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## Mononuclear Copper(I) Complexes Containing Redox-Active 1,2-Bis(arylimino)acenaphthene Acceptor Ligands: Synthesis, Crystal Structures and **Tuneable Electronic Properties**

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A series of pseudo-tetrahedral copper(I) complexes carrying bis(imino)acenaphthene (BIAN) ligands as acceptor subunits and various phosphane derivatives was prepared and characterized by elemental analysis, X-ray crystallography and spectroscopic techniques. The electronic spectra of the compounds are dominated by low-lying metal-to-ligand charge transfer (MLCT) transitions which could be systematically modified by different substituent patterns at the diimine acceptor subunit and by variations of the electron donating properties and bite angles of the phosphane moiety. A qualitative model based on frontier-orbital overlap arguments is

## Introduction

There is currently an increasing interest in the development of novel catalyst systems based on cheap, abundant and environmentally benign metal ions. Especially, the replacement of quite expensive second- and third-row transition elements, such as the commonly employed rhenium, ruthenium, iridium, palladium or platinum coordination compounds by first-row transition metals or main group elements as catalytically active centres is gaining more and more attention.<sup>[1-5]</sup> In this context, copper-based reagents offer an attractive alternative to complexes of the noble metals, according to their prominent role in enzymatic redox catalysis<sup>[6,7]</sup> and to the significance of Cu-containing heterogeneous catalysts<sup>[8,9]</sup> already used in many important technical processes.

In order to promote multi-electron transfer reactivity, which is crucially required for many permanent substrate transformation processes, individual copper centres are frequently attached to other redox-active subunits. This may be achieved by the formation of multinuclear metal complexes or by establishing an efficient coupling to organic

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introduced to describe the observed variations in optical spectra, excited state energies, solvatochromic behaviour, charge transfer character, and extent of electronic coupling following moderate changes in orbital mixing. Due to their readily tuneable properties and the potential of the BIAN ligands to reversibly store up to four redox equivalents, these systems are of considerable interest for the development of novel multi-electron transfer photosensitizers which are based on the abundant and environmentally benign transition metal copper.

ligands, which are acting as electron transfer cofactors. Following this latter strategy, we have combined a mononuclear copper centre with 1,2-bis(arylimino)acenaphthene (Ar-BIAN) derivatives as redox-active bidentate N-donor chelates.<sup>[10,11]</sup> The strong  $\pi$ -acceptor properties of Ar-BIAN ligands have already been successfully employed to introduce exceptionally low-lying metal-to-ligand charge transfer (MLCT) transitions in several d<sup>6</sup> chlorotricarbonyl Re<sup>I</sup> complexes.<sup>[12]</sup> and the beneficial properties of these compounds have soon led to interesting applications such as low-band-gap sensitizers in bulk-heterojunction photovoltaic devices.<sup>[13,14]</sup> Similar bathochromic shifts of charge transfer transitions expanding far into the visible spectral region of the solar spectrum could also be expected for the corresponding d<sup>10</sup> Cu<sup>I</sup> derivatives of 1,2-bis(arylimino)acenaphthene, which should be able to significantly improve the efficiency of new types of solar cells based on conventional copper 2,2'-bipyridine sensitizers.<sup>[15,16]</sup> Moreover, the properties of Ar-BIAN derivatives are particularly attractive for the development of novel types of photocatalysts, since the delocalized  $\pi$ -electron system of these ligands has recently been demonstrated to reversibly store up to four electrons upon consecutive two-electron reductions,[17] thus acting as a potential electron reservoir for catalytic multielectron reactions.

Here, we report the synthesis, structural characterization and spectroscopic properties of a series of air-stable mononuclear  $Cu^{I}$  Ar-BIAN systems with Ar = phenyl, *p*-tolyl, *p*-methoxyphenyl or *o*-bis(isopropyl)phenyl and additional phosphane-based mono- or bidentate P, PP and PO ligands

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in the coordination sphere of the copper centre. The suitability of these systems to accumulate reduction equivalents and to act as a redox relay for catalytic applications will also be discussed in this paper.

## **Results and Discussion**

#### Syntheses

The series of Ar-BIAN compounds (1a-1d) and phosphane derivatives (2a-2d) studied as ligands for copper(I) in this work is summarized in Scheme 1.



Scheme 1.

Reaction of the 1,2-bis(arylimino)acenaphthene derivatives 1a-1d with [Cu(NCCH<sub>3</sub>)<sub>4</sub>]PF<sub>6</sub> as a low-valent copper precursor and different phosphane ligands in CH<sub>2</sub>Cl<sub>2</sub> leads to deeply coloured compounds, which are obtained as crystalline materials upon precipitation with *n*-pentane. All metal complexes isolated were stable in the solid state with respect to air and moisture. They were characterized by elemental analysis and <sup>1</sup>H NMR, FTIR and ESI-MS spectroscopic methods. In the case of the heteroleptic compounds 1-3 carrying mono or bidentate phosphane ligands, red or violet crystals were formed according to the stoichiometric reaction shown in Scheme 2.



Scheme 2.

In another case, the initially expected formation of the heteroleptic Ar-BIAN phosphane derivative was incomplete, and a defined copper(I) complex 4 carrying only one phosphorus donor 2d was obtained following the general conditions of Scheme 2. This compound could also be produced in comparable yield, when the correct 1:1 stoichiometry was applied. Surprisingly, the combinations 1c/2a and 1a/2d result in the formation of a product mixture in only low yields. Recrystallisation gave only a few crystals of the unintended compounds shown in Figure S1–S3 (Supporting



Information). Therefore, no further chemical analyses were performed. Interestingly, with some other substituents  $\mathbf{R}$  in the Ar-BIAN ligand series, the homoleptic bis-1,2-diimine complexes were isolated as unexpected main products under the standard reaction conditions applied. These almost black compounds showed very interesting spectroscopic and redox properties, which will be presented in a separate publication.

The remarkable variety of coordination patterns of the isolated species formed by a supposedly straightforward synthetic procedure is a typical feature, which reflects the well-known lability of copper(I) phosphane complexes in solution.<sup>[18,19]</sup> Therefore, it is important to keep in mind that the preparation of defined species requires a delicate balance and control of the reaction conditions, and that a thorough structural characterization of the products becomes necessary. On the other hand, however, this feature may be quite advantageous for potential catalytic applications of such systems, since rapid ligand exchange at a labile substrate binding site similar to the reduced forms of mononuclear "type 2" copper centres in oxidoreductases<sup>[7]</sup> is a highly desirable feature for functional enzyme mimics and bio-inspired catalysis.<sup>[3]</sup>

#### Structural Studies

Single crystals suitable for X-ray diffraction of compounds 1, 2, and 4 were obtained from acetonitrile/pentane. Crystals of 1 and 2 are monoclinic with  $P2_1/n$  (Z = 4). 4 crystallizes in the monoclinic space group  $P2_1/c$  (Z = 4) with one molecule of ethyl ether in the asymmetric unit. Characteristic bond lengths and angles are summarized in Table 1. In compounds 1 and 2, the copper atom is coordinated by the BIAN and phosphane ligands in a distorted tetrahedral environment (see Figures 1 and 2). In analogy to other Cu<sup>I</sup> complexes of **2b** there are no sub-van der Waals contacts between the oxygen atom of the phosphane ligand and the copper atom in 2.<sup>[20]</sup> In contrast, the copper centre in complex 4 is coordinated by the BIAN and one phosphane ligand and shows a distorted trigonal-planar coordination geometry (Figure 3). Due to the weak contacts between the copper centre and the oxygen atom of the alde-

Table 1. Bond lengths and angles of 1, 2, and 4.

Bond length [Å]	1	2	4
Cu1–N1	2.132(3)	2.068(2)	2.045(2)
Cu1–N2	2.088(3)	2.087(2)	2.080(2)
Cu1–P1	2.246(1)	2.252(1)	2.172(1)
Cu1–P2	2.280(1)	2.224(1)	-
Cu1–O1	-	-	2.495(2)
Bond angles [°]			
N1–Cu1–N2	79.2(1)	80.1(1)	81.8(1)
P1–Cu1–P2	119.4(1)	112.3(1)	_
P1-Cu1-O1	-	-	75.9(1)
N1–Cu1–P1	121.1(1)	105.9(1)	141.1(1)
N2–Cu1–P2	108.4(1)	112.6(1)	_
N2–Cu1–P1	118.9(1)	111.7(1)	133.6(1)
N2-Cu1-O1	-	-	108.7(1)

hyde function [Cu1–O1 2.495(2) Å] the copper atom lies out of the plane defined by the atoms N1, N2, and P1. With the exception of the Cu1–N1 distance in **1** [2.132(3) Å] all Cu–N distances are very similar (2.045–2.088 Å). Likewise, **1** and **2** exhibit similar Cu–P distances (2.224 and 2.280 Å),

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Figure 1. Complex cation in crystals of 1 (ORTEP, displacement ellipsoids at the 50% probability level).



Figure 2. Complex cation in crystals of 2.



Figure 3. Complex cation in crystals of 4.

whereas in **4** this bond is significantly shorter [Cu1–Pl 2.172(1) Å]. The bite angle of the BIAN ligand lies in a narrow range  $[79.2(1)-81.8(1)^{\circ}]$  comparable to other Cu–BIAN complexes.<sup>[11]</sup> The lower steric flexibility of the chelating DPEPhos ligand **2b** leads to a smaller P–Cu–P angle in **2** compared to **1** [**1**: 119.4(1)° vs. **2**: 112.3(1)°].

#### **Electronic Spectra**

The absorption spectra of all copper(I) Ar-BIAN complexes investigated in this study display various electronic transitions below 400 nm and an additional broad chromophoric feature in the visible spectral region (Figure 4, Table 2).



Figure 4. Electronic absorption spectra of compounds 1–4 in DCM solutions.

Table 2. UV/Vis spectroscopic data of the complexes 1-4 in DCM solution at 298 K.

$\lambda_{\max} \text{ [nm] } (\varepsilon \text{ [L/(mol cm)]})$
461 (7400), 332 sh (16400), 319 (18100), 255 sh (45000)
481 (12100), 333 sh (28500), 315 sh (40900)
518 (6800), 310 sh (29800), 289 sh (33100)
405 sh (7500), 340 sh (7400), 323 (33300), 312 sh (31700),
257 sh (62200)

The shorter-wavelength bands are dominated by the typical structured intraligand (IL) transitions localized at the Ar-BIAN  $\pi$ -electron system,<sup>[12]</sup> which are only slightly shifted with respect to the corresponding UV absorptions of the free diimine ligands. The broad chromophoric visible bands are ascribed to metal-to-ligand charge transfer (MLCT) transitions from predominately copper(I) localized d-electrons to the lowest unoccupied  $\pi^*$ -orbitals of the Ar-BIAN ligand.<sup>[21]</sup> While metal centered ds- and dp-excited states may be present at higher energies, no other low-lying transitions involving the copper valance electrons are expected due to the d<sup>10</sup> electronic configuration of the central metal. The phosphane moiety of the complexes also does not directly contribute to significant spectral features, since the IL bands of these subunits are covered by the more intense diimine-based  $\pi\pi^*$ -transitions of the compounds.

The charge transfer assignment of the visible spectral bands of the complexes, which is in agreement with the regular spectroscopic properties of many other copper(I) diimine systems such as the extensively studied phenanthroline derivatives,<sup>[22–24]</sup> is strongly supported by the occurrence of a conspicuous negative solvatochromism, shifting the visible absorption maxima of all compounds to higher energy with increasing solvent polarity. This characteristic effect, resulting in drastic colour changes in compounds such as **1**, can be quantified by applying different solvent polarity scales such as the empirical  $E^*_{\text{MLCT}}$  parameters<sup>[25]</sup> (Figure 5).



Figure 5. Correlation of the charge transfer transition energies of compounds 1 ( $\blacktriangle$ ) and 2 ( $\blacksquare$ ) with the  $E^*_{\text{MLCT}}$  values of different solvents.

A reasonably linear correlation is observed for the solvatochromic behaviour of all compounds investigated in this study, although for 1 a significant deviation from a simple polarity character of solvent interactions seems to be operative in systems containing a carbonyl group, such as DMF and acetone (Figure 5). In this context it is interesting to recall that the preparation of copper Ar-BIAN complex with the carbonyl containing phosphane ligand (compound 4) also leads to larger deviations from the regular synthetic pathways. Therefore, it is tempting to speculate about dominant exchange equilibria between phosphane and carbonyl ligands in solution as a general property of these copper(I) compounds. This feature should be very useful for the development of catalytic cycles involving carbonyl group containing substrates, but still has to be further confirmed by a more systematic study exceeding the scope of this work.

Another support for the proposed MLCT assignment of the lowest-lying electronic transitions of the copper Ar-BIAN complexes is provided by the results of TD-DFT calculations, which clearly indicate the charge transfer character of the frontier orbital (HOMO–LUMO) transition resulting in a shift of electron density from the electron-rich copper phosphane donor moiety to the 1,2-diimine acceptor side of the molecule. The excited state with the highest calculated oscillator strength results predominately from such a transition (Figure 6, S6, and Table S2).



Figure 6. Contour plots of the highest occupied (left) and the lowest unoccupied molecular orbitals of complex 1 [DFT calculation at the B3LYP/6-31G(d,p) level].

It turns out that the HOMO of the heteroleptic complexes is not purely localized at the copper d-orbitals, but also carries a substantial portion of admixed phosphane ligand character, as illustrated in Figure 6. Therefore, the phosphane moiety, although spectroscopically attracting minor attention, can not only be regarded as a spectator subunit with regard to the photophysical properties, but significantly modifies the electronic structure and orbital coupling of the systems as will be described later in more detail. The LUMO predominately consists of the  $\pi$ -electron system of the coordinating diazabutadiene moiety (N=C-C=N), which is forced to stay rigid because of the aromatic acenaphthene backbone.<sup>[10]</sup> The LUMO-energy of the ligands can be moderately influenced by variations of substituents R, which are situated in *p*-position of the non-coplanar aryl groups directly attached to the nitrogen atoms of the diazabutadiene moiety. This allows to lower the MLCT transition energies by increasing the  $\pi$ -acceptor strength of the Ar-BIAN system. In a certain solvent, the bathochromic shift of the charge-transfer band maximum slightly increases in the series R = OMe < Me < H < COOMe, which linearly correlates to the trend predictable by the Hammet  $\sigma_p$  parameters, as already observed before in a similar system.<sup>[12]</sup>

A much more drastic effect on the electronic structure, however, is induced by small modifications at the phosphane moiety of the heteroleptic Ar-BIAN copper complexes. For example, the exchange of R = H(1a) vs. Me (1b) at the Ar-BIAN acceptor side should induce a moderate blue-shift of approximately 500 cm<sup>-1</sup> for the MLCT transition of complex 2 relative to 1.<sup>[12]</sup> In contrast to this prediction, the MLCT band of 2 is actually 900 cm<sup>-1</sup> redshifted, because the additional structural variation at the phosphane moiety overcompensates the expected effect of the methyl groups. It therefore turns out that the partially mixed copper-phosphane character of the metal-dominated donor subunit of the complexes deserves more attention for a detailed discussion of origin and properties of the lowestlying charge transfer transitions. In Figure 7, a simplified MO picture is provided to illustrate some of the relevant interactions involving the  $d\pi$  and  $\pi^*$  frontier orbitals of the compounds, assuming a pseudo-tetrahedral ligand sphere around the copper(I) center.



Figure 7. Metal–ligand frontier orbital overlap interactions in pseudotetrahedral copper(I) diazabutadiene complexes carrying additional P-donor ligands.

As shown in this qualitative picture, the P-localized lonepairs of the phosphane  $\sigma$ -donor moiety may directly interact with one of the occupied  $d\pi$ -orbitals of the copper center in a tetrahedral environment. This orbital interaction induces a destabilization of the copper(I) oxidation state and thus should lead to a decreasing excitation energy (bathochromic shift) of the corresponding MLCT transitions in heteroleptic complexes carrying 1,2-diimine acceptor ligands. According to angular orbital model considerations, the destabilization of the copper d-orbital shown in Figure 7 can be minimized by increasing the angle  $\theta$  between the Cu-center and the two  $\sigma$ -donor ligands situated at the corners of the tetrahedron. In fact, when two individual phosphane ligands are coordinated, as is the case in compound 1, a quite large distortion from the idealized tetrahedral geometry occurs, and the P–Cu–P angle  $\theta$  reaches a value of 119.4°, which is exceeding the hypothetical rectangular arrangement corresponding to a maximum d-orbital overlap by almost 30°. In the case of compound 2, where a P-Cu-P angle of 112.3° is imposed by the chelating bisphosphane ligand, the corresponding overlap integral should be larger due to the reduced bite angle.<sup>[26]</sup> Therefore, the d-orbital destabilization (wavelength of the MLCT maximum) and the effects of admixed phosphane electron density are expected to be higher in 2 ( $\lambda_{max} = 481 \text{ nm}$ ) compared to 1 ( $\lambda_{max}$  = 461 nm). Within a series of phosphanes of very similar basicity, as is the case with the coordinating P atoms in the  $\sigma$ -donor ligands **2a** and **2b**, in fact the bite angle  $\theta$  seems to be a dominant parameter for tuning the excited state energies of such types of complexes. A calculated Walsh diagram supporting such arguments is given in Figure 8: whereas the HOMO energy is pushed up with decreasing P–Cu–P angle  $\theta$  the energies of the LUMOs are hardly effected upon changing of  $\theta$  (Figure S8).

Besides variations in the P–Cu–P angle, larger changes of the  $\sigma$ -donor strength of different phosphane ligands will also lead to modifications of orbital mixing and MLCT energies, with electron rich phosphanes such as **2c** resulting in even stronger effects than decreasing bite-angles, and thus shifting the lowest-lying electronic transitions significantly to the red ( $\lambda_{max} = 518$  nm in **3**).<sup>[27]</sup> Removal of one of the phosphorus ligands and thus lowering the average ligand field around the copper center has the opposite effect, resulting in higher MLCT transition energies in compounds such as **4**.

While all these electronic effects discussed here certainly determine the optical properties of the compounds, another crucial frontier orbital interaction has the potential to



Figure 8. Walsh-diagram illustrating the effects of variable phosphane bite angles  $\theta$  on the three highest occupied orbital energies of the copper complex cation [(Ph-BIAN)Cu(PPh\_3)<sub>2</sub>]<sup>+</sup> obtained by single point calculations at the B3LYP/6-31G(d,p) level.

strongly influence the chromophore delocalization and therefore the actual charge transfer character of the corresponding excited states, which again will control the expected photoreactivity of the compounds. As can be seen in Figure 7, the copper  $d\pi$ -orbital directly influenced by the phosphane donor moiety has the proper symmetry to interact with the  $\pi$ -electron system of the 1,2-diimine acceptor site. Since the N-Cu-N bite angle of the Ar-BIAN ligands (79° in 1 and 80° in 2) is quite small and nearly approaches the 72° value of an aromatic five-membered ring such as a cyclopentadienyl anion, this  $\pi$ -interaction should not be neglected. In principle, for symmetry reasons, the  $\pi$ -orbital overlap with the copper center may only influence the HOMO-1 ( $\psi_1$ ) and the LUMO ( $\psi_3^*$ ) of the diazabutadiene fragment (see Figures 7 and 9), while the HOMO ( $\psi_2$ ) and LUMO+1 ( $\psi_4^*$ ) linear combinations remain non-bonding. The lowest unoccupied MO ( $\psi_3^*$ ) of the Ar-BIAN ligand depicted in Figure 9 has the largest orbital coefficients at the nitrogen atoms directly connected to the copper(I) center.<sup>[28]</sup> Therefore, the LUMO is predominately affected by this orbital interaction.

Whenever the electron density of the copper phosphane donor fragment is rising and the energy of the  $d\pi$ -orbital is high, also the mixing with the 1,2-diimine-based LUMO becomes more pronounced. As a consequence, the MLCT states are not only red-shifted, but at the same time become more delocalized between the copper center and the Ar-BIAN acceptor side. The corresponding excited states will no longer display pure charge transfer properties and less pronounced dipole moment changes will occur between ground- and MLCT-excited states. Experimentally, this feature is drastically illustrated by the different solvatochromic behaviour of complexes 1 and 2 (Figure 5), where the less delocalized derivative 1 carrying monophosphane ligands contains the more typical charge transfer chromophore with obviously much larger electron density rearrangements occurring in the lowest excited state.



Figure 9. Approximate composition of the  $\pi$ -molecular orbitals of 1,4-diazabutadiene.

When such typical MLCT states with a pronounced charge transfer characteristics are populated, the transition metal center in terms of a classical radical pair model formally reaches the copper(II) oxidation state with a d<sup>9</sup> electron configuration. At the same time, the Ar-BIAN ligand is formally reduced by one electron to form a radical anion. According to the Jahn-Teller effect, a distortion of the pseudo-tetrahedral coordination sphere around copper(II) occurs when the molecule is relaxing from the initial Franck-Condon state to reach a significantly flattened thermally equilibrated excited state geometry.<sup>[22]</sup> In the course of this relaxation process, the copper(II) oxidation state is stabilized and nucleophilic substrate or solvent molecules may approach the coordinatively unsaturated "axial" sites at the Cu center. In terms of the orbital interactions discussed above, it is important to note that this well-established flattening distortion occurring in the charge transfer excited state will also lead to an orbital decoupling of the donor and acceptor subunits in the compounds, since the  $d\pi$ -overlap of copper with the diazabutadiene moiety shown in Figure 7 is gradually lost with an increasing distortion of the tetrahedron and should even vanish completely in a square planar system.

By comparison of the redox properties of known rhenium(I) Ar-BIAN complexes<sup>[12]</sup> with the corresponding data available for phenanthroline-copper(I) and -rhenium(I) complexes,<sup>[18,29]</sup> it can be predicted that the MLCT-excited copper(I) Ar-BIAN systems such as 1 should be very versatile redox reagents for photoinduced electron transfer processes in solution.<sup>[30]</sup> Besides the possibility of back-electron transfer re-forming the copper(I) ground state species, the decoupled 1,2-diimine radical anion subunit of the MLCT excited species might for example further react in a secondary electron transfer process by reductive quenching involving a donor substrate. This type of reaction, which is expected to be favoured due to a low reorganization energy, should then result in the formation of the diamagnetic Ar-BIAN<sup>2-</sup> dianion<sup>[17,29]</sup> in the coordination sphere of copper and thus could store two reduction equivalents on an elecEurjic ef horganic chemis

tronically decoupled acceptor ligand. Such a process is extremely useful for the development of photocatalytic systems suitable for multi-electron transfer reactions similar to the ones involving biologically relevant organic redox cofactors such as hydroquinones, NADH or reduced flavines, which have evolved in natural systems as efficient redox relays for the prevention of free radical product formation and undesired catalyst degradation processes.

Of course, this ideal situation for photoredox reactivity gradually changes in the more delocalized MLCT cases occurring in compounds such as **3**, where the formal copper oxidation states are less settled and coupling between the copper center and the Ar-BIAN ligand might be dominant also in the excited states due to the larger orbital interactions. As a consequence, besides the differences in solvatochromic features also the structural changes following the MLCT excitation should be less pronounced in this case. Such drastic differences in excited state distortion are wellknown to strongly influence the luminescence properties and photochemical reactivity of other copper 1,2-diimine complexes.<sup>[22]</sup> A systematic study, which is certainly necessary to further support all the basic concepts developed in the present work is currently underway.

## Conclusions

Pseudo-tetrahedral copper(I) complexes carrying bis-(imino)acenaphthene ligands are versatile new photosensitizers with rather low-lying metal-to-ligand charge transfer (MLCT) states which are expected to be suitable for photoredox processes. Their electronic properties can be systematically modified by different substituents at the diimine acceptor subunit and by variations of the electron donating properties and bite angles of the phosphane moiety. Especially, the delocalization between central metal and the ligands is quite sensitive to minor structural distortions at the phosphane ligand site and thus can be exploited to dictate excitation energies, solvatochromism, charge transfer reactivity and the stability of the copper(I) oxidation state in these complexes. The suitability of such systems for the accumulation of reduction equivalents and to act as a multielectron redox reagent for catalytic applications seems very promising. Therefore, such copper-based systems may become an attractive alternative to classical photosensitizers such as ruthenium polypyridine complexes in the context of typical applications such as dye-sensitized solar cells or photocatalytic redox reactions.

## **Experimental Section**

**General Methods:** All chemicals were purchased in reagent-grade quality and directly used as received. Unless otherwise stated, commercially available organic solvents of standard quality were purified and dried according to the accepted general procedures. Elemental analyses were performed at the Centre for Chemical Analysis of the Faculty of Natural Sciences of the University of Regensburg. Electronic absorption spectra were recorded with a Cary 300 Bio UV/Vis spectrophotometer using 1-cm quartz cells. NMR spectra were recorded with a Bruker Digital Avance NMR spectrometer DPX200 (<sup>1</sup>H: NMR 200.1 MHz; <sup>13</sup>C: 50.3 MHz; T = 303 K). The chemical shifts are reported in ppm relative to external standards (solvent residual peak), and coupling constants are given in Hertz. The spectra were analysed as being first order. Error of reported values: 0.01 ppm for <sup>1</sup>H NMR, 0.1 ppm for <sup>13</sup>C NMR and 0.1 Hz for coupling constants. The solvent used is reported for each spectrum. Mass spectra were recorded with a LCQ DECA XP Plus (ESI). Infrared spectra were recorded with a FT-IR-Spectrometer Paragon PC.

Computational Details: The Gaussian03 program was used in the calculations.[31] Initial coordinates were taken from the corresponding X-ray crystal structure if available. All quantum-chemical calculations were carried out using a density functional theory (DFT) based method with the hybrid B3LYP<sup>[32]</sup> functional. The 6-31G(d,p) basis set<sup>[33]</sup> was used through the calculations, whereas for the complexed metal a LanL2DZ basis set<sup>[34]</sup> was applied. The obtained geometries were verified to correspond to a real minimum by establishing an absence of imaginary IR frequencies. The electronic transition energies and oscillator strengths were calculated using the time-dependent density functional response theory (TD-DFT)<sup>[35]</sup> at the B3LYP/6-31G(d',p') level.<sup>[36]</sup> Single point energies were calculated applying the B3LYP/6-31G(d,p) method. The parameters from the optimized geometry were held fixed while the bond P–Cu–P angle  $\theta$  were changed from 95–135° in intervals of 5°.

**Synthesis:** The preparation of all compounds described in this work was carried out according to the following general procedure: stoichiometrical amounts of  $[Cu(NCCH_3)_4]PF_6$  and the phosphane ligand in 20 mL of dichloromethane were stirred at room temperature for 2 h and then combined with a solution of the Ar-BIAN ligand in 5 mL of dichloromethane. This reaction mixture was stirred for an additional hour. After this period, approximately 10 mL of *n*-pentane were added to fully precipitate the complex

formed. The product was washed with *n*-pentane, filtered and dried in vacuo.

**[(Ph-BIAN)(Ph<sub>3</sub>P)<sub>2</sub>Cu]PF<sub>6</sub> (1):** Reaction of  $[Cu(NCCH_3)_4]PF_6$ (100 mg, 0.27 mmol) with Ph-BIAN (**1a**, 89.29 mg, 0.27 mmol) and PPh<sub>3</sub> (**2a**, 140.74 mg, 0.54 mmol) yielded 208.68 mg (73%) as a red powder. <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>):  $\delta = 8.19$  (d, <sup>3</sup>J = 8.54 Hz, 2 H, *o*-H-An), 8.13 (d, <sup>3</sup>J = 7.02 Hz, 2 H, *p*-H-An), 7.86 (dd, <sup>3</sup>J =7.88 Hz, 2 H, *p*-H-An), 7.62–7.34 (m, 40 H, Ph-H) ppm. <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>):  $\delta = 162.45$  (+, N=C, 2 C), 146.43 (+, N-C, 2 C), 129.36–133.38 (-, aromatic, 4 C), 130.84 (+, 6 C), 125.23 (+, 4 C) ppm. MS (ESI, MeOH/CHCl<sub>3</sub>): m/z (%) = 658.28 (100) [M – PPh<sub>3</sub>]<sup>+</sup>, 436.00 (24.33) [(Ph – BIAN)Cu + MeCN]<sup>+</sup>, 395.20 (1.91) ](Ph – BIAN)Cu]<sup>+</sup>. C<sub>60</sub>H<sub>46</sub>CuF<sub>6</sub>N<sub>2</sub>P<sub>3</sub> (1065.5): calcd. C 67.64, H 4.35, N 2.63; found C 68.76, H 4.48, N 2.30. UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda$ (log  $\varepsilon$ ) = 255 sh (4.65), 319 (4.26), 332 sh (4.22), 461 nm (3.87). IR (KBr):  $\tilde{v} = 3054$  (m, =C–H), 1736 (s, C=O), 1652 (s, C=N–), 1440 (s, P–C), 1280 (s, C–N), 840 (ss, P–F) cm<sup>-1</sup>.

**[(Tol-BIAN)(DPEPhos)Cu]PF<sub>6</sub> (2):** Reaction of  $[Cu(NCCH_3)_4]PF_6$ (100 mg, 0.27 mmol) with Tol-BIAN (1b, 97.25 mg, 0.27 mmol) and DPEPhos (2b, 144.50 mg, 0.27 mmol) yielded 234.75 mg (79%) as a violet powder. <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>):  $\delta = 8.29$  (d, <sup>3</sup>J =8.54 Hz, 2 H, *o*-H-An), 8.13 (d, <sup>3</sup>J = 7.70 Hz, 2 H, *p*-H-An), 7.58 (dd, <sup>3</sup>J = 7.68 Hz, 2 H, *m*-H-An), 6.74–7.65 (m, 34 H, Ph-H), 6.30 (d, <sup>3</sup>J = 8.55 Hz, 2 H, Ph-H), 2.40 (s, 6 H, Me) ppm. MS (ESI, MeOH/CHCl<sub>3</sub>): *m*/*z* (%) = 962.28 (100) [M]<sup>+</sup>, 601.33 (53.98) [M – (Tol-BIAN)]<sup>+</sup>, 642.53 (14.19) [Cu + DPEPhos + MeCN]<sup>+</sup>. C<sub>62</sub>H<sub>48</sub>CuF<sub>6</sub>N<sub>2</sub>OP<sub>3</sub> (1107.5): calcd. C 67.24, H 4.37, N 2.53; found C 66.93, H 4.56, N 2.22. UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda$  (log  $\varepsilon$ ) = 315 *sh* (4.61), 333 *sh* (4.46), 481 nm (4.08). IR (KBr):  $\tilde{v} =$  3054 (m, =C–H), 1654 (s, C=N–), 1436 (s, P–C), 1280 (w, C–N), 842 (ss, P–F) cm<sup>-1</sup>.

**[(MeO-Ph-BIAN)(dppe)Cu]PF<sub>6</sub> (3):** Reaction of  $[Cu(NCCH_3)_4]PF_6$ (100 mg, 0.27 mmol) with MeO-Ph-BIAN (1c, 105.3 mg, 0.27 mmol) and dppe (2c, 106.9 mg, 0.27 mmol) yielded 211.83 mg

	1	2	4
Formula	$C_{60}H_{46}CuN_2P_2 \cdot PF_6$	C <sub>62</sub> H <sub>48</sub> CuN <sub>2</sub> OP <sub>2</sub> ·PF <sub>6</sub>	$C_{55}H_{55}CuN_2OP \cdot C_4H_{10}O \cdot PF_6$
$M_{\rm W}$ [g/mol]	1065.50	1107.48	1073.62
Crystal size [mm]	$0.28 \times 0.24 \times 0.20$	$0.22 \times 0.18 \times 0.12$	$0.32 \times 0.29 \times 0.11$
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/c$
a [Å]	15.262(12)	14.395(10)	15.4477(1)
<i>b</i> [Å]	17.002(16)	17.457(10)	18.3784(1)
c [Å]	20.145(18)	21.240(2)	19.3020(1)
a [°]	90	90	90
β [°]	8.65(10)	94.68(9)	98.518(1)
γ [°]	90	90	90
V[Å <sup>3</sup> ]	5168.1(8)	5319.64(7)	5419.47(6)
$\rho_{\rm ber}  [{\rm mg}  {\rm cm}^{-3}]$	1.369	1.383	1.316
Ζ	4	4	4
$\mu [{ m mm}^{-1}]$	0.579	1.982	1.662
<i>T</i> [K]	296(1)	123	123
Θ range [°]	2.57-26.94	3.28-62.24	2.89-62.21
λ [Å]	0.71073	1.54184	1.54184
Reflections collected	70487	25805	71918
Unique reflections	11172 [R(int) = 0.1468]	8146 [R(int) = 0.0273]	8517 [R(int) = 0.0398]
Observed reflections $[I > 2\sigma(I)]$	4427	6201	6579
Data/restraints/parameters	11172/0/649	8146/0/679	8517/0/659
Absorption correction	analytical	semi-empirical	semi-empirical
$T_{\min}, T_{\max}$	0.9212, 0.7981	1.00000, 0.77370	1.00000, 0.59687
$\sigma_{\text{fin.}}$ (max/min) [eÅ <sup>-3</sup> ]	0.425/-0.252	0.707/-0.475	0.896/-0.394
$R_1 \left[ I \ge 2\sigma(I) \right]$	0.0477	0.0369	0.0394
wR <sub>2</sub>	0.1060	0.1015	0.1165

Table 3. Crystal data, data collection and structure refinement for compounds 1, 2, and 4.

(79%) as a red powder. <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>):  $\delta = 8.62$  (d, <sup>3</sup>*J* = 8.02 Hz, 2 H, *o*-H-An), 6.84–7.49 (m, 32 H, Ph-H), 3.93 (s, 6 H, Me), 2.39 (t, <sup>3</sup>*J* = 5.32 Hz, 4 H) ppm. <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>):  $\delta = 24.94$  (+, dd, <sup>2</sup>*J*<sub>CP</sub> = 18.95 Hz; 2 C), 55.30 (-, 2 C), 114.53 (-, 4 C), 131.87 (-, dd, *J* = 7.95 Hz, Ph), 131.41 (+, Ph), 130.75 (+, Ph), 130.46 (-, Ph), 128.69 (-, m, Ph), 127.82 (-, Ph), 124.08 (-, Ph), 158.42 (-, 2 C) ppm. C<sub>52</sub>H<sub>44</sub>CuF<sub>6</sub>N<sub>2</sub>O<sub>2</sub>P<sub>3</sub> (999.39): calcd. 62.50, H 4.44, N 2.80; found C 61.97, H 4.09, N 2.68. UV/ Vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda$  (log  $\varepsilon$ ) = 289 *sh* (4.52), 310 *sh* (4.47), 518 nm (3.83). IR (KBr):  $\tilde{v} = 3052$  (m, =C–H), 1638 (s, C=N–), 1446 (s, P–C), 1295 (s, C–N), 1246 (s, C–O), 839 (ss, P–F) cm<sup>-1</sup>.

**[(***i***Pr<sub>2</sub>-Ph-BIAN)(PCHO)Cu]PF<sub>6</sub> (4):** Reaction of [Cu(NCCH<sub>3</sub>)<sub>4</sub>]-PF<sub>6</sub> (100 mg, 0.27 mmol) with Pr<sub>2</sub>-Ph-BIAN (1d, 134.3 mg, 0.27 mmol) and PCHO (2d, 140.7 mg, 0.54 mmol) yielded 168.95 mg (63%) of a brown powder. <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>):  $\delta = 9.67$  (s, 1 H, CHO), 8.21 (d, <sup>3</sup>J = 8.14 Hz, 2 H, *o*-H-An), 7.93–7.99 (m, 1 H), 7.77 (dd, <sup>3</sup>J = 7.64 Hz, 1 H), 7.16–7.62 (m), 6.97 (m, 4 H), 6.86 (d, <sup>3</sup>J = 7.17 Hz, 2 H), 3.07 (sept, <sup>3</sup>J = 6.68 Hz, Me<sub>2</sub>C-*H*), 1.26 (br., 1 H, Me), 0.93 (br., 23 H, Me) ppm. C<sub>55</sub>H<sub>55</sub>CuF<sub>6</sub>-N<sub>2</sub>OP<sub>2</sub> (999.54): calcd. C 66.09, H 5.55, N 2.80; found C 64.36, H 4.62, N 2.68. UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>): λ (log ε) = 257 sh (4.79), 312 sh (4.60), 323 (4.52), 340 sh (3.87), 405 sh nm (3.88). IR (KBr):  $\tilde{v} = 2959$  (m, -C-H), 1670 (s, C=O), 1641 (s, C=N–), 1435 (s, P–C), 1297 (s, C–N), 837 (ss, P–F) cm<sup>-1</sup>.

**Crystal Structures:** Diffraction data for crystals of the compounds **1** and **8** were collected with a STOE-IPDS diffractometer<sup>[37]</sup> with graphite-monochromated Mo- $K_{\alpha}$  radiation ( $\lambda = 0.71073$  Å), whereas crystal data of **2**, **4**, **6** and **7** were collected with an Oxford Diffraction Gemini Ultra CCD diffractometer with multilayer optics and Cu- $K_{\alpha}$  radiation ( $\lambda = 1.5418$  Å). Further crystallographic and refinement data can be found in Table 3 and Table S1. The structures were solved by direct methods (SIR-97)<sup>[38]</sup> and refined by full-matrix least-squares an  $F^2$  (SHELXL-97).<sup>[39]</sup> The H atoms were calculated geometrically and a riding model was applied during the refinement process.

CCDC-756603 (for 1), -756606 (for 2) and -756601 (for 4), contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data\_request/cif.

**Supporting Information** (see also the footnote on the first page of this article): Further experimental details on synthesis, structures, and quantum chemical calculations.

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