales Salazar, E. Mijangos, S. Pullen, M. Gao, A. Orthaber, *Chem. Commun.* 53 (2017) 1120–1123.