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# Unprecedented Formation of π-Copper Complexes during Sonogashira Coupling: Synthesis of a Unique, Recyclable, Ethynyl Ferrocene Derived Cu(I) Specific Ligand

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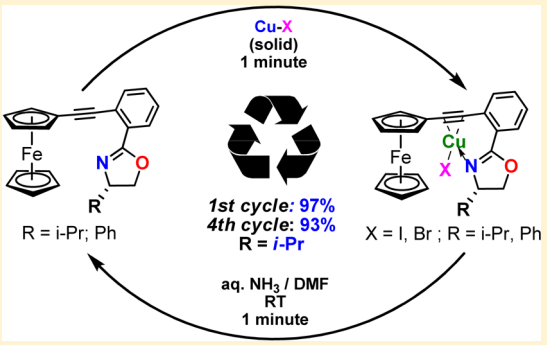
Supporting Information

**ABSTRACT:** During the synthesis of a chiral oxazolinyl-derived ethynyl ferrocene {Fc-C≡C−$C_6H_4$-o-(4-iPr-2-Ox)} (Fc = ferrocenyl; Ox = oxazolinyl), we observed an unprecedented formation of highly air stable and monomeric π-copper(I) complexes **4a** and **4b**, which were structurally characterized. CuI was used as a cocatalyst in this Sonogashira coupling. By the reaction of **4a** with aqueous $NH_3$/DMF, the CuI was removed from the complex and the metal-free compound **5a** was obtained. This was found to be an excellent ligand for selectively binding Cu(I) halides. Analogous 4-Ph-substituted oxazoline-based ligand **5b** and its Cu−I complex **4c** were also isolated and characterized. The possible role of these complexes in explaining the copper cycle proposed for Sonogashira coupling has also been discussed.




## INTRODUCTION

Since its discovery, Sonogashira coupling has been one of the most robust and effective tools for coupling alkynes with aryl/vinyl halides[1] and has been used in the synthesis of a diverse range of natural products, pharmaceuticals,[2] polymers,[3] and functional materials.[4] Although the palladium cycle of the Sonogashira coupling is well understood, the cocatalytic copper cycle, wherein a Cu(I) halide is used to activate the alkyne, is still not fully understood.[1c,e] This has mostly been due to the absence of properly characterized intermediates, unavailability of methods to trap such intermediates, and difficulty in synthesizing monomeric Cu(I) complexes that mimic the conditions present in the copper cycle. The main problem with many Cu(I) monomeric complexes is their inherent instability, due to which they tend to disproportionate to Cu(II) and Cu(0).[5] Although monomeric Cu(I) complexes are reported in the literature with different ligands[6] and of differing geometry and nuclearity,[7] most of them suffer from poor air and moisture stability.

Recently Driess, Hartwig, and co-workers reported a nickel(II)-catalyzed Sonogashira coupling using silylene- and germylene-based pincer ligands, in which a CuBr-trapped intermediate, prior to the transmetalation step, was isolated and structurally characterized. The nature of the CuBr in this intermediate was found to be quite complex, as the Cu(I) was at bonding distances with not only the alkyne carbon but also Ni(II) along with Ge/Si. The Ni, Cu, Ge/Si, and the alkynyl carbon showed a four-membered cyclic arrangement (Figure 1). This has been described by them as a "nonclassical end-on" type bonding. This complex, to the best of our knowledge, is the only example of a copper(I) halide bound complex, observed from a Sonogashira coupling.[8]

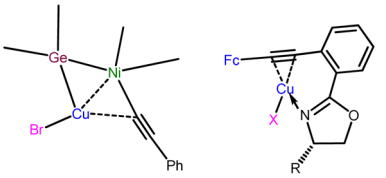



**Figure 1.** Cu−X complexes observed in Sonogashira coupling.

It may be noted that in the mechanisms proposed for Sonogashira coupling both σ- and π-alkyne-coordinated species have been given as intermediates as a part of the copper cycle.[1c,e,9] In this article we report, for the first time, an example of a Sonogashira coupling wherein the coupled product holds CuX (X = I, Br) as a "classical side-on" type complex, which has been found to be highly air and moisture stable as well.

## RESULTS AND DISCUSSION

The role of metal sandwich derived chiral oxazolinyl ligands in the synthesis of chiral catalysts for various asymmetric organic transformations is well documented.[10] In our attempts to prepare bifunctional alkynyl-derived *ortho*-chiral oxazolinyl ligands, the corresponding *ortho*-halobenzoic acids were first converted to oxazolines **2a−c** followed by coupling through a Sonogashira reaction (Scheme 1). Interestingly, when the *ortho*-oxazolinyl halobenzenes **2a−c** were subjected to Sonogashira coupling, a 3% yield of the Sonogashira-coupled product was obtained where CuI was found to be complexed to the coupled

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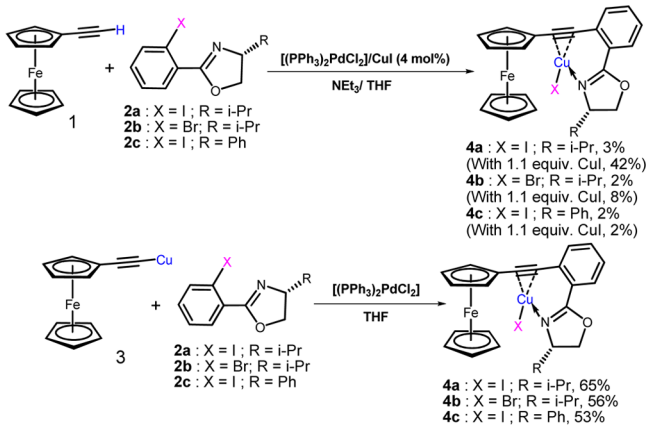
**Scheme 1. Synthesis of $\pi$-Copper Complexes**




product. Not even traces of the expected metal-free alkyne-coupled product were obtained from the reaction mixture. When CuI was used in stoichiometric amounts in the same reaction, the Cu(I)-complexed Sonogashira coupled products **4a**–**c** were obtained in yields ranging from 2% to 42% (see Table S1, in the Supporting Information).

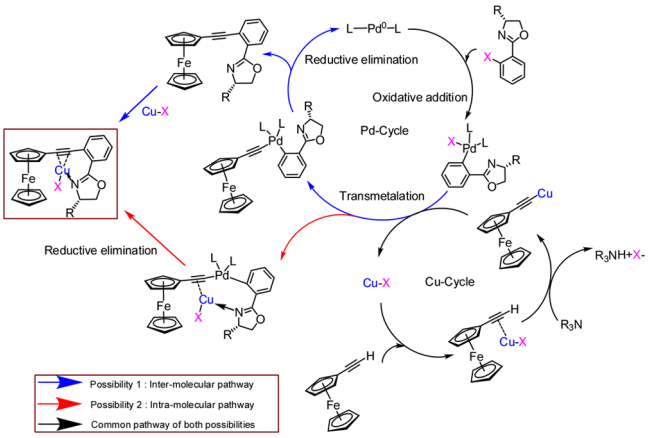
The role of the base used in the classic Sonogashira coupling has been proposed as to activate the acetylenic proton of the $\pi$-copper-bound terminal alkyne and to convert it to a terminal copper acetylide, which transfers the alkynyl group to the palladium in the rate-determining transmetalation step.[1c,e] For a better understanding of our observations, we carried out the coupling reaction by directly using cuprous acetylide under base-free conditions. Cuprous acetylide of the ethynyl ferrocene **3** was prepared and was reacted with the chiral *ortho*-oxazolinyl derivatives **2a**–**c** along with Pd catalyst. This resulted in the same $\pi$-copper complexes **4a**–**c** within a period of 1–3 h of stirring even at room temperature in better yields ranging from 53% to 65%.

We were keen to determine the origin of the halide bound to Cu(I) in the complexes **4a**–**c**, whether it came from the added cocatalyst, CuX, or from Ar–X. A reaction of chiral-oxazolinyl bromobenzene **2b** was carried out with cuprous acetylide **3**, synthesized using CuI, and purified by filtration and repeatedly washing with ethanol, water, and diethyl ether.[10] The resulting reaction yielded complex **4b**, which indicated that CuBr was bound to the ligand. The generation and X-ray structural characterization of complex **4b** provide experimental evidence that in the copper cycle of Sonogashira coupling the aryl halide supplies the halide needed to form CuX after the transmetalation step. Interestingly, a Sonogashira coupling of ethynyl ferrocene with oxazolinyl bromobenzene **2b** using $Pd(PPh_3)_2Cl_2$ along with CuI yielded both CuI- and CuBr-bound complexes **4a** and **4b**. This observation clearly indicates that the chiral ethynyl ferrocene ligand formed has a high propensity to form Cu(I) complexes, and there can be more than one possible pathway for the formation of $\pi$-copper complexes.

To explore the possibility of isolating complexes with similar ligands, we have prepared the cuprous acetylide of phenyl acetylene and reacted it with oxazolinyl iodobenzene **2a** under similar reaction conditions. There occurs a reaction, but the formed light green colored product was found to be too unstable for isolation and characterization. The oxazolinyl iodobenzene having R = H also did not yield any $\pi$-copper halide complex, whereas R = i-Pr, Ph yielded Cu(I)-bound complexes (Scheme 1). Hence the presence of an alkyl or aryl substituent is necessary for the stabilization of the monomeric Cu(I) complexes reported in this study. We believe that the *ortho*-oxazolinyl fragment in the vicinity of the alkyne unit is ideal in size and shape to bind to Cu halide in its reach. We have also carried out reactions of **3** with *meta*-oxazolinyl iodobenzene, which produced the normal Cu-free Sonogashira coupled product. The selectivity of the analogous *ortho*-derivatives could not be achieved by the *meta*-oxazolinyl derivatives. The ferrocene unit is possibly providing enough steric bulkiness protecting the Cu(I) center and giving the complex stability that the phenyl group could not offer.

On the basis of these observations, we propose a plausible mechanism for the formation of the Cu(I)-complexed Sonogashira coupled products **4a**–**c** (Scheme 2). As shown,

**Scheme 2. Plausible Mechanistic Pathways of the Formation of the $\pi$-Copper Complexes in Sonogashira Coupling**




two pathways are possible, namely, intermolecular and intramolecular. In the intermolecular route the cuprous acetylide eliminates CuX in the transmetalation step and the Pd complex generated undergoes reductive elimination to give the coupled product. Since this product has a high propensity to form Cu(I) complexes, it recombines with the Cu(I) species present in the medium and forms complexes **4a**–**c**. The low yields of the CuX-bound complexes **4a**–**c** indicate that the CuX regenerated is less available for transfer of HX to the base ($Et_3N$). In the intramolecular pathway, the CuX generated during transmetalation may remain bound to the alkyne unit and the oxazolinyl nitrogen. This Pd-*cis*-oriented complex further undergoes reductive elimination to form the aryl–alkyne bond. From the type of complexes obtained in this study, both pathways seem to be equally possible.

## STRUCTURAL STUDIES

Figures 2, 3, and 4 show the molecular structures of compound **4a**, **4b**, and **4c**, respectively. (For details of selected bond angles and bond lengths, see Supporting Information Tables S4, S5, and S6.) The molecular structures show that the coordination of Cu(I) to the alkyne is symmetrical. The Cu–X (X = I, Br) distances are $d$(Cu–I) = 2.515 Å and $d$(Cu–Br) = 2.307 Å, and the Cu–N distances are $d$(Cu–N1) = 1.963 Å for **4a** and $d$(Cu–N1) = 1.971 Å for **4b**, respectively. The Cu–alkyne distances are $d$(Cu–C11) = 2.017 Å and $d$(Cu–C12) = 1.967 Å for **4a**, resulting in a $\Delta d$ (Cu–C11 vs Cu–C12) = 0.05, giving a "classical side-on" (less than 0.150 Å)[12] coordination to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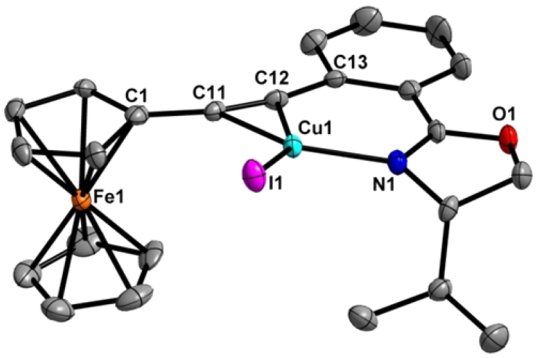



**Figure 2.** Molecular structure of compound **4a**. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): N(1)−Cu(1) 1.963(6); I(1)−Cu(1) 2.5151(11); C(11)−C(12) 1.233(10); Cu(1)−C(11) 2.017(7); Cu(1)−C(12) 1.966(7); N(1)−Cu(1)−C(12) 94.3(3); N(1)−Cu(1)−C(11) 129.6(3); C(12)−Cu(1)−C(11) 36.0(3); N(1)−Cu(1)−I(1) 112.87(18); C(11)−Cu(1)−I(1) 117.5(2).

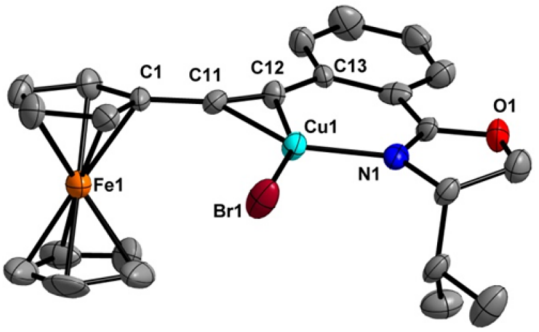



**Figure 3.** Molecular structure of compound **4b**. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): N(1)−Cu(1) 1.971(11); Br(1)−Cu(1) 2.307(2); C(11)−C(12) 1.261(17); Cu(1)−C(11) 1.996(12); Cu(1)−C(12) 1.927(12); C(12)−Cu(1)−N(1) 95.2(5); N(1)−Cu(1)−C(11) 132.6(5); C(12)−Cu(1)−C(11) 37.4(5); N(1)−Cu(1)−Br(1) 111.8(3); C(11)−Cu(1)−Br(1) 115.5(4).

the alkyne. On the other hand, the angles $C_1-C_{11}\equiv C_{12}$ and $C_{11}\equiv C_{12}-C_{13}$ are 159.5° and 162.9°, respectively, for **4a**, supporting a side-on $\pi$-coordination (expected angle for side-on: 156-165°; end-on: 170−180°[12e,f]).

## COPPER(I) BINDING STUDIES AND RECYCLABILITY

The new monomeric Cu−X complexes **4a−c** are quite stable to air and moisture, and it was observed that the removal of the Cu−X unit from the complex was cumbersome. Attempts to use well-known Cu(I) scavengers such as triphenylphosphine or ethylenediamine in common organic solvents such as dichloromethane or THF were unsuccessful in removing the CuX unit. Interestingly, a reaction of the complexes **4a−c** with aqueous $NH_3$ in *N*,*N*-dimethylformamide (DMF) was found to remove the Cu(I) from the complexes at room temperature within a minute. The aqueous solution with released Cu(I) was found to get oxidized, giving a blue-colored solution of $[Cu(NH_3)_4(H_2O)_2]^{2+}$ (confirmed by UV−vis studies;[13] see Supporting Information for details), and the copper-free oxazolinyl-derived ethynyl ferrocene was isolated from the ethyl acetate layer in almost quantitative yield. The metal-free

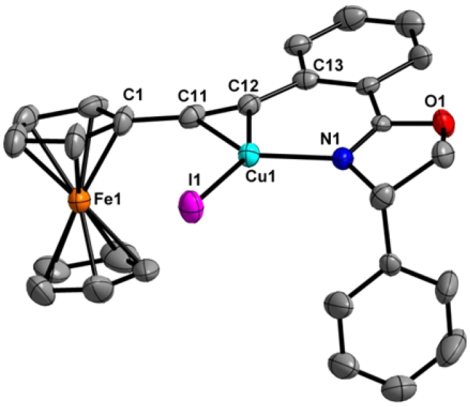
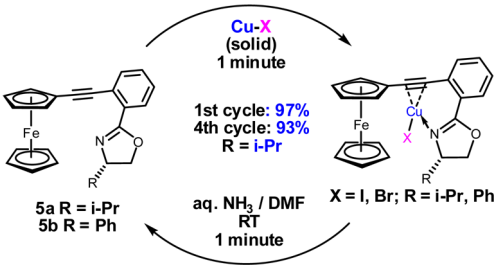



**Figure 4.** Molecular structure of compound **4c**. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): I(1)−Cu(1) 2.5008(11); Cu(1)−C(12) 1.947(7); Cu(1)−N(1) 1.951(6); Cu(1)−C(11) 2.004(7); C(11)−C(12) 1.226(10); C(12)−Cu(1)−N(1) 94.7(3); C(12)−Cu(1)−C(11) 36.1(3);N(1)−Cu(1)−C(11) 130.8(3); C(12)−Cu(1)−I(1) 151.2(2); N(1)−Cu(1)−I(1) 113.90(19); C(11)−Cu(1)−I(1) 115.3(2).

compounds **5a,b**, upon mixing with Cu(I)−X (X= Br, I), even as a suspension, formed the CuX-bound complexes instantaneously and almost quantitatively.

**Scheme 3. Synthesis of Free Ligands 5a,b and the Cu(I) Halide Selectivity and Recyclability**




The copper-free oxazolinyl-derived ethynyl ferrocenes **5a,b** were found to be quite robust and highly stable to air and water. A stoichiometric reaction of the copper-free alkyne **5a** with CuI gave $\pi$-complex **4a** in 97% yield, immediately. The recyclability of **5a** was also explored. Even after four cycles of complexation followed by removal of Cu(I) by aqueous $NH_3$/DMF the alkyne ligand **5a** was found to be quite efficient in forming the Cu(I) complex with a yield of 93% for the fourth cycle.

To further explore the selectivity of the oxazolinyl-derived ethynyl ferrocene for Cu(I) salts, we have carried out the reaction of Cu-free ligand **5a** with a mixture of metal salts in dichloromethane. The solvent dichloromethane was chosen intentionally, as the free ligand **5a** remains soluble in it, whereas the metal salts are left in a suspended form. After workup it was observed that the ligand takes up only Cu(I)X (X = Br, I) salts from the suspension. TLC indicates the formation of CuI- and CuBr-bound $\pi$-complexes (Scheme 4).

## CONCLUSIONS

In conclusion, we report first isolation and structural characterization of alkyne "side-on"-bound CuX complexes observed during a Sonogashira coupling. By carrying out a direct reaction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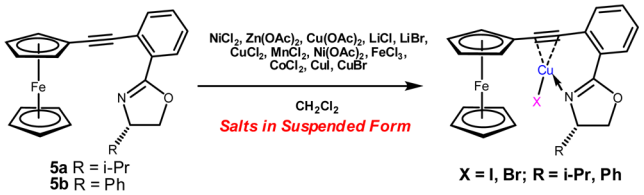
**Scheme 4. Cu(I)−X Selectivity of Oxazolinyl-Derived Ethynyl Ferrocenes 5a,b vs Other Metal Salts**




of cuprous acetylide with oxazolinyl bromobenzene and isolating the CuBr-bound alkyne complexes, we have provided evidence for the source of halide in the Sonogashira coupling. With specific focus on the copper cycle of Sonogashira coupling, regeneration of CuX after the transmetalation has been experimentally demonstrated by isolating and structurally characterizing the CuX-bound alkyne complexes. By chemically removing CuX from the complexes we have prepared the metal-free ethynyl ferrocene derived oxazolinyl ligands, and interestingly, this ligand was found to have high specificity toward Cu(I) halides. The utility of these ligands to selectively bind CuX (X = Br, I) from a mixture of metal salts as well as the recyclability of the ligand **5a** has also been demonstrated.

## EXPERIMENTAL SECTION

**Synthesis and Reagents.** All reactions were carried out under pure nitrogen following Schlenk-line techniques. Solvents were dried under their respective suitable drying agents such as THF on sodium/benzophenone and $CH_2Cl_2$ on dry phosphorus pentoxide and so on. All compounds were purified by column chromatography using silica gel of 60−120 mesh. $^1$H and $^{13}$C{$^1$H} NMR spectra were recorded on a Bruker Spectrospin DPX-300 NMR spectrometer at 300 and 75.4 MHz, respectively. $CDCl_3$ was the solvent utilized for NMR studies unless otherwise specified. Mass spectra were recorded on a Bruker Micro-TOF QII quadrupole time-of-flight (Q-TOF) mass spectrometer. IR spectra in the range 4000−250 cm$^{-1}$ were recorded on a Nicolet Protége 460 FT-IR spectrometer as KBr pellets. Elemental analyses were carried out on a Carlo Erba CHNSO 1108 elemental analyzer. Optical rotations of the chiral compounds were measured on an Autopol V (Rudolph Research, Flanders, NJ, USA) instrument. All the rotations were measured at 589 nm (sodium D line) using dichloromethane as solvent.

*General Procedure for Making Oxazolinyl Halobenzene Derivatives (**2a−c**).* The 2-halobenzoic acids were taken in an oven-dried one-neck round-bottom flask, cooled under nitrogen, and dissolved in dry dichloromethane. Oxalyl chloride was added into the reaction mixture, and 2 or 3 drops of *N*,*N*-dimethylformamide as a catalyst was also added. It was allowed to stir at room temperature for 1 h, solvent was removed under rotary evaporation, and the residue was added to a 1:1 mixture of DCM/triethylamine in a dry two-neck round-bottom flask. The chiral amino alcohol was dissolved in 20 mL of DCM, and this was added to the reaction mixture. It was allowed to stir for 2 h at room temperature. After that the reaction mixture was cooled at 0 °C, methanesulfonyl chloride was added, and the mixture was stirred for 16 h at room temperature. The reaction mixture was washed with (2 × 40 mL) saturated $NaHCO_3$ solution and 50 mL of brine solution, dried on $Na_2SO_4$, filtered, and chromatographed using a column of silica gel (hexane/ethyl acetate, 9:1). This yielded the product as colorless or pale yellow oil.

*Synthesis of 2-(4-iPr-2-oxazolinyl)iodobenzene (**2a**):*[14] colorless, viscous oil. Yield: 48%. $^1$H NMR ($CDCl_3$): $\delta$ 7.85−7.82 [1H, d, Ph−*H*], 7.56−7.53 [1H, d, Ph−*H*], 7.29−7.20 [1H, dd, Ph−*H*], 7.02−6.91 [1H, dd, Ph−*H*], 4.4−4.31 [1H, m, Ox−$CH_2CH$−], 4.11−4.03 [2H, m, Ox−$CH_2CH$−], 1.86−1.78 [1H, m, −$CH(CH_3)_2$], 1.01−0.96 [3H, d, −$CH(CH_3)(CH_3)$], 0.93−0.80 [3H, d, −$CH(CH_3)(CH_3)$]. $^{13}$C{$^1$H} NMR ($CDCl_3$): $\delta$ 163.81 (*C*═N), 140.40−127.78 (Ph*C*), 73.12 [(−$CHCH_2$)], 70.51 [(−$CHCH_2$)], 32.80 [$CH(CH_3)_2$], 18.45, 18.95 [−$CH(CH_3)_2$]. HRMS: calcd *m*/*z* for $C_{12}H_{15}NOI$ [M + H]$^+$ 316.0192; found 316.0199.

*Synthesis of 2-(4-iPr-2-oxazolinyl)bromobenzene (**2b**):*[14b] colorless, viscous oil. Yield: 42%. $^1$HNMR ($CDCl_3$): $\delta$ 7.65−7.58 [2H, d, Ph−*H*], 7.30−7.23 [2H, dd, Ph−*H*], 4.5−4.41 [1H, m, Ox−$CH_2CH$−], 4.2−4.14 [2H, m, Ox−$CH_2CH$−], 1.99−1.92 [1H, m, −$CH(CH_3)_2$], 1.08−1.06 [3H, d, −$CH(CH_3)$ ($CH_3$)], 1.02−0.99 [3H, d, −$CH(CH_3)(CH_3)$]. $^{13}$C{$^1$H} NMR ($CDCl_3$): $\delta$ 162.92 (*C*═N), 133.84−121.78 (Ph*C*), 74.70 [(−$CHCH_2$)], 70.34 [(−$CHCH_2$)], 32.65 [$CH(CH_3)_2$], 18.99, 17.33 [−$CH(CH_3)_2$]. HRMS: calcd *m*/*z* for $C_{12}H_{15}BrNO$ [M + H]$^+$ 268.0331; found 268.0323.

*Synthesis of 2-(4-Ph-2-oxazolinyl)iodobenzene (**2c**):*[14a] colorless, viscous oil. Yield: 40%. $^1$HNMR ($CDCl_3$): $\delta$ 8.01−7.98 [1H, d, Ph−*H*], 7.76−7.68 [1H, d, Ph−*H*], 7.46−7.40 [5H, m, Ph−*H*], 7.37−7.30 [1H, m, Ph−*H*], 7.19−7.13 [1H, dd, Ph−*H*], 5.51−5.44 [1H, t, Ox−$CH_2CH$−], 4.9−4.83 [1H, t, Ox−$CH_2CH$−], 4.35−4.32 [1H, t, Ox−$CH_2CH$−]. $^{13}$C{$^1$H} NMR ($CDCl_3$): $\delta$ 165.24 (*C*═N), 142.00−126.88 (Ph*C*), 75.04 [(−$CHCH_2$)], 70.53 [(−$CHCH_2$)]. HRMS: calcd *m*/*z* for $C_{15}H_{13}NOI$ [M + H]$^+$ 350.0036; found 350.0035.

*General Procedure for Synthesis of Cuprous Acetylide of Ethynyl Ferrocene (**3**).* Cuprous acetylide of ethynyl ferrocene (**3**) was prepared using a known literature procedure.[11] Ethynyl ferrocene was dissolved in 20 mL of ethanol, and CuI was dissolved in 30 mL of aqueous 30% ammonia solution, which was added to the former solution. A yellow precipitate was obtained, instantaneously. The precipitate was filtered, washed with water, ethanol, and diethyl ether, and dried in an oven. This was used without any further purification.

*General Procedure for Sonogashira Coupling Using Stoichiometric CuI.* Ethynyl ferrocene (1.2 equiv), 2-oxazolinyl halobenzene (1 equiv), [$(PPh_3)_2PdCl_2$] (10 mol %), and CuI (1.1 equiv) were added to a two-necked round-bottomed flask, and 30 mL of triethylamine (excess) was added to it as a sole solvent as well as base. The mixture was allowed to stir for 24 h at room temperature (for iodobenzenes) or at 50 °C (for bromobenzenes). The resultant mixture was filtered, and the filtrate was concentrated under rotary evaporation and purified by column chromatography in a silica gel column using hexane/ethyl acetate (9:1) as eluent. Products **4a−c** formed and were characterized by spectroscopic techniques (see Supporting Information, Table S1, entries 1, 2, 3).

*General Procedure for Preparation of π-Copper Complexes (**4a−c**).* The *ortho*-oxazolinyl aryl halides (**2a−c**) and the palladium catalyst [$(PPh_3)_2PdCl_2$] were taken in a two-necked round-bottomed flask under nitrogen, 20 mL of THF was added to it, and the mixture was allowed to stir for 5 min. The cuprous acetylide **3** of ethynyl ferrocene was added to it. The mixture was allowed to stir for 3−4 h at room temperature. The reaction mixtures were evaporated under vacuum and chromatographed through a silica gel column using hexane/ethyl acetate (85:15) as eluent.

*Synthesis of {Fc-C≡C-$C_6H_4$-o-(4-iPr-2-Ox)CuI} (**4a**).* Fc-C≡C−Cu (150 mg, 0.550 mmol), **2a** (145 mg, 0.460 mmol), [$(PPh_3)_2PdCl_2$] (17 mg, 5 mol %). Red solid. Yield: 211 mg, 0.360 mmol, 65.4%. Mp: 120−122 °C. $[\alpha]^{25}_D$ = +28.73 (*c* 0.052, $CH_2Cl_2$). Anal. Found: C, 49.22; H, 3.84; N, 2.31. Calcd for $C_{24}H_{23}CuNOFeI$: C, 49.04; H, 3.94; N, 2.38. IR ($\nu$, cm$^{-1}$): 1989 (coordinated C≡C). $^1$H NMR ($CDCl_3$): $\delta$ 7.49−8.13 [4H, 2d, 2t, Ph−*H*], 5.08−5.18 [2H, 2s, Ox−$CH_2$−], 4.13 [5H, s, $C_5H_5$ of Fc], 4.58−4.81 [4H, m, $C_5H_4$ of Fc], 2.86 [1H, m, −$CH(CH_3)_2$], 1.03[3H, d, −$CH(CH_3)(CH_3)$], 0.75 [3H, d, −$CH(CH_3)(CH_3)$]. $^{13}$C{$^1$H} NMR ($CDCl_3$): $\delta$ 164.41 (*C*═N), 133.68−122.05 (Ph*C*), 73.72, 73.43 (*C*≡*C*), 70.64, 70.49 (Cp*C*), 68.23 (−$CHCH_2$), 65.96 (−$CHCH_2$), 30.42 [−$CH(CH_3)_2$], 18.92, 13.94 [−$CH(CH_3)_2$].

*Synthesis of {Fc-C≡C-$C_6H_4$-o-(4-iPr-2-Ox)CuBr} (**4b**).* Fc−C≡C−Cu (70 mg, 0.256 mmol), **2b** (57.4 mg, 0.214 mmol), [$(PPh_3)_2PdCl_2$] (16 mg, 10 mol %). Red solid. Yield: 65 mg, 0.120 mmol, 56.2%. Mp: 82−83 °C (dec). $[\alpha]^{25}_D$ = +19.46 (*c* 0.046, $CH_2Cl_2$). Anal. Found: C, 53.11; H, 4.38; N, 2.65. Calcd for $C_{24}H_{23}BrCuFeNO$: C, 53.31; H, 4.29; N, 2.59. IR ($\nu$, cm$^{-1}$): 1986.43, (coordinated C≡C) Cu π-complexed. $^1$H NMR ($CDCl_3$): $\delta$ 7.46−8.11 [4H, 2d, 2t, Ph−*H*], 5.00−5.10 [2H, 2s, Ox−$CH_2$−], 4.27 [5H, s, $C_5H_5$ of Fc], 4.42−4.72 [4H, m, $C_5H_4$ of Fc], 2.86 [1H, m, −$CH(CH_3)_2$], 1.02 [3H, d,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−CH(C$H_3$) ($CH_3$)], 0.77 [3H, d, −CH($CH_3$)(C$H_3$)]. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 164.65 (C═N), 133.62−122.05 (PhC), 73.38, 73.13 (C≡C), 68.31 (−CHC$H_2$), 65.89 (−C$H$C$H_2$), 70.67, 70.51 (CpC), 30.13 [−H($CH_3$)$_2$], 19.04, 14.18 [−CH(C$H_3$)$_2$].

*Synthesis of {Fc-C≡C-$C_6H_4$-o-(4-Ph-2-Ox)CuI}(**4c**).* Fc−C≡C−Cu (65.6 mg, 0.240 mmol), **2c** (70 mg, 0.200 mmol), [($PPh_3$)$_2$$PdCl_2$] (15 mg, 10 mol %). Red solid. Yield: 66 mg, 0.106 mmol, 53%. Mp: 74−75 °C (dec). $[\alpha]^{25}_D$ = +135.14 (*c* 0.074, $CH_2Cl_2$). Anal. Found: C, 52.25; H, 3.37; N, 2.22. Calcd for $C_{27}H_{21}CuNOFeI$: C, 52.16; H, 3.40; N, 2.25. IR (ν, $cm^{-1}$): 1990.74 (coordinated C≡C). $^1H$ NMR: δ 7.12−8.36 [4H + 5H, 2d, 2t, m Ph-*H*], 5.81 [1H, dd, C*H*Ph−], 4.59 [2H, m, −Ox−C$H_2$], 4.24−4.41 [9H, Fc]. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 164.59 (C═N), 137.45−125.42 (PhC), 73.84, 70.79 (C≡C), 70.66−69.93 (CpC), 68.86−68.56 [Ox−C$H_2$], 64.23 [CHPh].

*General Procedure of Synthesis of Metal-Free Cu(I) Specific Ligands (**5a,b**).* An oven-dried two-necked round-bottom flask was charged with the π-copper complexes **4a−c** under nitrogen, which were dissolved in 10−15 mL of DMF. Excess (10 mL) aqueous ammonia solution was added to it, and the mixture was stirred for about a minute. The reaction mixture was fractionated using 50 mL of water and 50 mL of ethyl acetate. The organic layer was washed (5 × 50 mL) with water. The organic layer was dried over anhydrous $Na_2SO_4$, filtered, evaporated, and purified by column chromatography using silica gel with a 2% ethyl acetate/hexane mixture as eluent.

*Synthesis of {Fc-C≡C-$C_6H_4$-o-(4-iPr-2-Ox)} (**5a**).* **4a** (300 mg, 0.511 mmol) was dissolved in DMF, and aqueous $NH_3$ was added. The product was purified as mentioned in procedure **E**. Yellow semisolid. Yield: 202 mg, 0.506 mmol, 99%. $[\alpha]^{25}_D$ = −58.11 (*c* 0.00074, $CH_2Cl_2$). IR (ν, $cm^{-1}$): 2251, (C≡C). $^1H$ NMR ($CDCl_3$): δ 7.83−7.80 [1H, d, Ph−*H*], 7.6−7.57 [1H, d, Ph−*H*], 7.4−7.28 [2H, m, Ph−*H*], 4.52−4.45 [3H, m, Ox−C$H_2$−], 4.27−4.24 [7H, s, α protons of $C_5H_4$ + $C_5H_5$ of Fc], 4.22−4.19 [2H, m, β protons of $C_5H_4$ of Fc], 2.00−1.9 [1H, m, −C*H*($CH_3$)$_2$], 1.13−1.09 [3H, d, −CH(C$H_3$) ($CH_3$)], 1.02−1.00 [3H, d, −CH($CH_3$)(C$H_3$)]. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 163.42 (C═N), 133.47−123.49 (PhC), 73.38, 73.00−71.42 (C≡C), 70.17, 68.86 (CpC), 68.17 (−CHC$H_2$), 65.50 (−C$H$C$H_2$), 28.94 [−C$H$($CH_3$)$_2$], 19.00, 18.34 [−CH(C$H_3$)$_2$]. HRMS: calcd *m*/*z* for $C_{24}H_{24}NOFe$ [M + H]$^+$ 398.1202; found 398.1209.

*Synthesis of {Fc-C≡C-$C_6H_4$-o-(4-Ph-2-Ox)} (**5b**).* **4c** (125 mg, 0.201 mmol) was dissolved in DMF, and aqueous $NH_3$ was added. The product was purified as mentioned in procedure **E**. Yellow semisolid. Yield: 83 mg, 0.191 mmol, 95%. $[\alpha]^{25}_D$ = −30.76 (*c* 0.00026, $CH_2Cl_2$). IR (ν, $cm^{-1}$): 2258 (C≡C). $^1H$ NMR ($CDCl_3$): δ 7.85−7.83 [1H, d, Ph−*H*], 7.55−7.53 [1H, d, Ph−*H*], 7.4−7.28 [7H, m, Ph−*H*], 5.41 [1H, dd, C*H*Ph−], 4.79 [1H, dd, Ox−C$H_2$−], 4.37−4.13 [10H, 1H, dd, Ox−C$H_2$− + all protons of Fc]. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 164.84 (C═N), 142.58−123.69 (PhC), 74.90, 71.52 (C≡C), 69.93−68.91 (CpC), 68.86−68.56 [Ox−C$H_2$], 65.29 [CHPh]. HRMS: calcd *m*/*z* for $C_{27}H_{22}NOFe$ [M + H]$^+$ 432.1045; found 432.1046.

**Crystal Structure Determination.** Suitable crystals of compounds **4a−c** were obtained by slow evaporation of their saturated solutions in suitable solvent mixtures. Single-crystal diffraction studies were carried out on a Bruker SMART APEX CCD diffractometer with a Mo Kα (λ = 0.710 73 Å) sealed tube. All crystal structures were solved by direct methods. The program SAINT (version 6.22) was used for integration of the intensity of reflections and scaling. The program SADABS was used for absorption correction. The crystal structures were solved and refined using the SHELXTL (version 6.12) package.[15] All hydrogen atoms were included in idealized positions, and a riding model was used. Non-hydrogen atoms were refined with anisotropic displacement parameters. Table S7 lists the data collection and structure solving parameters for compounds **4a−c** (see Supporting Information). Selected bond distances and angles for all the compounds are given in the Supporting Information (Tables S4, S5, and S6).

## ■ ASSOCIATED CONTENT

### Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.6b00069.

Experimental data and tables giving selected bond lengths and angles and crystallographic data for compounds **4a−c** (PDF)

Crystallographic data for compounds **4a−c** (CIF)

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### Notes

The authors declare no competing financial interest.

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