

Synthesis, characterization, and the role of counterion in cyclopropanation of styrene catalyzed by $[\text{Cu}^{\text{I}}(2,2'\text{-bpy})(\pi\text{-CH}_2\text{=CHC}_6\text{H}_5)][\text{A}]$ ($\text{A} = \text{ClO}_4^-$, PF_6^- and CF_3SO_3^-) complexes

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Abstract

Copper(I)/2,2'-bipyridine complexes, $[\text{Cu}^{\text{I}}(\text{bpy})(\pi\text{-CH}_2\text{CHC}_6\text{H}_5)][\text{A}]$ ($\text{A} = \text{CF}_3\text{SO}_3^-$ (**1**), PF_6^- (**2**)) have been synthesized and characterized. The equilibrium constants for the coordination of styrene to $[\text{Cu}^{\text{I}}(\text{bpy})]^+$ cations at 300 K were determined to be 4.3×10^3 (**1**), 4.4×10^3 (**2**) and $3.8 \times 10^3 \text{ M}^{-1}$ ($\text{A} = \text{ClO}_4^-$, **3**). These data suggested that the axial coordination of the counterion in these complexes observed in the solid state (2.4297(11) Å **1**, 2.9846(12) Å **2**, and 2.591(4) Å **3**) did not significantly affect the binding constant of styrene to $[\text{Cu}^{\text{I}}(\text{bpy})]^+$ cations in solution. In cyclopropanation reactions catalyzed by **1–3**, similar product distribution was obtained. The rate of decomposition of EDA in the presence of styrene at room temperature catalyzed by **3** ($k_{\text{obs}} = (7.7 \pm 0.32) \times 10^{-3} \text{ min}^{-1}$) was slower than the rate observed for **1** ($k_{\text{obs}} = (1.4 \pm 0.041) \times 10^{-2} \text{ min}^{-1}$) or **2** ($k_{\text{obs}} = (1.0 \pm 0.025) \times 10^{-2} \text{ min}^{-1}$).

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Keywords: Copper(I); 2,2'-Bipyridine; Styrene; Crystal structure; Cyclopropanation

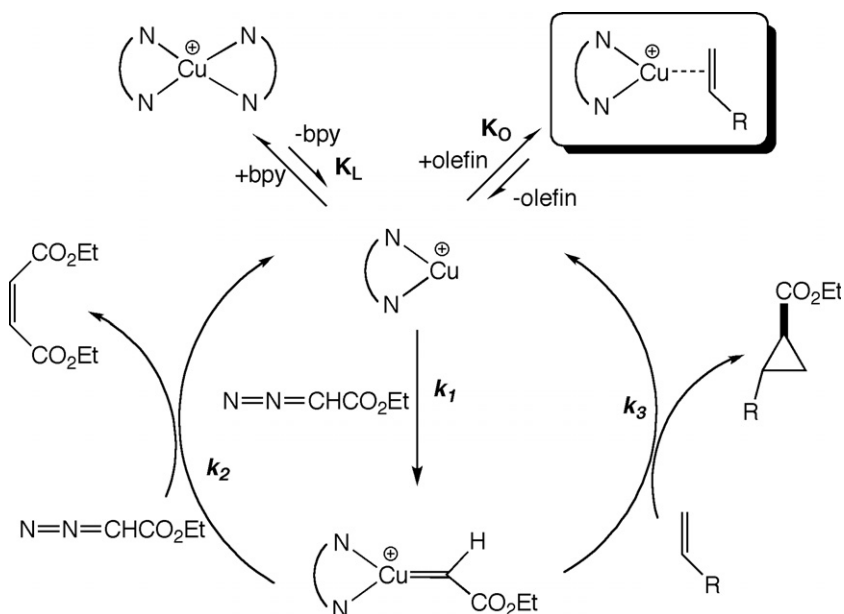
1. Introduction and background

In recent years, a considerable effort has been devoted to the development of transition metal catalysts for diastereo- and enantioselective cyclopropanation [1–4] and aziridination [5,6] of olefins. Effective catalytic system for the cyclopropanation of alkenes with diazo reagents requires the use of a transition metal complex which facilitates the loss of N_2 from the diazo reagent, as well as stabilizes intermediate carbene species against competing carbene dimerization [7–10]. A variety of transition metal complexes have been found to be active in cyclopropanation reactions and they include the complexes of Fe [11], Rh [12], Ru [13,14] and Cu [4]. Copper appears to be particularly attractive because of its low cost relative to other transition metal complexes.

So far, cationic copper(I) complexes in conjunction with a C_2 -symmetric ligand, such as bis(oxazoline) [15], 2,2'-bipyridine (bpy) [16], 2,2':6',2''-terpyridine [16–18] and 1,10-phenanthroline (phen) [16,19], and neutral copper(I) complexes with semicorrin [20], polypyrazolylborates [21–23], iminophosphoramidates [24,25] and β -diketiminates [26] have been successfully used in cyclopropanation reactions. However, despite a tremendous effort directed towards empirical catalyst development, mechanism of these very important synthetic reactions is still not fully understood. It is generally accepted that the copper catalyzed cyclopropanation reactions proceed via a copper–carbene complex, as indicated in Scheme 1 for cyclopropanation catalyzed by copper(I)/2,2'-bipyridine complex [1,2,15]. However, the details of this process are not well-known.

Only, very recently, copper–carbene complexes have been detected as reaction intermediates in cyclopropanation reactions utilizing low temperature NMR

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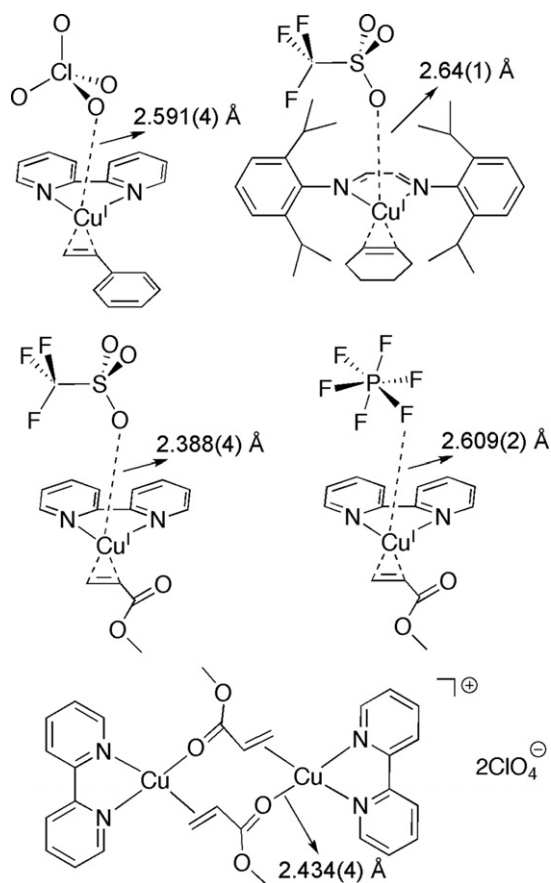
Scheme 1. Proposed mechanism for copper(I)/2,2'-bipyridine catalyzed cyclopropanation of olefins.

measurements [24,25] and X-ray diffraction [26]. Another key mechanistic feature of these reactions includes the role of monomer and counterion, both of which are poorly understood. Mechanistic [15,27] and computational [28,29] studies have indicated that copper(I)/olefin complexes in these systems might act as either catalytically active species or resting states. Furthermore, the reactivity of cationic copper(I) complexes is strongly influenced by the counterion. Triflates and hexafluorophosphates [15,30] were found to be highly effective catalysts whereas halides, cyanides, acetates and perchlorate showed little or no catalytic activity.

Cationic copper(I)/alkene complexes with bidentate nitrogen based ligands are very rare and so far only two complexes with nonpolar olefins such as styrene [31] and cyclohexene [32] have been isolated (Scheme 2). In both complexes, the geometry around copper(I) atom was found to be trigonal pyramidal, due to the weak interaction with the counterion. Recently, we have successfully isolated and structurally characterized $[\text{Cu}^{\text{I}}(\text{bpy})(\pi\text{-CH}_2\text{CHCOOCH}_3)][\text{A}]$ ($\text{A} = \text{CF}_3\text{SO}_3^-$, PF_6^- and ClO_4^-) complexes (Scheme 2). These complexes represented the first class of trigonal pyramidal copper(I) complexes with π -coordinated electron poor olefins. Weak coordination of the counterion was observed in the case of CF_3SO_3^- ($\text{Cu}-\text{O} = 2.388(4) \text{ \AA}$) and PF_6^- ($\text{Cu}-\text{F} = 2.609(2) \text{ \AA}$) complexes. The counterion ClO_4^- , on the other hand, was noncoordinating and the corresponding copper(I) complex was dimeric in the solid state with oxygen atoms of the carbonyl moieties in methyl acrylate bridging two copper(I) centers ($\text{Cu}-\text{O} = 2.434(4) \text{ \AA}$).

In this article, we report the synthesis and characterization of copper(I)/bpy complexes $[\text{Cu}^{\text{I}}(\text{bpy})(\pi\text{-CH}_2=\text{CH-C}_6\text{H}_5)][\text{A}]$ ($\text{A} = \text{CF}_3\text{SO}_3^-$ (1), PF_6^- (2)). Furthermore,

the role of counterion in cyclopropanation of styrene with ethyldiazoacetate (EDA) catalyzed by these complexes and $[\text{Cu}^{\text{I}}(\text{bpy})(\pi\text{-CH}_2=\text{CHC}_6\text{H}_5)][\text{ClO}_4]$ (3) is also discussed.



Scheme 2. Structures of cationic copper(I)/alkene complexes with bidentate nitrogen based ligands.

2. Experimental

2.1. General

$[\text{Cu}^{\text{I}}(\text{CF}_3\text{SO}_3)_2] \cdot \text{C}_6\text{H}_5\text{CH}_3$ (99.99%, Aldrich), $[\text{Cu}^{\text{I}}(\text{CH}_3\text{CN})_4][\text{PF}_6]$ (98+%, Strem) and 2,2'-bipyridine (99+%, Acros) were used as received. $[\text{Cu}^{\text{I}}(\text{CH}_3\text{CN})_4][\text{ClO}_4]$ was synthesized according to the literature procedure [33]. Styrene (99%, Acros) was stirred over CaH_2 for 24 h and distilled under argon. Solvents (methylene chloride, pentane, acetonitrile and methanol) were degassed and deoxygenated using Innovative Technology solvent purifier. Ethyl diazoacetate (EDA, 99% Aldrich) was degassed prior to use. All manipulations were performed under argon atmosphere in a dry box (<1.0 ppm of O_2 and <0.5 ppm of H_2O) or using standard Schlenk line techniques. ^1H NMR spectra were obtained using Bruker Avance 300 and 400 MHz spectrometers and chemical shifts are given in ppm relative to residual solvent peaks ($\delta(\text{CD}_2\text{Cl}_2) = 5.32$ and $\delta(\text{CDCl}_3) = 7.26$). IR spectra were recorded in the solid state or solution using Nicolet Smart Orbit 380 FT-IR spectrometer (Thermo Electron Corporation). Elemental analyses for C, H and N were obtained from Midwest Microlab, LLC. *Caution:* Perchlorate metal salts are potentially explosive and were handled in small quantities under argon atmosphere (Fig. 1).

2.2. $[\text{Cu}^{\text{I}}(\text{bpy})(\pi\text{-CH}_2=\text{CHC}_6\text{H}_5)][\text{CF}_3\text{SO}_3]$ (1)

$[\text{Cu}^{\text{I}}(\text{CF}_3\text{SO}_3)_2] \cdot \text{C}_6\text{H}_5\text{CH}_3$ (0.100 g, 1.93×10^{-4} mol) and styrene (1.33 mL, 1.16×10^{-2} mol) were dissolved in 2.0 mL of dry and degassed methanol and the solution stirred at room temperature for 20 min. 2,2'-Bipyridine (0.0604 g, 3.86×10^{-4} mol) was then added and the solution stirred for additional 30 min. Pentane (2.0 mL) was layered on top of methanol and the solution placed inside

dry box refrigerator at -35°C . After 24 h, colorless crystals were formed, which were washed with 10 mL of pentane and dried under vacuum to yield 0.120 g (68%) of $[\text{Cu}^{\text{I}}(\text{bpy})(\pi\text{-CH}_2=\text{CH-C}_6\text{H}_5)][\text{CF}_3\text{SO}_3]$. ^1H NMR (300 MHz, CD_2Cl_2 , 250 K): δ 8.39 (d, $J = 5.0$ Hz, 2H, $\text{H}_6 + \text{H}'_6$), δ 8.24 (d, $J = 8.1$ Hz, 2H, $\text{H}_3 + \text{H}'_3$), δ 8.11 (t, $J = 7.7$ Hz, $\text{H}_4 + \text{H}'_4$), δ 7.60 (m, 2H, $\text{H}_5 + \text{H}'_5$), δ 7.51 (d, $J = 7.5$ Hz, 2H, Sty), δ 7.27–7.36 (m, 3H, Sty), δ 6.32 (dd, $J_{\text{trans}} = 16$ Hz, $J_{\text{cis}} = 10$ Hz, 1H, H^α), δ 5.06 (d, $J_{\text{trans}} = 16$ Hz, 1H, $\text{H}^\beta_{\text{trans}}$), δ 4.73 (d, $J_{\text{cis}} = 10$ Hz, 1H, $\text{H}^\beta_{\text{cis}}$). FT-IR (solid): $\nu(\text{C}=\text{C}) = 1529 \text{ cm}^{-1}$. Anal. Calc. for $\text{C}_{19}\text{H}_{16}\text{CuF}_3\text{N}_2\text{O}_3\text{S}$: C, 48.25; H, 3.41; N, 5.92. Found: C, 48.36; H, 3.42; N, 5.87%.

2.3. $[\text{Cu}^{\text{I}}(\text{bpy})(\pi\text{-CH}_2=\text{CHC}_6\text{H}_5)][\text{PF}_6] \cdot 1/2\text{CH}_2=\text{CHC}_6\text{H}_5$ (2)

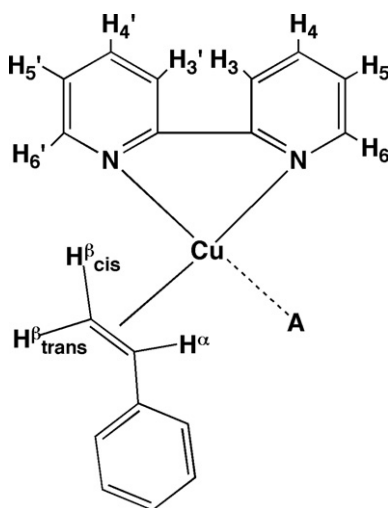
The complex was prepared using the procedure for $[\text{Cu}^{\text{I}}(\text{bpy})(\pi\text{-CH}_2=\text{CH-C}_6\text{H}_5)][\text{CF}_3\text{SO}_3]$ except that $[\text{Cu}^{\text{I}}(\text{CH}_3\text{CN})_4][\text{PF}_6]$ (0.100 g, 2.68×10^{-4} mol) was used instead of $[\text{Cu}^{\text{I}}(\text{CF}_3\text{SO}_3)_2] \cdot \text{C}_6\text{H}_5\text{CH}_3$. Yield = 0.105 g (75%). ^1H NMR (300 MHz, CD_2Cl_2 , 180 K): δ 8.55 (ddd, $J_1 = 5.0$ Hz, $J_2 = 1.5$ Hz, $J_3 = 0.90$ Hz, 2H, $\text{H}_6 + \text{H}'_6$), δ 8.41 (dt, $J_1 = 8.0$ Hz, $J_2 = 1.0$ Hz, 2H, $\text{H}_3 + \text{H}'_3$), δ 8.32 (dt, $J_1 = 8.0$ Hz, $J_2 = 1.7$ Hz, 2H, $\text{H}_4 + \text{H}'_4$), δ 7.80 (m, 2H, $\text{H}_5 + \text{H}'_5$), δ 7.5–7.6 (m, 7.5H, Sty), δ 6.31 (dd, $J_{\text{trans}} = 16$ Hz, $J_{\text{cis}} = 10$ Hz, 1.5H, H^α), δ 5.23 (d, $J_{\text{trans}} = 16$ Hz, 1.5H, $\text{H}^\beta_{\text{trans}}$), δ 4.74 (d, $J_{\text{cis}} = 10$ Hz, 1.5H, $\text{H}^\beta_{\text{cis}}$). FT-IR (solid): $\nu(\text{C}=\text{C}) = 1527 \text{ cm}^{-1}$. Anal. Calc. for $\text{C}_{44}\text{H}_{40}\text{Cu}_2\text{F}_{12}\text{N}_4\text{P}_2$: C, 50.72; H, 3.87; N, 5.38. Found: C, 50.57; H, 3.88; N, 5.18%.

2.4. $[\text{Cu}^{\text{I}}(\text{bpy})(\pi\text{-CH}_2=\text{CHC}_6\text{H}_5)][\text{ClO}_4]$ (3)

The complex was synthesized according to the modified literature procedure, starting from $[\text{Cu}^{\text{I}}(\text{CH}_3\text{CN})_4][\text{ClO}_4]$, 2,2'-bipyridine and excess styrene [31]. The complex was obtained in 83% yield. ^1H NMR (300 MHz, CD_2Cl_2 , 220 K): δ 8.40 (d, $J = 4.5$ Hz, 2H, $\text{H}_6 + \text{H}'_6$), δ 8.25 (d, $J = 8.1$ Hz, 2H, $\text{H}_3 + \text{H}'_3$), δ 8.15 (dt, $J_1 = 7.8$ Hz, $J_2 = 1.7$ Hz, 2H, $\text{H}_4 + \text{H}'_4$), δ 7.64 (m, 2H, $\text{H}_5 + \text{H}'_5$), δ 7.51 (d, $J = 6.9$ Hz, 2H, Sty), δ 7.30–7.40 (m, 3H, Sty), δ 6.33 (dd, $J_{\text{trans}} = 16$ Hz, $J_{\text{cis}} = 10$ Hz, 1H, H^α), δ 5.17 (d, $J_{\text{trans}} = 16$ Hz, 1H, $\text{H}^\beta_{\text{trans}}$), δ 4.75 (d, $J_{\text{cis}} = 10$ Hz, 1H, $\text{H}^\beta_{\text{cis}}$). FT-IR (solid): $\nu(\text{C}=\text{C}) = 1525 \text{ cm}^{-1}$.

2.5. General procedure for cyclopropanation of styrene

In a 20-mL Schlenk flask, catalyst precursor (0.0250 mmol, 1 equiv.), 2,2'-bipyridine (0.0038 g, 0.025 mmol, 1 equiv.) and styrene (1.40 mL, 12.2 mmol, 500 equiv.) were suspended in CH_2Cl_2 (1.4 mL) and stirred at room temperature for 10 min. To the homogenous solution, EDA (130 μL , 1.24 mmol, 50 equiv.) was added in one portion and stirred for 2 h. Completeness of the reaction was determined by IR spectroscopy, as indicated by the disappearance of the absorption of the diazo group ($-\text{N}=\text{N}-$) at



A = PF_6^- , CF_3SO_3^- and ClO_4^-

Fig. 1. ^1H NMR labeling scheme.

2112 cm⁻¹. The reaction mixture was then exposed to air and the remaining copper(II) complex was removed by passing through a basic alumina column. The solvent was removed by vacuum evaporation and the product distribution determined by ¹H NMR in CDCl₃.

2.6. Kinetic studies

A solution at time zero was prepared separately by mixing EDA (260 μL, 2.47 mmol), styrene (2.8 mL, 24.4 mmol) and CH₂Cl₂ (2.8 mL) and the IR spectrum was recorded ($\nu_{\text{N}=\text{N}} = 2112 \text{ cm}^{-1}$). In a 20-mL Schlenk flask, the solution was prepared by dissolving the catalyst precursor (0.0100 mmol, 1.0 equiv.) and 2,2'-bipyridine (0.0016 g, 0.010 mmol, 1.0 equiv.) in styrene (2.80 mL, 24.7 mmol, 2500 equiv.) and CH₂Cl₂ (2.80 mL). The solution was stirred at room temperature until it became homogeneous (10 min). EDA (260 μL, 2.47 mmol, 250 equiv.) was then added in one portion. The consumption of EDA was monitored by collecting 0.2 mL of the reaction solution every 15 min and recording the IR spectrum for a period of 3 h.

2.7. X-ray crystallography

The X-ray intensity data were collected at room temperature using graphite-monochromated Mo K α radiation

($\lambda = 0.71073 \text{ \AA}$) on a Bruker Smart Apex II CCD diffractometer. Data reduction included absorption corrections by the multiscan method using SADABS [34]. Crystal data and experimental conditions are given in Table 1. Structures were solved by direct methods and refined by full-matrix least squares using SHELXTL 6.1 bundled software package [35]. The H atoms were positioned geometrically (aromatic C–H = 0.93 Å, methylene C–H = 0.97 Å and methyl C–H = 0.96 Å) and treated as riding atoms during subsequent refinement, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ or $1.5U_{\text{eq}}$ (methyl C). Crystal maker 7.2 was used to generate molecular graphics.

3. Results and discussion

3.1. X-ray crystallography

[Cu^I(bpy)(π -CH₂=CHC₆H₅)] [A] (A = CF₃SO₃⁻ (**1**), PF₆⁻ (**2**) and ClO₄⁻ (**3**)) were synthesized by reacting [Cu^I(CF₃SO₃)₂ · C₆H₅CH₃], [Cu^I(CH₃CN)₄][PF₆]⁻ and [Cu^I(CH₃CN)₄][ClO₄]⁻, respectively, with the stoichiometric amounts of 2,2'-bipyridine (bpy) and large excess of styrene (typically 30 equiv). Slow crystallization from methanol at -35 °C afforded colorless crystals of **1–3** in reasonable yields. Shown in Fig. 2 is the molecular structure of complex **1**. Selected bond distances and angles are listed in

Table 1
Crystallographic data and experimental details for **1** and **2**

Compound	[Cu ^I (bpy)(π -CH ₂ =CHC ₆ H ₅)] [CF ₃ SO ₃] (1)	[Cu ^I (bpy)(π -CH ₂ =CHC ₆ H ₅)] [PF ₆] · 1/2Sty (2)
Formula	C ₁₉ H ₁₆ CuF ₃ N ₂ O ₃ S	C ₄₄ H ₄₀ Cu ₂ F ₁₂ N ₄ P ₂
Color/shape	Colorless/needles	Colorless/needles
Formula weight	472.94	1041.82
Crystal system	Monoclinic	Monoclinic
Space group	<i>P</i> 2(1)/ <i>c</i>	<i>P</i> 2(1)/ <i>c</i>
Temperature (K)	150(2)	150(2)
Cell constants		
<i>a</i> (Å)	8.36140(10)	22.3107(7)
<i>b</i> (Å)	15.6925(2)	12.2893(4)
<i>c</i> (Å)	14.8425(2)	16.5493(5)
α (°)	90.	90.
β (°)	98.4940(10)	107.63(4)
γ (°)	90.	90.
<i>V</i> (Å ³)	1926.14(4)	4324.5(2)
Formula units/unit cell	4	4
<i>D</i> _{calc} (g cm ⁻³)	1.631	1.600
μ (mm ⁻¹)	1.294	1.148
<i>F</i> (000)	960	2112
Diffractometer	Bruker Smart Apex II	Bruker Smart Apex II
Radiation, graphite-monochromated	Mo K α ($\lambda = 0.71073 \text{ \AA}$)	Mo K α ($\lambda = 0.71073 \text{ \AA}$)
Crystal size (mm)	0.25 × 0.14 × 0.08	0.49 × 0.29 × 0.17
θ Range (°)	1.90 < θ < 30.97	0.96 < θ < 32.47
Range of <i>h, k, l</i>	±12, ±22, ±21	±32, ±18, ±24
Reflections collected/unique	33538/6103	53954/14828
<i>R</i> _{int}	0.0280	0.0476
Refinement method	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	6103/0/265	14828/0/577
Goodness-of-fit on <i>F</i> ²	1.023	0.745
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0288, <i>wR</i> ₂ = 0.0716	<i>R</i> ₁ = 0.0325, <i>wR</i> ₂ = 0.0975
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0391, <i>wR</i> ₂ = 0.0764	<i>R</i> ₁ = 0.0503, <i>wR</i> ₂ = 0.1104
Maximum residual peaks (e Å ⁻³)	0.426 and -0.304	0.668 and -0.461

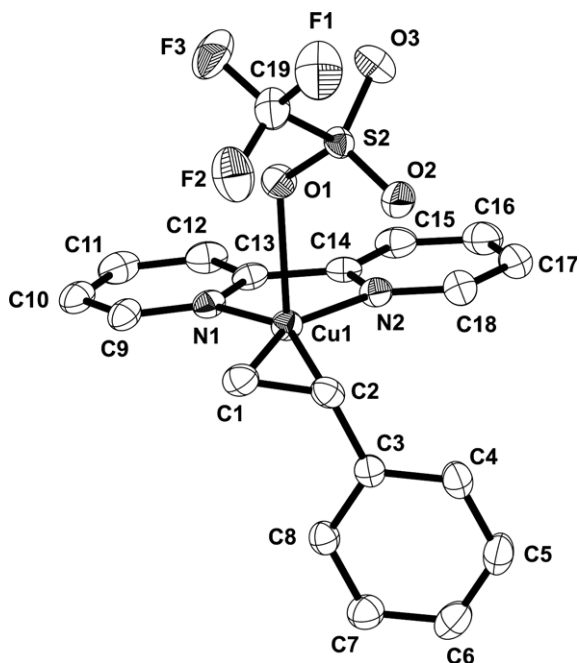


Fig. 2. Molecular structure of $[\text{Cu}^{\text{I}}(\text{bpy})(\pi\text{-CH}_2=\text{CHC}_6\text{H}_5)][\text{CF}_3\text{SO}_3]$ (**1**), shown with 50% probability displacement ellipsoids. H atoms have been omitted for clarity.

Table 2. Complex **1** is distorted trigonal pyramidal in geometry and copper(I) atom is coordinated by two nitrogen atoms of bpy ligand, two olefinic carbon atoms of styrene at the equatorial position, and an oxygen atom of CF_3SO_3^- anion at the axial position. The dihedral angle between the planes defined by the copper and two nitrogen atoms of the bpy molecule and by the copper and two carbon atoms of styrene is $19.63(4)^\circ$. The $\text{Cu}^{\text{I}}\text{-N}$ bond distances ($\text{Cu}(1)\text{-N}(1) = 1.9998(12) \text{ \AA}$, $\text{Cu}(1)\text{-N}(2) = 1.9978(12) \text{ \AA}$) are in the range generally found for copper(I) complexes with bpy containing ligands ($1.93\text{--}2.16 \text{ \AA}$) [36]. The $\text{Cu}^{\text{I}}\text{-O}(\text{SO}_2\text{CF}_3)$ distance ($2.4297(11) \text{ \AA}$) is longer than the sum of ionic radii for Cu^{I} (0.96 \AA) and O^- (1.40 \AA), and is also longer than $2.388(4) \text{ \AA}$ observed in structurally related π -methyl acrylate complex, $[\text{Cu}^{\text{I}}(\text{bpy})(\pi\text{-CH}_2=\text{CHCOOCH}_3)][\text{CF}_3\text{SO}_3]$ [37]. The two $\text{Cu}\text{-C}$ bond distances ($\text{Cu}(1)\text{-C}(1) = 2.0033(14) \text{ \AA}$, $\text{Cu}(1)\text{-C}(2) = 2.0304(14) \text{ \AA}$) are slightly shorter than those found in tetrahedral $\text{Cu}^{\text{I}}(\text{PMDETA})(\pi\text{-CH}_2=\text{CHC}_6\text{H}_5)[\text{BPh}_4]$ (PMDETA = N,N,N',N'',N''' -pentamethyldiethylenetriamine) complex ($\text{Cu}^{\text{I}}\text{-C} = 2.052(2)$ and $2.108(2) \text{ \AA}$) [38]. Furthermore, the $\text{C}=\text{C}$ double bond distance of the coordinated styrene ($1.383(2) \text{ \AA}$) is slightly longer than those reported for other free olefin molecules ($1.355 \pm 0.005 \text{ \AA}$) [38,39]. The crystal structure of **1** is stabilized by $\pi\text{-}\pi$ stacking interactions between bpy units (perpendicular separation between least-squares planes = $3.304(6) \text{ \AA}$). Such interactions are very common in copper(I) complexes with bipyridine based ligands and are typically in the range $3.30\text{--}3.60 \text{ \AA}$ [40,41].

The crystals of complex **2** contain two crystallographically independent molecules, $[\text{Cu}^{\text{I}}(\text{bpy})(\pi\text{-CH}_2=\text{CH-}$

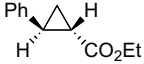
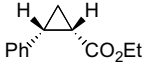
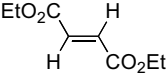
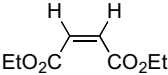
Table 2
Selected bond distances (\AA) and angles ($^\circ$) for **1** and **2**

Distances	Angles		
$[\text{Cu}^{\text{I}}(\text{bpy})(\pi\text{-CH}_2=\text{CHC}_6\text{H}_5)][\text{CF}_3\text{SO}_3]$ (1)			
$\text{Cu}(1)\text{-N}(1)$	1.9998(12)	$\text{N}(2)\text{-Cu}(1)\text{-N}(1)$	82.88(5)
$\text{Cu}(1)\text{-N}(2)$	1.9978(12)	$\text{N}(2)\text{-Cu}(1)\text{-C}(1)$	156.03(6)
$\text{Cu}(1)\text{-C}(1)$	2.0033(14)	$\text{N}(1)\text{-Cu}(1)\text{-C}(1)$	119.27(6)
$\text{Cu}(1)\text{-C}(2)$	2.0304(14)	$\text{N}(2)\text{-Cu}(1)\text{-C}(2)$	115.92(6)
$\text{Cu}(1)\text{-O}(1)$	2.4297(11)	$\text{N}(1)\text{-Cu}(1)\text{-C}(2)$	153.24(5)
$\text{C}(1)\text{-C}(2)$	1.383(2)	$\text{C}(1)\text{-Cu}(1)\text{-C}(2)$	40.11(6)
		$\text{N}(2)\text{-Cu}(1)\text{-O}(1)$	91.31(4)
		$\text{N}(1)\text{-Cu}(1)\text{-O}(1)$	94.77(4)
		$\text{C}(1)\text{-Cu}(1)\text{-O}(1)$	95.49(5)
		$\text{C}(1)\text{-C}(2)\text{-C}(3)$	125.04(13)
$[\text{Cu}^{\text{I}}(\text{bpy})(\pi\text{-CH}_2=\text{CHC}_6\text{H}_5)][\text{PF}_6] \cdot 1/2\text{Sty}$ (2)			
$\text{Cu}(1)\text{-N}(1)$	1.9779(13)	$\text{N}(1)\text{-Cu}(1)\text{-N}(2)$	83.40(5)
$\text{Cu}(1)\text{-N}(2)$	1.9964(13)	$\text{N}(1)\text{-Cu}(1)\text{-C}(1)$	117.64(6)
$\text{Cu}(1)\text{-C}(1)$	2.0144(15)	$\text{N}(2)\text{-Cu}(1)\text{-C}(1)$	158.31(6)
$\text{Cu}(1)\text{-C}(2)$	2.0167(14)	$\text{N}(1)\text{-Cu}(1)\text{-C}(2)$	156.27(6)
$\text{C}(1)\text{-C}(2)$	1.378(2)	$\text{N}(2)\text{-Cu}(1)\text{-C}(2)$	118.37(6)
$\text{Cu}(2)\text{-N}(3)$	1.9713(12)	$\text{C}(1)\text{-Cu}(1)\text{-C}(2)$	39.99(6)
$\text{Cu}(2)\text{-N}(4)$	1.9621(12)	$\text{C}(1)\text{-C}(2)\text{-C}(3)$	124.80(14)
$\text{Cu}(2)\text{-C}(19)$	1.9706(15)	$\text{N}(4)\text{-Cu}(2)\text{-C}(19)$	115.05(6)
$\text{Cu}(2)\text{-C}(20)$	2.0131(14)	$\text{N}(4)\text{-Cu}(2)\text{-N}(3)$	84.01(5)
$\text{Cu}(2)\text{-F}(9)$	2.9846(12)	$\text{C}(19)\text{-Cu}(2)\text{-N}(3)$	159.80(6)
$\text{C}(19)\text{-C}(20)$	1.388(2)	$\text{N}(4)\text{-Cu}(2)\text{-C}(20)$	155.71(6)
		$\text{C}(19)\text{-Cu}(2)\text{-C}(20)$	40.76(6)
		$\text{N}(3)\text{-Cu}(2)\text{-C}(20)$	119.75(6)
		$\text{C}(19)\text{-C}(20)\text{-C}(21)$	125.19(14)

$\text{C}_6\text{H}_5)(\text{PF}_6)]$ and $[\text{Cu}^{\text{I}}(\text{bpy})(\pi\text{-CH}_2=\text{CHC}_6\text{H}_5)][\text{PF}_6]$ (Fig. 3) and styrene solvate. The structure of $[\text{Cu}^{\text{I}}(\text{bpy})(\pi\text{-CH}_2=\text{CHC}_6\text{H}_5)(\text{PF}_6)]$ is very similar to **1**. The copper(I) atom is coordinated by two nitrogen atoms from bpy ligand ($\text{Cu}(2)\text{-N}(3) = 1.9713(12) \text{ \AA}$, $\text{Cu}(2)\text{-N}(4) = 1.9621(12) \text{ \AA}$), two carbon atoms from styrene in equatorial position ($\text{Cu}(2)\text{-C}(19) = 1.9706(15) \text{ \AA}$, $\text{Cu}(2)\text{-C}(20) = 2.0131(14) \text{ \AA}$), and a fluorine atom from PF_6^- anion ($\text{Cu}(2)\text{-F}(9) = 2.9846(12) \text{ \AA}$) in the axial position. Relatively long $\text{Cu}^{\text{I}}\text{-F}(\text{PF}_5)$ distance ($2.9846(12) \text{ \AA}$) indicates that counterion in this complex is weakly coordinated to the copper(I) center. The $\text{C}=\text{C}$ bond length of coordinated styrene is $1.388(2) \text{ \AA}$. The dihedral angle between $\text{Cu}(2)\text{-C}(19)\text{-C}(20)$ and $\text{Cu}(2)\text{-N}(3)\text{-N}(4)$ planes in **2** is $6.34(3)^\circ$, which is much smaller than $19.63(4)^\circ$ and $12.60(5)^\circ$ observed in **1** and $[\text{Cu}^{\text{I}}(\text{bpy})(\pi\text{-CH}_2=\text{CHC}_6\text{H}_5)][\text{ClO}_4]$ (**3**) [31], respectively. This result indicates that $\text{Cu}^{\text{I}}(\text{bpy})(\pi\text{-CH}_2=\text{CHC}_6\text{H}_5)^+$ moiety in **2** is more trigonal planar in geometry than in **1** and **3**. The $[\text{Cu}^{\text{I}}(\text{bpy})(\pi\text{-CH}_2=\text{CHC}_6\text{H}_5)]^+$ cations in **2** form $\pi\text{-}\pi$ stacking interactions between bpy planes (perpendicular separation between least-squares planes = $3.303(5) \text{ \AA}$).

In the molecular structure of complex **3**, which has been published previously (Scheme 2) [31], the copper(I) center is distorted trigonal pyramidal in geometry. Bipyridine ligand coordinates to the copper(I) atom in a bidentate fashion ($\text{Cu}\text{-N} = 1.985(4)$ and $2.014(5) \text{ \AA}$). Additionally, two coordination sites are occupied by olefinic carbon atoms from styrene in equatorial position ($\text{Cu}\text{-C} = 2.014(5)$ and $1.985(6) \text{ \AA}$) and an oxygen atom from ClO_4^- anion

Table 4
Cyclopropanation of styrene in the presence of EDA catalyzed by **1–3**^a

Catalyst				
1	58.0	27.0	8.0	7.0
2	58.7	25.3	9.9	6.1
3	66.9	14.7	6.7	11.7

^a Solvent = CH₂Cl₂, reaction time = 2h, [Cu^I]₀:[2,2'-bpy]₀:[EDA]₀:[Styrene]₀ = 1:1:50:500, [Cu^I]₀ = 1.7 × 10⁻³ M, % yield based on ¹H NMR.

(14.7 mol%). However, surprisingly, the diethyl fumarate to diethyl maleate ratio does not follow the same trend. Cyclopropanation of styrene catalyzed by complex **3** leads to a 36:64 mol% ratio, favoring the formation of diethyl maleate, whereas the same ratio for complexes **1** and **2** was determined to be 53:47 mol% and 62:38 mol%, respectively. We are presently conducting kinetic measurements in the absence of styrene to gain further information on the effect of counterion on the ratio of EDA decomposition products. Overall, based on the results presented in this article, it appears that **1–3** showed similar *trans:cis* cyclopropane selectivity.

The effect of counterion in **1–3** on the cyclopropanation of styrene in the presence of EDA was additionally examined by monitoring the rate of decomposition of EDA. The decomposition of EDA in the presence of **1–3** was very fast and quantitative conversions were achieved within 2 min at room temperature. However, the presence of externally added styrene dramatically slowed down the

reaction rate. This result was expected due to the known fact that the coordination of olefin to the copper(I) center inhibits the diazocarbene decomposition (Scheme 1) [45,46]. Shown in Fig. 4 are the plots for the pseudo-first order decomposition of EDA in the presence of styrene and **1–3**.

Linearity was observed for all three complexes, enabling the determination of the observed rate constant (k_{obs}). The observed rate constant (k_{obs}), as pointed out by detailed kinetic studies with anionic poly(pyrazolyl) borate ligands [45], is a complex function of the total copper(I) and styrene concentration, equilibrium constant for styrene coordination to the copper(I) center (K_0 , Scheme 1), and the rate constant for the formation of copper(I) carbene complex (k_1 , Scheme 1). The rate of decomposition of EDA catalyzed by **3** ($k_{\text{obs}} = (7.7 \pm 0.32) \times 10^{-3} \text{ min}^{-1}$) is slower than the rate observed for **1** ($k_{\text{obs}} = (1.4 \pm 0.041) \times 10^{-2} \text{ min}^{-1}$) or **2** ($k_{\text{obs}} = (1.0 \pm 0.025) \times 10^{-2} \text{ min}^{-1}$). This result is consistent with the cyclopropanation of styrene catalyzed by copper(I) complexes with bis(oxazolines) in which the presence of ClO₄⁻ counterion resulted in a decrease in the catalytic activity [15,30]. Furthermore, the decrease in the observed rate constant for EDA decomposition in the case of ClO₄⁻ counterion cannot be explained in terms of equilibrium constant for styrene coordination to the copper(I) center because variable temperature ¹H NMR measurements have indicated similar binding constant of styrene to **1** ($4.3 \times 10^3 \text{ M}^{-1}$), **2** ($4.4 \times 10^3 \text{ M}^{-1}$) and **3** ($3.8 \times 10^3 \text{ M}^{-1}$). We believe that the counterion in **1–3** can also have an effect on the formation of tetrahedral [Cu^I(2,2'-bpy)₂]⁺ cations [33,36,40,47,48], which are commonly present in these systems (Scheme 1), and would additionally slow down the rate of decomposition of EDA. This possibility is currently under investigation.

In summary, novel copper(I)/2,2-bipyridine complexes with π -coordinated styrene have been synthesized and characterized. These complexes are used as catalysts in copper(I) mediated cyclopropanation of styrene. The equilibrium constants for the coordination of styrene to [Cu^I(bpy)]⁺ cations at 300 K were determined to be 4.3×10^3 , 4.4×10^3 and $3.8 \times 10^3 \text{ M}^{-1}$ for **1**, **2** and **3**, respectively. These data suggested that the axial coordination of the counterion in these complexes observed in the solid state (2.4297(11) Å **1**, 2.9846(12) Å **2**, and 2.591(4) Å **3**) did not significantly affect the binding constant of styrene

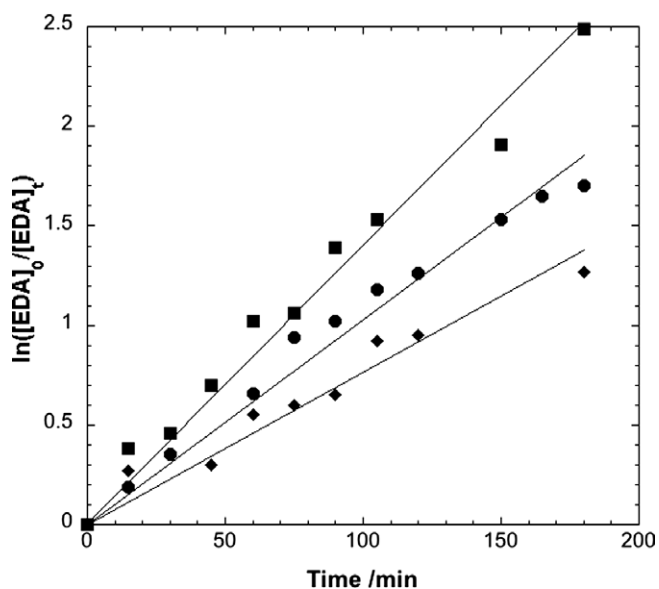


Fig. 4. Plots of $\ln([EDA]_0/[EDA]_t)$ vs. time for the cyclopropanation of styrene with EDA in CH₂Cl₂ at 25 °C catalyzed by **1** (■, $k_{\text{obs}} = (1.4 \pm 0.041) \times 10^{-2} \text{ min}^{-1}$), **2** (●, $k_{\text{obs}} = (1.0 \pm 0.025) \times 10^{-2} \text{ min}^{-1}$) and **3** (◆, $k_{\text{obs}} = (7.7 \pm 0.32) \times 10^{-3} \text{ min}^{-1}$). [Cu^I]₀:[EDA]₀:[Styrene]₀ = 1:250:2500, [Cu^I]₀ = 1.71 × 10⁻³ M. Errors are given at 95% confidence limits.

to $[\text{Cu}^{\text{I}}(\text{bpy})]^+$ cations in solution. In cyclopropanation reactions catalyzed by **1–3**, similar product distribution was obtained. Furthermore, the rate of decomposition of EDA in the presence of styrene catalyzed by **3** ($k_{\text{obs}} = (7.7 \pm 0.32) \times 10^{-3} \text{ min}^{-1}$) was slower than the rate observed for **1** ($k_{\text{obs}} = (1.4 \pm 0.041) \times 10^{-2} \text{ min}^{-1}$) or **2** ($k_{\text{obs}} = (1.0 \pm 0.025) \times 10^{-2} \text{ min}^{-1}$).

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Appendix A. Supplementary material

CCDC No. 649535 and 649536 contain the supplementary crystallographic data for **1** and **2**. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorganchem.2007.07.045](https://doi.org/10.1016/j.jorganchem.2007.07.045).

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