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Heterobimetallic Cu-dppf (dppf = 1,1'-Bis(diphenylphosphino)ferrocene) Complexes with "Click" Derived Ligands: A Combined Structural, Electrochemical, Spectroelectrochemical, and Theoretical Study

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Supporting Information

ABSTRACT: Heterodinuclear complexes of the form $[(dppf)Cu(L)](BF_4)$ (dppf = 1,1'-bis(diphenylphosphino)ferrocene), where L are the chelating, substituted 4,4'-bis(1,2,3-triazole) or 4-pyridyl(1,2,3-triazole) ligands, were synthesized by reacting $[Cu(dppf)(CH_3CN)_2](BF_4)$ with the corresponding "click" derived ligands. Structural characterization of representative complexes revealed a distorted-tetrahedral coordination geometry around the Cu(I) centers, with the donor atoms being the P donors of dppf and the N donors of the substituted triazole ligands. The "local-pseudo" symmetry around the iron center in all the investigated complexes of dppf is between that of the idealized D_{5h} and D_{5d} . Furthermore, for the complex with the mixed pyridine and triazole donors, the Cu–N bond distances were found to be shorter for the triazole N donors in comparison to those for the pyridine N donors. Electrochemical studies on the complexes revealed the presence of one oxidation and one



reduction step for each. These studies were combined with UV–vis–near-IR and EPR spectroelectrochemical studies to deduce the locus of the oxidation process (Cu vs Fe) and to see the influence of changing the chelating "click" derived ligand on both the oxidation and reduction processes and their spectroscopic signatures. Structure-based DFT studies were performed to get insights into the experimental spectroscopic results. The results obtained here are compared with those of the complex $[(dppf)Cu(bpy)](BF_4)$ (bpy = 2,2′-bipyridine). A comparison is made among bpy, pyridyl-triazole, and bis-triazole ligands, and the effect of systematically replacing these ligands on the electrochemical and spectroscopic properties of the corresponding heterodinuclear complexes is investigated.

INTRODUCTION

The metalloligand 1,1'-bis(diphenylphosphino)ferrocene (dppf) occupies a special place in organometallic and catalysis research.¹ Reasons for this are manifold: the presence of two strong P donors, a redox-active ferrocene backbone, and an unusual bite angle produced at the additional metal center by the two P donors.^{1c} dppf provides an ideal starting point for generating heterodinculear complexes because of the ability of the P donors to bind to a variety of metal centers.¹ One research direction that has been followed with the dppf metalloligand is to generate metal complexes with an additional metal center that is then connected to either a redox-inert or a redox-active coligand (Scheme 1).²

The locus of oxidation in such heterobimetallic complexes (Scheme 1) is often strongly dependent on the nature of the additional metal center and the coligands attached to it.² Examples of definitive proof of the preferred oxidation of the additional metal center are prevalent in the literature.^{2b} We have recently shown that the presence of zwitterion-derived

Scheme 1. Schematic Representation of Heterodinuclear Complexes with dppf and an Additional Metal Center with the Arrows Pointing to the Possible Locus of Oxidation





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Scheme 2. Synthesis of Complexes^a



^aThe synthesis of 7 was adapted from the literature.¹²

redox-active ligands on the copper center bound to the dppf unit actually results in the shift of the oxidation step to the redox-active ligand.³ There are examples available of heterobimetallic complexes where the oxidation steps are actually predominantly localized on the dppf part of the molecule.^{2b} Furthermore, the presence of redox-active ligands often allows the observation of reduction processes based on those ligands.^{2c,3}

"Click"-derived substituted 1,2,3-triazole⁴ ligands have been extensively used in coordination chemistry in recent years.⁵ Metal complexes derived from such ligands have found use in electron transfer chemistry,⁶ photochemistry,⁷ homogeneous catalysis,⁸ magnetic studies,⁹ and supramolecular chemistry,¹⁰ just to name a few fields. Our group has been interested in the use of these ligands in coordination chemistry^{5d} and the applications thereof.¹¹ For the present work, we asked ourselves the following questions.

(a) Where would the locus of oxidation be (Cu or dppf) in heterodinuclear complexes where a copper(I) center bound to dppf has additional "click"-derived ligands? This question is an interesting one, considering that both copper(I) and the ferrocene unit are considered to be redox centers that are relatively easy to oxidize.

(b) How would the oxidation processes as well as possible reduction processes change on changing the coligand on copper(I) from a bis(1,2,3-triazole) through a pyridyl-triazole to 2,2'-bipyridine (bpy)?

(c) What would be the spectroscopic signatures for the various redox states of these heterodinuclear complexes, and what influence would the "click"-derived coligands have on these spectroscopic signatures?

The ligands $L^1 = 1,1'$ -bis(phenyl)-4,4'-bis(1,2,3-triazole), $L^2 = 1,1'$ -bis(benzyl)-4,4'-bis(1,2,3-triazole), and $L^3 = 1,1'$ -bis(2-

(methylthio)phenyl)-4,4'-bis(1,2,3-triazole), containing substituted bis-triazole ligands, and the ligands $L^4 = 1$ -(phenyl)-4-(2pyridyl)-1,2,3-triazole, $L^5 = 1-(benzyl)-4-(2-pyridyl)-1,2,3$ triazole, and $L^6 = 1-(2-(methylthio)phenyl)-4-(2-pyridyl)-$ 1,2,3-triazole, containing substituted pyridyl-triazoles, were used to synthesize the complexes $[(dppf)Cu(L^1)](BF_4)$ (1), $[(dppf)Cu(L^2)](BF_4)$ (2), $[(dppf)Cu(L^3)](BF_4)$ (3), [(dppf)- $Cu(L^4)](BF_4)$ (4), $[(dppf)Cu(L^5)](BF_4)$ (5), and [(dppf)Cu- (L^{6})](BF₄) (6). Structural characterization, electrochemical studies, and UV-vis-near-IR and EPR spectroelectrochemical studies, together with DFT calculations on these complexes, are presented below to address the questions formulated above. Furthermore, the complex $[(dppf)\hat{C}u(bpy)](BF_4) (7)^{12}$ is used as a standard to discuss the structural, electrochemical, and spectroelectrochemical results of the novel complexes presented here. This is also the first time that a structural characterization of 7 is being presented.

RESULTS AND DISCUSSION

Synthesis and Crystal Structures. The ligand L^3 was synthesized by modification of a route reported in the literature for similar ligands such as L^1 and $L^{2.6c,13,14}$ The reaction of bis(trimethylsilyl)butadiyne with 2-(thiomethyl)phenyl azide under click conditions resulted in the formation of L^3 in reasonable yields (see the Experimental Section). Single crystals of L^3 were obtained by condensation of a diethyl ether/THF solution. L^3 crystallizes in the monoclinic $P2_1/n$ space group (Table S1, Supporting Information). The N–N and C–N bond lengths in L^3 are in the expected range and fit well with data reported for related 1,2,3-triazole ligands.^{11a} The two 1,2,3-triazole moieties are *anti* to each other, and the molecule is centrosymmetric (Figure S1, Supporting Information). The



Figure 1. ORTEP plots of **2** (left) *anti* conformation (with respect to the benzyl groups) of L^2 ; (right) *syn* conformation (with respect to the benzyl groups) of L^2 . Ellipsoids are drawn at the 50% probability level. Hydrogen atoms, solvent molcules, and counteranions have been omitted for clarity.

phenyl rings are twisted with respect to the planes containing the 1,2,3-triazole rings, the dihedral angle being $55.34(1)^{\circ}$.

The heterodinuclear complexes 1-6 were synthesized by the reaction of $[Cu(dppf)(CH_3CN)_2](BF_4)$ with the corresponding substituted 1,2,3-triazole ligands (Scheme 2). After precipitation of the product, a simple filtration yielded pure compounds in excellent yields (see the Experimental Section). The identity and purity of the metal complexes were established by ¹H and ³¹P NMR spectroscopy, and mass spectrometry. The presence of a single peak in the ³¹P NMR spectrum (at a ppm value different from that of the precursor; see the Experimental Section) of the complexes was usually a first indication for the formation of the new complexes. In addition to 1-6, the reported compound 7^{12} with bpy was also synthesized for comparison purposes and for determining its structural, electrochemical, and spectroscopic signatures, which to the best of our knowledge have not been reported previously.

The compounds **2**, **6**, and 7 containing a substituted bis(1,2,3-triazole), a substituted pyridyl(1,2,3-triazole), and bpy, respectively, as ligands were crystallized for single-crystal X-ray diffraction studies by condensation of a diethyl ether/ acetone solution. **2**•C₂H₆O and **6** crystallize in the monoclinic *Cc* and *C*2/*c* space groups, respectively, and 7•2C₂H₆O crystallizes in the triclinic *P*I space group (Table S1, Supporting Information). The copper(I) centers in complexes **2**, **6**, and 7 are each in a distorted-tetrahedral environment (Figures 1–3).

For 2, both the *syn* and *anti* isomers (with respect to the benzyl substituents) were detected within the same crystal (Figure 1). The Cu–N distances to the triazole donors are in the range 2.08–2.13 Å (Table 1). The Cu–P distances are in the range 2.22–2.24 Å and match well with Cu–P distances reported in the literature for copper(I) complexes with dppf.^{2c,3} For a disubstituted ferrocene ligand such as dppf, the so-called tilt and twist angles have been recently defined in the literature.^{15a} These angles are exactly the same as the torsional (θ) and tilt (τ) angles well established for ligands such as dppf.^{15b} For 2, the θ and τ angles are 2.39 (*anti*), 1.46° (*syn*) and 34.08 (*anti*), 38.93 (*anti*)°, respectively. The Fe–Cu distance in 2 is 4.10 Å for the *anti* isomer and 4.06 Å for the *syn* isomer.



Figure 2. ORTEP plot of 6. Ellipsoids are drawn at the 50% probability level. Hydrogen atoms and the counteranion have been omitted for clarity.



Figure 3. ORTEP plot of 7. Ellipsoids are drawn at the 50% probability level. Hydrogen atoms, solvent molecules, and the counteranion have been omitted for clarity.

For 6, which contains a mixed pyridyl-triazole ligand, the Cu1-N1 distance to the triazole N atom of 2.055(4) Å is

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Table 1. Selected Bond Lengths in Å and Bond Angles in deg for the Complexes

	$2 \cdot C_2 H_6 O$			
	syn	anti	6	$7 \cdot 2C_2 H_6 O$
Cu1-N1	2.092(3)	2.083(3)	2.055(4)	2.058(2)
Cu1-N1'	2.086(3)	2.128(3)	2.109(4)	
Cu-P	2.242(1)	2.238(1)	2.231(2)	2.2517(7)
Cu–P'	2.223(1)	2.2380(9)	2.267(2)	
N1-Cu-N1'	79.1(1)	79.5(1)	79.5(2)	80.3(1)
N1-Cu-P1	104.36(8)	121.00(8)	120.4(1)	109.28(5)
N1-Cu-P1'	123.61(8)	111.11(8)	102.8(1)	121.27(6)
N1'-Cu-P1	113.48(8)	123.42(8)	125.9(1)	
N1'-Cu-P1'	119.77(8)	106.58(8)	108.5(1)	
P1-Cu-P1'	112.23(3)	111.31(3)	113.66(6)	112.49(4)

shorter than the Cu1–N1′ distance of 2.109(4) Å to the pyridine N atom. This observation for metal complexes of such mixed donor ligands likely depicts the better donor ability of the triazole N atom in comparison to the pyridine N atom.^{11a,b} The Cu–P distances in **6** are similar to those in **2** (Table 1). The phenyl ring containing the SMe group has a dihedral angle of 69.98(1)° with respect to the plane of the triazole ring. The θ and τ angles for **6** are 39.98 and 1.05°, respectively, and the Fe–Cu distance is 4.03 Å.

In 7, there is a local mirror plane running through the molecule. The Cu1–N1 distance is 2.058(2) Å. The Cu–P distances in 7 are comparable to those of 2 and 6. The θ and τ angles are 44.98 and 2.33°, respectively, and the Fe–Cu distance is 4.03 Å.

Some general and interesting observations can be made by comparing the structures of the three complexes. The N-N and C-N bond distances within the triazole rings point to a short central N=N "azo"-like double bond, flanked by C-N and N-N single bonds.^{11a,b} The local "pseudo" symmetry about the ferrocene ring in all the complexes is between D_{5d} and D_{sht} depicting the conformation of the substituted Cp rings between those of eclipsed and staggered. Intriguingly, only in the complex that contains a mixed pyridyl-triazole ligand (6) is the Cu-N(triazole) bond distance shorter than the Cu-N(pyridine) bond distance. For 7, which contains bpy as a ligand, the Cu-N(pyridine) bond length is shorter than the Cu-N(triazole) bond length for 2, which contains a bis-triazole ligand (Table 1). The percentage buried volume of dppf for complexes 2, 6, and 7, which contain different chelating nitrogen donating ligands, are 57.5, 60.0, and 56.3%, respectively, showing that dppf displays the largest percentage buried volume with the mixed-donor ligand.¹⁵⁰

Cyclic Voltammetry and UV–Vis Spectroscopy. The presence of two redox-active metal centers (Cu and Fe) and the potentially redox active nitrogen donor ligands make the complexes presented here ideal candidates for investigating their redox properties. The investigated complexes all display a one-electron oxidation, as well as a one-electron reduction process in THF/0.1 M Bu_4NPF_6 at 295 K (Figure 4 and Table 2). It was not possible to record a reasonable cyclic voltammogram of 1 because of its poor solubility in THF. The dichloromethane solvent window is not broad enough for the detection of the reduction step.

Whereas the oxidation steps are reversible for all the investigated complexes, the reduction steps are either reversible or quasi-reversible. A closer look at Figure 4 and Table 2 makes it clear that the oxidation potential is about 0.5 V for all



Figure 4. Cyclic voltammograms of complexes **3**, **6**, and 7 in THF/0.1 M Bu_4NPF_6 at 295 K. Ferrocene/ferrocenium was used as an internal standard.

Table 2	. Elec	ctrochemical	Potentials	from	Cyclic
Voltam	metry	Measureme	nts ^a		

	$E_{\rm pa}/{ m V}$	$E_{\rm pc}/{ m V}$
1 ^b		
2	0.56	-2.66
3	0.55	-2.69
4	0.46	-2.51
5	0.53	-2.57
6	0.50	-2.53
7	0.55	-2.15

^{*a*}Measurements in THF/0.1 M NBu₄PF₆ at 295 K. Scan rate: 100 mV/s. ^{*b*}Measurements were precluded due to the poor solubility of this complex in THF.

complexes and is not affected by changes in the nitrogendonating ligands. This however, is not the case for the reduction step, which seems to be influenced by the nature of the nitrogen-donating coligand. Of the complexes investigated here, 2 and 3, which contain substituted bis-triazoles as ligands, have the most cathodically shifted (-2.66 and -2.69 V)respectively) reduction potentials. For complexes 4-6, containing substituted pyridyl-triazole ligands, the potentials are less negative at -2.51, -2.57, and -2.53 V, respectively. For 7, which contains bpy, the reduction potential is the least negative at -2.15 V. Thus, stepwise substitution of the pyridine units with 1,2,3-triazole units leads to cathodic shifts of the reduction potentials. This observation is related to the fact that the π^* LUMO of the complexes is shifted to higher energies on replacing pyridines with 1,2,3-triazoles.^{6f,g} The changes in reduction potentials on stepwise changes of the ligands are not uniform. The effect of replacing one pyridine unit in bpy with a triazole unit has a greatly pronounced effect on the reduction potentials in comparison to the replacement of the second unit (Table 2). Apparently, the destabilization of the π^* LUMO is more significant on replacing one pyridine unit in comparison to both pyridines in bpy. The reversibility of the reduction step is the best for complex 7, which contains a bpy ligand. Complete electrochemical reversibility becomes attenuated on introducing the 1,2,3-triazole units, probably due to the extremely high basicity of the reduced forms of this ligand and their high sensitivity toward all existing electrophiles. The substituents on the 1,2,3-triazole rings do not seem to have any significant influence on the reduction potentials, as can be seen on comparing the potentials of **2** and **3** or **4**, **5**, and **6** (Table 2).

The trend observed in the redox potentials of the complexes is also reflected in the metal to ligand charge transfer (MLCT) bands of these compounds. Each of the complexes displays an absorption band in the UV region, which can be assigned to an intraligand transition (Figure 5 and Table 3). Additionally, an MLCT band is observed for the complexes. For complexes 1-3 this band is merged with the intraligand band, as can be seen in Figure 6 for 3.



Figure 5. UV-vis spectra of complexes 3, 6, and 7 in THF at 295 K.

Table 3. UV-Vis Data of the Complexes



Figure 6. Changes in the UV–vis spectrum of 3 during the first oxidation in THF/0.1 M Bu_4NPF_{67} from OTTLE spectroelectrochemistry at 295 K.

For complexes **4–6**, the MLCT band appears at 362, 360, and 348 nm, respectively, and that for 7 appears at 387 nm. Thus, the position of the MLCT band correlates well with the kind of nitrogen-donating ligands in the complexes and with the trends in the redox potentials observed in the cyclic voltammetric experiments. The appearance of the MLCT band for 7 at the lowest energy in comparison to all the complexes investigated here matches well with the least negative reduction potential observed for this complex and, hence, a correspondingly low HOMO–LUMO gap. As the pyridine ligands are progressively replaced by the substituted 1,2,3-triazole ligands, the MLCT band is shifted to higher energies (for **4–6** and **1–3** respectively), as is expected for a higher lying π^* LUMO and hence a larger HOMO–LUMO gap.

Spectroelectrochemistry and DFT Calculations. In order to shed light on the observed redox processes, and to possibly detect the locus of the oxidation and reduction steps, UV–vis–near-IR and EPR spectroelectrochemistry measurements were carried out on the complexes. As the substituents

on the 1,2,3-triazole rings have been shown above to have a negligible effect on the electrochemical and spectroscopic properties of the complexes, spectroelectrochemical measurements were carried out only on 3, 6, and 7. Hence, the data can be used to compare complexes, each of which contains a different type of nitrogen-donating ligand. On one-electron oxidation of the complexes, the bands in the UV region remain largely unaffected. The MLCT bands lose intensity in each case, and a new band grows at lower energies (Figures 6 and 7,



Figure 7. Changes in the UV–vis–near-IR spectrum of 7 during the first oxidation (top) and first reduction (bottom), from OTTLE spectroelectrochemistry in THF/0.1 M Bu_4NPF_6 at 295 K.

Table 4. UV–Vis–Near-IR Data of the Complexes in Various Redox States a

	λ /nm (ϵ /10 ³ M ⁻¹ cm ⁻¹)
3	292 (5.5)
3 ⁺	289 sh (5.2); 429 (0.34)
6	292 (17.3); 348 (3.8)
6 ⁺	247 sh (31.8); 287 sh (18.7); 359 (2.3); 452 (1.0)
7^{-}	270 (14.2); 385 (7.8); 531 (2.2); 665 (0.7); 850 (0.9); 983 (0.8)
7	294 (10.6); 387 (1.6)
7+	249 sh (13.9); 291 (10.4); 392 (1.0)
[*] From	OTTLE spectroelectrochemistry in THF/0.1 M $\mathrm{Bu}_4\mathrm{NPF}_6$

Figure S2 (Supporting Information), and Table 4). This new band can be assigned to a ligand to metal charge transfer (LMCT) transition. Such LMCT bands that appear at lower energy on oxidation of the complexes have been observed previously for metal complexes of dppf.^{2b,3c}

For 3 and 6, the reduction steps were not completely reversible and hence the spectroelectrochemistry results for those two complexes will not be discussed here. One-electron reduction of 7 leads to the appearance of multiple bands in the vis-near-IR region (Figure 7). This pattern is reminiscent of a reduced (bpy)^{•-} and has been observed previously for the spectrum of (bpy)^{•-} as well as metal-bound (bpy)^{•-.16} The multiple bands arise due to intraligand transitions within the

 $(bpy)^{\bullet-}$ radical, as well as MLCT transitions. Hence, from the UV-vis-near-IR spectroelectrochemical data, the best formulation for the one-electron reduced species can be safely formulated as $[(dppf)Cu^{I}(bpy)^{\bullet-}]$.

To further probe the oxidation steps of all the complexes, and the reduction of 3 and 6, EPR spectroelectrochemical measurements and DFT calculations were carried out. The oneelectron oxidized forms of 3, 6, and 7 were EPR silent at temperatures down to 110 K. This is a strong indication for the oxidation taking place on dppf. Oxidation of Cu(I) to Cu(II) should produce a typical axially symmetric EPR signal, usually with hyperfine coupling to the copper nucleus. Such signals are always detectable at 110 K.¹⁷ Oxidation of the ferrocene, on the other hand, is known to produce species with extremely fast spin-lattice relaxation, which leads to "EPR silence" at 110 K.^{3c,18} Thus, this result would point to oxidation taking place predominantly on the dppf part of the molecule and to a best description of the one-electron oxidized forms of the complexes as $[(dppf)^{\bullet+}Cu^{I}(L)]^{2+}$. Confirmation of this fact also came from structure-based DFT calculations of spin density using the B3LYP functional. For complexes containing the bis-triazole and pyridyl-triazole ligands, the substituents were truncated to save computing time. A look at the spin densities by using the Löwdin population analysis shows that for 3^+ , 6^+ (models), and 7^+ , 96, 96, and 90%, respectively, of the spin densities are located on the dppf part (Figure 8 and Figures S3 and S4



Figure 8. Spin density plot for the one-electron oxidized form of a model complex containing a bis-triazole ligand.

(Supporting Information)). This result thus strongly corroborates the "EPR silence" of these species at 110 K and confirms the formulation $[(dppf)^{\bullet+}Cu^{I}(L)]^{2+}$.

For the one-electron reduced forms, on the other hand, the spin density is primarily located on the nitrogen-donating ligands, as has been experimentally proven for complex $7^{\bullet-}$ above (Figure 9 and Figures S5 and S6 (Supporting Information)). DFT calculations thus also provide evidence



Figure 9. Spin density plot for the one-electron reduced form of a model complex containing a bis-triazole ligand.

for spin localization on the nitrogen-donating ligands [(dppf)- $Cu^{I}(L)^{\bullet-}$] for the one-electron reduced species 3 and 6, where the reduction process could not be experimentally investigated because of its irreversible nature.

Surprisingly, the one-electron reduced complex $7^{\bullet-}$ also did not display EPR signals down to 110 K. While it is to be expected that such a metal-bound radical should show detectable EPR signals under conventional X-ray EPR conditions, in the present case, close-lying states likely lead to fast relaxations and line broadening beyond detection even at 110 K. However, the UV-vis-near-IR data and the spin density calculations unequivocally establish the reduced form of 7 as [(dppf)Cu¹(bpy)^{•-}].

The HOMO-LUMO gap for the three cases discussed above were calculated by using canonical orbitals to be as follows: Δ (HOMO-LUMO) of **3** (model), 4.43 eV; Δ (HOMO-LUMO) of **6** (model), 3.78 eV; Δ (HOMO-LUMO) of **7**, 3.38 eV. The trend in the HOMO-LUMO gap thus nicely matches with those observed in cyclic voltammetry and UV-vis experiments.

CONCLUSIONS

In conclusion, we have presented here the synthesis and characterization of six new heterodinuclear Cu–dppf complexes with "click"-derived substituted 1,2,3-triazole ligands and we have compared these with the analogous compound with bpy. Structural characterizations of representative complexes show a stronger Cu–N(triazole) bond in comparison to the Cu–N(pyridine) bond in complexes with mixed-donor ligands. All complexes display one oxidation and one reduction process in their cyclic voltammogram. Whereas the oxidation step is not influenced by the nature of the coligand, the reduction step displays a cathodic shift as a function of the number of 1,2,3-triazole units, owing to energetically higher lying π^* LUMO's. Accordingly, the HOMO–LUMO gap also increases as a function of the triazole units and results in a high-energy shift of the MLCT band. Results from UV–vis–near-IR and EPR

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spectroelectrochemistry and DFT calculations unequivocally point to dppf being the locus of oxidation in all complexes and the nitrogen-donating ligands being the locus of reduction. Our results here provide convenient routes for preparing heterodinuclear complexes with "click"-derived ligands and introducing a ferrocene backbone into such complexes. We have also shown the tuning of redox and spectroscopic properties that is possible on carrying out a systematic variation of such 1,2,3triazole ligands. Such tuning can be used for scanning a range of redox potentials as well as optimizing the wavelength of the MLCT transitions. To the best of our knowledge, this is one of the rare occasions^{6d} that such combined structural, electrochemical, and UV-vis-near-IR and EPR spectroelectrochemical studies together with DFT calculations have been applied to metal complexes of the emerging class of "click"-derived ligands.

EXPERIMENTAL SECTION

General Considerations. $[(dppf)Cu(CH_3CN)_2](BF_4)$, ¹² L^{1,13} L^{2,14} L^{4,6c} L^{5,19} L^{6,11b} and 7¹² were synthesized according to the literature. All other reagents are commercially available and were used as received. All solvents were dried and distilled using common techniques unless otherwise mentioned.

Instrumentation. ¹H and ³¹P NMR spectra were recorded with a JEOL Lambda 400 (400 MHz) instrument. EPR spectra in the X band were recorded with a Bruker System EMX instrument. Quantitative UV-vis-near-IR absorption spectra were recorded on a Perkin-Elmer Lambda 9 spectrometer. Cyclic voltammetry at 100 mV/s was carried out in 0.1 M Bu₄NPF₆ solution using a three-electrode configuration (glassy-carbon working electrode, Pt counter electrode, Ag wire as pseudoreference) and a PAR VersaSTAT 4 (Ametek) potentiostat. The working electrode was 2 mm in diameter. The ferrocene/ ferrocenium couple served as internal reference. Spectroelectrochemical measurements were carried out using an optically transparent thinlayer electrochemical (OTTLE) cell consisting of platinum-grid working and auxiliary electrodes and a silver quasi-reference electrode sealed between optical windows.²⁰ The cell was mounted on an Avantes spectrometer system (diode-array spectrometer), and the spectra were collected continuously during the potential scan within the redox steps. Elemental analysis was performed on a Elementar Vario EL III instrument. Mass spectrometry experiments were carried out on an Agilent 6210 ESI-TOF mass spectrometer (Agilent Technologies, Santa Clara, CA, USA).

Synthesis. Ligand L³. 2-Thiomethylphenyl azide (495 mg; 3 mmol), bis(trimethylsilyl)butadiyne (0.291 mg; 1.5 mmol), potassium carbonate (414 mg; 4 mmol), CuSO₄·5H₂O (150 mg; 0.6 mmmol), and sodium ascorbate (240 mg; 1.2 mmol) were dissolved in tert-butyl alcohol (15 mL), water (15 mL), and pyridine (1.2 mL). The solution was stirred for 3 days at room temperature. Afterward, the organic phase was extracted with DCM $(3 \times 15 \text{ mL})$, it was washed with a 1 M EDTA solution (3 \times 15 mL), and it was dried over Na₂SO₄. Recrystallization from DCM/hexane yielded a white product (342 mg; 0.90 mmol) in 60% yield. Crystals suitable for X-ray diffraction could be grown by condensation of diethyl ether on top of a THF solution. The low solubility of 3 in common solvents omitted characterization by ¹³C NMR spectroscopy. HRMS (ESI): calcd for C₁₈H₁₆N₆NaS₂ $([M + Na]^+) m/z$ 403.0770, found 403.0783. ¹H NMR (400 MHz, d_6 -DMSO): δ 2.46 (s, 6H, S(CH₃)), 7.42 (t, ${}^{3}J_{H-H}$ = 7.2 Hz, 2H, Ph), 7.57 (m, 4H, Ph), 7.63 (t, ${}^{3}J_{H-H} =$ 7.6 Hz, 2H, Ph), 8.89 (s, 2H, triazole-CH).

Complexes 1–6 were synthesized according to a general procedure: under an inert atmosphere, a ligand (0.13 mmol) and $[(dppf)Cu-(CH_3CN)_2](BF_4)$ (100 mg; 0.13 mmol) were dissolved in DCM (5 mL). The solution was stirred for 30 min, and afterward, a yellow product precipitated after the addition of pentane (15 mL). The product could be isolated by filtration in excellent yields.

Complex 1. The product (119 mg, 0.12 mmol) could be isolated in 95% yield. HRMS (ESI): calcd for $C_{50}H_{40}CuFeN_6P_2$ ($[M - BF_4]^+$) m/

z 905.1430, found 905.1549. ³¹P NMR (170 MHz, CD₂Cl₂): δ –12.0. ¹H NMR (400 MHz, CD₂Cl₂): δ 4.38 (s, 4H, Cp), 4.45 (s, 4H, Cp), 7.26 – 7.39 (m, 12H, Ph), 7.43 – 7.51 (m, 8H, Ph), 7.55 (t, ³J_{H-H} = 7.3 Hz, 2H, Ph), 7.62 (t, ³J_{H-H} = 7.0 Hz, 4H, Ph), 7.80 (d, ³J_{H-H} = 7.7 Hz, 4H, Ph), 9.10 (s, 2H, triazole-CH).

Complex **2**. The product (122 mg, 0.12 mmol) could be isolated in 95% yield. Crystals suitable for X-ray diffraction could be grown by condensation of diethyl ether on top of an acetone solution. HRMS (ESI): calcd for $C_{52}H_{44}CuFeN_6P_2$ ($[M - BF_4]^+$) m/z 933.1774, found 933.1852. ³¹P NMR (170 MHz, CD₂Cl₂): δ –11.6. ¹H NMR (400 MHz, CD₂Cl₂): δ 4.33 (s, 4H, Cp), 4.43 (s, 4H, Cp), 5.57 (s, 4H, CH₂), 7.17–7.52 (m, 30H, Ph), 8.43 (s, 2H, triazole-CH).

Complex **3**. The product (130 mg, 0.12 mmol) could be isolated in 95% yield. HRMS (ESI): calcd for $C_{52}H_{44}CuFeN_6P_2S_2$ ($[M - BF_4]^+$) m/z 997.1186, found 997.1172. ³¹P NMR (170 MHz, CD_2Cl_2): δ -11.2. ¹H NMR (400 MHz, CD_2Cl_2): δ 2.42 (s, 6H, SCH₃), 4.34 (s, 4H, Cp), 4.42 (s, 4H, Cp), 7.28–7.52 (m, 26H, Ph), 7.59 (t, ³J_{H-H} = 7.6 Hz, 2H, Ph), 8.73 (s, 2H, triazole-CH).

Complex **4**. The product (105 mg, 0.11 mmol) could be isolated in 90% yield. HRMS (ESI): calcd for $C_{47}H_{38}CuFeN_4P_2$ ($[M - BF_4]^+$) m/z 839.1212, found 839.1245. ³¹P NMR (170 MHz, CD_2Cl_2): δ -9.9. ¹H NMR (400 MHz, CD_2Cl_2): δ 4.27–4.50 (m, 8H, Cp), 7.19–7.43 (m, 21H, Ph), 7.55–7.65 (m, 3H, Ph), 7.70 (m, 2H, aromatic), 8.04 (t, ³J_{H-H} = 7.8 Hz, 1H, Py), 8.16 (d, ³J_{H-H} = 7.8 Hz, 1H, Py), 8.44 (d, ³J_{H-H} = 4.8 Hz, 1H, Py), 8.93 (s, 1H, triazole-CH).

Complex **5**. The product (95 mg, 0.10 mmol) could be isolated in 80% yield. HRMS (ESI): calcd for $C_{48}H_{40}CuFeN_4P_2$ ($[M - BF_4]^+$) m/z 853.1368, found 853.1433. ³¹P NMR (170 MHz, CD_2Cl_2): δ -11.4. ¹H NMR (400 MHz, CD_2Cl_2): δ 4.27–4.50 (m, 8H, Cp), 5.56 (s, 2H, CH₂), 7.22–7.44 (m, 26H, aromatic), 7.89 (d, ³J_{H-H} = 7.9 Hz, 1H, Py), 7.95 (t, ³J_{H-H} = 7.7 Hz, 1H, Py), 8.42 (d, ³J_{H-H} = 7.7 Hz, 1H, Py), 8.43 (s, 1H, triazole-CH).

Complex **6**. The product (116 mg, 0.12 mmol) could be isolated in 95% yield. Crystals suitable for X-ray diffraction could be grown by condensation of diethyl ether on top of an acetone solution. HRMS (ESI): calcd for $C_{48}H_{40}$ CuFeN₄P₂S ($[M - BF_4]^+$) m/z 885.1090, found 885.1093. ³¹P NMR (170 MHz, CD₂Cl₂): δ –11.5. ¹H NMR (400 MHz, CD₂Cl₂): δ –244 (s, 3H, SCH₃), 4.28–4.49 (m, 8H, Cp), 7.17 (d, ³J_{H-H} = 7.9 Hz, 1H, Ph), 7.24–7.45 (m, 22H, aromatic), 7.50 (d, ³J_{H-H} = 8.1 Hz, 1H, Ph), 7.61 (t, ³J_{H-H} = 7.8 Hz, 1H, Py), 8.01–8.09 (m, 2H, Py), 8.51 (d, ³J_{H-H} = 5.4 Hz, 1H, Py), 8.66 (s, 1H, triazole-CH).

Complex **7**. Crystals suitable for X-ray diffraction could be grown by condensation of diethyl ether on top of an acetone solution.

X-ray Crystallography. Single -rystal X-ray structural studies were performed on a Stoe X-Area or a Bruker Smart AXS diffractometer. Data were collected at 100(2), 133(2), or 293(2) K using graphite-monochromated Mo K α radiation ($\lambda_{\alpha} = 0.71073$ Å). The strategy for the data collection was evaluated by using the CrysAlisPro CCD software. The data were collected by the standard $\psi-\omega$ scan techniques and were scaled and reduced using CrysAlisPro RED software. The structures were solved by direct methods using SHELXS-97 and refined by full-matrix least squares with SHELXL-97,²¹ refining on F^2 .

The positions of all the atoms were obtained by direct methods. All non-hydrogen atoms were refined anisotropically. The remaining hydrogen atoms were placed in geometrically constrained positions and refined with isotropic temperature factors, generally 1.2 times the $U_{\rm eq}$ values of their parent atoms.

CCDC 925716–925719 contain CIF files for this paper. All these data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_requests/cif.

DFT Calculations. The program package ORCA 2.9.1 was used for all calculations.²² The geometry optimization and single-point calculations were performed by the spin-unrestricted DFT method with BP86 and B3LYP functionals, respectively.²³ Convergence criteria for the geometry optimization were set to default values (OPT), and "tight" convergence criteria were used for SCF calculations (TIGHTSCF). In all calculations, triple-ζ valence quality basis sets

(def2-TZVP) were used for all atoms.²⁴ The resolution of the identity approximation (RIJCOSX) was employed^{25,26} with matching auxiliary basis sets.²⁶ All spin densities were calculated according to Löwdin population analysis²⁷ and were visualized via the program Molekel.²⁸

ASSOCIATED CONTENT

S Supporting Information

CIF files and a table giving crystallographic data for L³, **3**, **6**, and 7, figures giving spin density plots and NMR spectra, and tables giving coordinates for DFT calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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