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Note

Synthesis, characterization, and the role of counterion in stabilizing trigonal pyramidal copper(I)/2,2′bipyridine complexes containing electron-poor methyl acrylate

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Abstract

Copper(I)/2,2′-bipyridine complexes, $[Cu^I(bpy)(\pi\text{-}CH_2CHCOOCH_3)][A]$ ($A = CF_3SO_3^-$ (**1**), ClO_4^- (**2**) and PF_6^- (**3**)) have been synthesized and characterized. These complexes are used in copper(I) mediated cyclopropanation and aziridination reactions of methyl acrylate and represent the first class of trigonal pyramidal copper(I) complexes with π-coordinated electron poor olefins. In the case of **1** and **3**, weak coordination of the counterion was observed. The counterion ClO_4^- was noncoordinating in complex **2**, which was dimeric in the solid state with the oxygen atoms of the carbonyl moieties in methyl acrylate bridging two copper(I) centers.

Keywords: Copper(I), 2,2′-bipyridine; Methyl acrylate; 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 [1–3] and aziridination [4,5] of olefins. One of the most effective catalytic systems involves a copper(I) complex in conjunction with a C_2-symmetric ligand, such as semicorrin [6], bis(oxazoline) [7], 2,2-bipyridine (bpy) [8] or 1,10-phenanthroline (phen) [8]. 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 and aziridination reactions proceed via a copper–carbene complex, as indicated in Scheme 1 for cyclopropanation [1,2,7].

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 measurements [9,10]. Another key mechanistic feature of these reactions includes the role of monomer and counterion, both of which are poorly understood. Mechanistic [7,11] and computational [12,13] studies have indicated that copper(I)/olefin complexes in these systems might act as either catalytically active species or resting states.

Cationic copper(I)/olefin complexes with bidentate nitrogen based ligands are very rare and so far only two complexes with nonpolar olefins such as styrene [14] and cyclohexene [15] 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, neutral copper(I) π-ethylene and π-norbornene complexes with anionic iminophosphanamide ligand [16] have been isolated and characterized using X-ray crystallography (Scheme 2). Both complexes showed a remarkable stability in the solid state and solution and were distorted trigonal planar in geometry.

In this paper, we report the synthesis and characterization of novel copper(I)/bpy complexes $[Cu^I(bpy)(\pi\text{-}CH_2CHCOOCH_3)][A]$ ($A = CF_3SO_3^-$ (**1**), ClO_4^- (**2**) and

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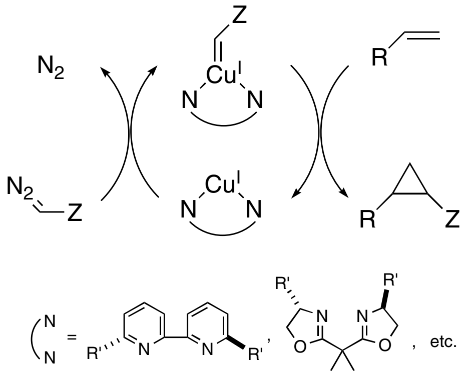
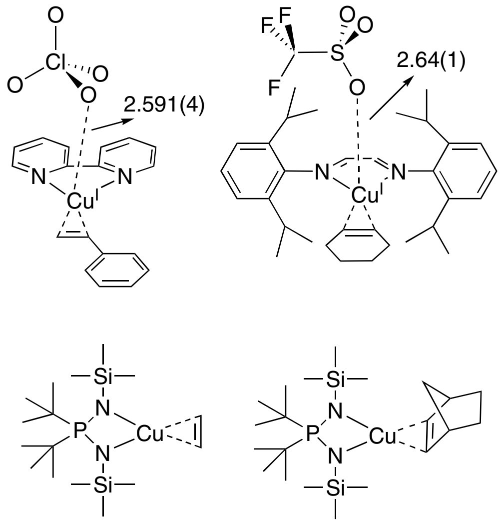


Scheme 1. Proposed catalytic cycle for copper(I) mediated asymmetric cyclopropanation.



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

PF_6^- (**3**)). These complexes are used as catalysts in copper(I) mediated cyclopropanation and aziridination reactions of methyl acrylate and represent the first class of trigonal pyramidal copper(I) complexes with electron poor olefins. Furthermore, the role of counterion in stabilizing trigonal pyramidal geometry is also discussed.

2. Experimental

2.1. General

$[Cu^I(CF_3SO_3)]_2 * C_6H_5CH_3$ (99.99%, Aldrich), $[Cu^I(CH_3CN)_4][PF_6]$ (98+%, Strem) and 2,2′-bipyridine (99+%, Acros) were used as received. $[Cu^I(CH_3CN)_4]$-$[ClO_4]$ was synthesized according to the literature procedure [17]. Methyl acrylate (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. 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 MHz spectrometer and chemical shifts are given in ppm relative to residual solvent peaks ($\delta(CD_2Cl_2) = 5.32$ and $\delta(CDCl_3) = 7.26$). IR spectra were recorded in the solid state or solution using Nicolet Smart Orbit 380 FT-IR spectrometer (Thermo Electron Corporation).

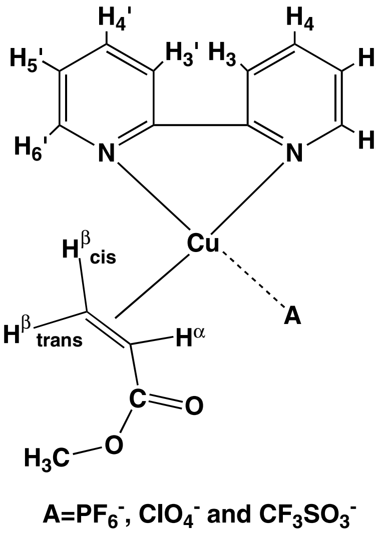


Fig. 1. ^1H NMR labeling scheme.

2.2. *$[Cu^I(bpy)(\pi\text{-}CH_2{=}CHCOOCH_3)][CF_3SO_3]$ (**1**)*

$[Cu^I(CF_3SO_3)]_2 * C_6H_5CH_3$ (0.0500 g, 9.66×10^{-5} mol) and methyl acrylate (17.4 μL, 1.93×10^{-4} mol) were dissolved in 5.0 ml of methylene chloride and the solution stirred at room temperature for 20 min. 2,2′-Bipyridine (0.0302 g, 1.93×10^{-4} mol) dissolved in 5.0 mL of methylene chloride was then added dropwise and solution stirred for additional 60 min. Solvent was removed under vacuum, product washed with pentane and dried under vacuum to yield 0.0760 g (96.5%) of orange powder. Slow evaporation of the methylene chloride solution of the complex afforded dark red and colorless crystals. Colorless crystals were selected for X-ray diffraction studies. ^1H NMR (300 MHz, CD_2Cl_2, RT): δ8.61 (bs, 2H, $H_6 + H'_6$), δ8.30 (d, $J = 6.0$ Hz, 2H, $H_3 + H'_3$), δ8.13 (t, J=6.0 Hz, 2H, $H_4 + H'_4$), δ7.64 (m, 2H, $H_5 + H'_5$), δ5.65 (dd, $J_{trans} = 15$ Hz, $J_{cis} = 9.0$ Hz, 1H, H^α), δ5.30 (d, $J = 15$ Hz, 1H, H^β_{trans}), δ5.05 (d, $J_{cis} = 9.0$ Hz, 1H, H^β_{cis}), δ3.71 (s, 3H, O–CH_3) (Fig. 1).

2.3. *$([Cu^I(bpy)(\pi\text{-}CH_2{=}CHCOOCH_3)][ClO_4])_2$ (**2**)*

$[Cu^I(CH_3CN)_4][ClO_4]$ (0.100 g, 3.06×10^{-4} mol) and 10 equivalents of methyl acrylate (275 μL, 3.06×10^{-3} mol) were dissolved in 2.5 ml of methanol and the solution stirred at room temperature for 20 min. 2,2′-Bipyridine

(0.0477 g, 3.06×10^{-4} mol) was then added and solution stirred for additional 5 min. Solvent was allowed to slowly evaporate under inert atmosphere until dryness. Pentane (10 mL) was then added and product separated by filtration. It was washed with additional 10 mL of pentane and dried under vacuum to yield 0.115 g (92.7%) of white prism like crystals which were suitable for X-ray diffraction. ^{1}H NMR (300 MHz, CD_2Cl_2, RT): δ8.67 (d, $J = 6.0$ Hz, 2H, $H_6 + H'_6$), δ8.28 (d, $J = 9.0$ Hz, 2H, $H_3 + H'_3$), δ 8.17 (t, $J = 9.0$ Hz, 2H, $H_4 + H'_4$), δ7.70 (m, 2H, $H_5 + H'_5$), δ5.63 (dd, $J_{trans} = 15$ Hz, $J_{cis} = 9.0$ Hz, 1H, H^{α}), δ 5.21 (d, $J = 15$ Hz, 1H, H^{β}_{trans}), δ 5.01 (d, $J_{cis} = 9.0$ Hz, 1H, H^{β}_{cis}), δ3.74 (s, 3H, O–CH_3). FT IR (solid): $\nu(C{=}O) = 1694\ cm^{-1}$, $\nu(C{=}C) = 1608\ cm^{-1}$.

2.4. $[Cu^I(bpy)(\pi\text{-}CH_2{=}CHCOOCH_3)][PF_6]$ (**3**)

The complex was prepared using the procedure for $[Cu^I(bpy)(\pi\text{-}CH_2{=}CHCOOCH_3)][ClO_4]$ except that $[Cu^I(CH_3CN)_4][PF_6]$ (0.100 g, 2.68×10^{-4} mol) was used instead of $[Cu^I(CH_3CN)_4][ClO_4]$. Yield = 0.130 g (79%). ^{1}H NMR (500 MHz, CD_2Cl_2, RT): δ8.66 (d, $J = 6.0$ Hz, 2H, $H_6 + H'_6$), δ 8.35 (d, $J = 9.0$ Hz, 2H, $H_3 + H'_3$), δ 8.27 (t, $J = 9.0$ Hz, 2H, $H_4 + H'_4$), δ 7.78 (m, 2H, $H_5 + H'_5$), δ 5.56 (dd, $J_{trans} = 15$ Hz, $J_{cis} = 9.0$ Hz, 1H, H^{α}), δ5.27 (d, $J = 15$ Hz, 1H, H^{β}_{trans}), δ 4.95 (d, $J_{cis} = 9.0$ Hz, 1H, H^{β}_{cis}), δ 3.80 (s, 3H, O–CH_3). FT IR (solid): $\nu(C{=}O) = 1705\ cm^{-1}$, $\nu(C{=}C) = 1601\ cm^{-1}$.

2.5. X-ray crystallography

The X-ray intensity data were collected at room temperature using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) on a Bruker Smart Apex II CCD diffractometer. Data reduction included absorption corrections by the multiscan method using SADABS [18]. 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 [19]. The H atoms were calculated geometrically and treated with a riding model in subsequent refinement cycles.

3. Results and discussion

$[Cu^I(bpy)(\pi\text{-}CH_2{=}CHCOOCH_3)][CF_3SO_3]$ (**1**) was synthesized by reacting $[Cu^I(CF_3SO_3)]_2 * C_6H_5CH_3$ with the stoichiometric amounts of bpy and methyl acrylate. $([Cu^I(bpy)(\pi\text{-}CH_2{=}CHCOOCH_3)][ClO_4])_2$ (**2**) and $[Cu^I(bpy)(\pi\text{–}CH_2{=}CHCOOCH_3)][PF_6]$ (**3**) were prepared in a similar way starting from $[Cu^I(CH_3CN)_4][ClO_4]$ and $[Cu^I(CH_3CN)_4][PF_6]$, respectively, except that excess

Table 1
Crystallographic data and experimental details for **1**–**3**

Compound	$[Cu^I(bpy)(\pi\text{-}MA)][CF_3SO_3]$ (**1**)	$([Cu^I(bpy)(\pi\text{-}MA)][ClO_4])_2$ (**2**)	$[Cu^I(bpy)(\pi\text{-}MA)][PF_6]$ (**3**)
Formula	$C_{15}H_{14}CuF_3N_2O_5S$	$C_{28}H_{28}Cl_2Cu_2N_4O_{12}$	$C_{14}H_{14}CuF_6N_2O_2P$
Color/shape	Colorless/needles	Colorless/needles	Colorless/prisms
Formula weight	454.88	775.07	450.78
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P21/n$	$P21/n$
Temperature (K)	298	298	298
Cell constants			
a (Å)	6.0741(14)	10.0179(12)	11.8256(13)
b (Å)	9.542(2)	10.2126(12)	7.9740(8)
c (Å)	16.804(4)	16.181(2)	18.2054(19)
α (°)	74.184(4)	90	90
β (°)	88.759(4)	101.260(2)	92.010(2)
γ (°)	77.189(4)	90.	90.
V (Å^3)	913.0(4)	1623.6(3)	1715.7(3)
Formula units/unit cell	2	2	4
D_{calcd} (g cm^{-3})	1.655	1.585	1.745
μ (mm^{-1})	1.369	1.459	1.439
$F(000)$	460	790	904
Diffractometer	Bruker Smart Apext II	Bruker Smart Apex II	Bruker Smart Apex II
Radiation, graphite monochr.	Mo Kα ($\lambda = 0.71073$ Å)	Mo Kα ($\lambda = 0.71073$ Å)	Mo Kα ($\lambda = 0.71073$ Å)
Crystal size (mm)	$0.32 \times 0.18 \times 0.10$	$0.11 \times 0.050 \times 0.030$	$0.47 \times 0.25 \times 0.17$
2θ Range (°)	$1.26 < 2\theta < 25.61$	$2.21 < 2\theta < 26.42$	$2.02 < 2\theta < 32.92$
Range of h,k,l	± 7, ± 11, ± 20	± 12, ± 12, ± 20	± 18, ± 12, ± 27
Reflections collected/unique	7688/3434	16,750/3332	21,793/6034
R_{int}	0.0380	0.0938	0.0178
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	3434/0/245	3332/0/218	6034/0/236
Goodness-of-fit on F^2	0.975	1.077	1.049
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0469$, $wR_2 = 0.1296$	$R_1 = 0.0487$, $wR_2 = 0.1267$	$R_1 = 0.0391$, $wR_2 = 0.1335$
R indices (all data)	$R_1 = 0.0758$, $wR_2 = 0.1593$	$R_1 = 0.1009$, $wR_2 = 0.1473$	$R_1 = 0.0561$, $wR_2 = 0.1480$
Max. resid. peaks (e Å^{-3})	0.509 and −0.397	0.764 and −0.339	0.498 and −0.457

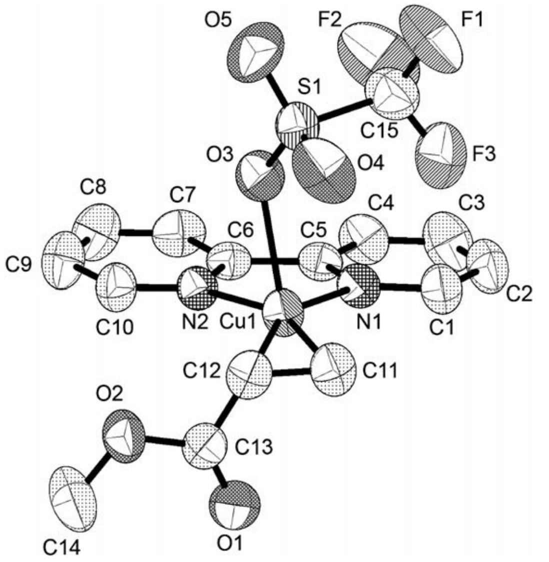


Fig. 2. Molecular structure of **1** with thermal ellipsoids at 50% probability. Hydrogen atoms have been omitted for clarity.

methyl acrylate was used (typically 10–20 equivalents) in order to completely displace coordinated CH_3CN. Colorless crystals of **1**–**3** suitable for X-ray analysis were obtained by slow evaporation of methanol with (**2** and **3**) or without (**1**) the presence of excess methyl acrylate.

Shown in Fig. 2 is the molecular structure of **1**. Selected bond distances and angles are listed in 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 methyl acrylate 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 methyl acrylate is 14.94(4)°. The Cu^{I}–N bond distances (Cu(1)–N(1) = 1.966(4) Å, Cu(1)–N(2) = 1.986(3) Å) are in the range generally found for copper(I) complexes with bpy containing ligands (1.93–2.16 Å) [20]. The Cu^{I}–O(SO_2CF_3) distance (2.388(4) Å) is slightly longer than the sum of ionic radii for Cu^{I} (0.96 Å) and O^- (1.40 Å), and is much shorter than 2.64(1) Å observed in structurally related π-cyclohexene complex with diazadiene ligand [15] (Scheme 2).

The two Cu–C bond distances (Cu(1)–C(11) = 2.002(5) Å, Cu(1)–C(12) = 2.012(4) Å) are slightly shorter than those found in tetrahedral Cu^{I}(PMDETA)(π-$CH_2CHCOOCH_3$)][BPh_4] (PMDETA = *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine) complex (Cu(1)–C(1) = 2.021(4) Å, Cu^{I}–C(2) = 2.067(4) Å) [21]. Furthermore, the C–C double bond distance of the coordinated methyl acrylate (1.374(7) Å) is slightly longer than those reported for other free olefin molecules (1.355 ± 0.005 Å) [22].

In the solid state, complex **2** exists as a dimer and each copper(I) center is trigonal pyramidal in geometry (Fig. 3). Copper(I) atom is coordinated by two nitrogen atoms from bpy ligand (Cu(1)–N(1) = 1.965(4) Å, Cu(1)–N(2) = 1.980 (4) Å), two carbon atoms from methyl acrylate in equatorial position (Cu(1)–C(11) = 1.994(5) Å, Cu(1)–C(12) = 2.002(5) Å), and an oxygen atom from carbonyl group of the adjacent methyl acrylate (Cu(1)–O(1) = 2.434(4) Å). Surprisingly, the counterion ClO_4^- is noncoordinating, since the shortest distance between Cu^{I} atom and O from ClO_4^- anion is 3.721 Å. This is contrary to structurally related [Cu^{I}(bpy)(π-styrene)][ClO_4] complex (Scheme 2) in which Cu–O(ClO_3) bond length was determined to be 2.591(4) Å [14]. 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 methyl acrylate is 19.45(2)°, indicating significant distortion from the ideal trigonal pyramidal geometry. The coordination

Table 2
Selected bond distances (Å) and angles (°) for **1**–**3**

[Cu^{I}(bpy)(π-MA)][CF_3SO_3] (**1**)		([Cu^{I}(bpy)(π-MA)][ClO_4])$_2$ (**2**)		[Cu^{I}(bpy)(π-MA)][PF_6] (**3**)	
Distances					
Cu(1)–N(1)	1.966(4)	Cu(1)–N(1)	1.965(4)	Cu(1)–N(1)	1.9767(16)
Cu(1)–N(2)	1.986(3)	Cu(1)–N(2)	1.980(4)	Cu(1)–N(2)	1.9678(16)
Cu(1)–C(11)	2.002(5)	Cu(1)–C(11)	1.994(5)	Cu(1)–C(11)	1.967(2)
Cu(1)–C(12)	2.012(4)	Cu(1)–C(12)	2.002(5)	Cu(1)–C(12)	2.0078(19)
Cu(1)–O(3)	2.388(4)	Cu(1)–O(1)	2.434(4)	Cu(1)–F(5)	2.609(2)
C(11)–C(12)	1.374(7)	C(11)–C(12)	1.369(7)	C(11)–C(12)	1.379(3)
Angles					
N(1)–Cu(1)–N(2)	83.62(15)	N(1)–Cu(1)–N(2)	83.48(17)	N(1)–Cu(1)–N(2)	83.87(6)
N(1)–Cu(1)–C(12)	153.41(19)	N(1)–Cu(1)–C(12)	114.5(2)	N(1)–Cu(1)–C(12)	122.16(8)
N(1)–Cu(1)–C(11)	115.58(19)	N(1)–Cu(1)–C(11)	149.67(19)	N(1)–Cu(1)–C(11)	161.36(9)
C(11)–Cu(1)–C(12)	40.0(2)	C(11)–Cu(1)–C(12)	40.1(2)	C(11)–Cu(1)–C(12)	40.57(9)
N(2)–Cu(1)–C(11)	156.32(19)	N(2)–Cu(1)–C(11)	118.84(19)	N(2)–Cu(1)–C(11)	112.96(8)
N(2)–Cu(1)–C(12)	117.79(18)	N(2)–Cu(1)–C(12)	158.4(2)	N(2)–Cu(1)–C(12)	153.52(8)
N(1)–Cu(1)–O(3)	97.61(14)	N(2)–Cu(1)–O(1)	90.54(14)	N(1)–Cu(1)–F(5)	89.16(6)
N(2)–Cu(1)–O(3)	85.65(13)	N(1)–Cu(1)–O(1)	98.58(15)	N(2)–Cu(1)–F(5)	96.71(8)
C(11)–C(12)–C(13)	121.6(5)	C(13A)–C(11)–C(12)	121.95(19)	C(11)–C(12)–C(13)	121.3(2)

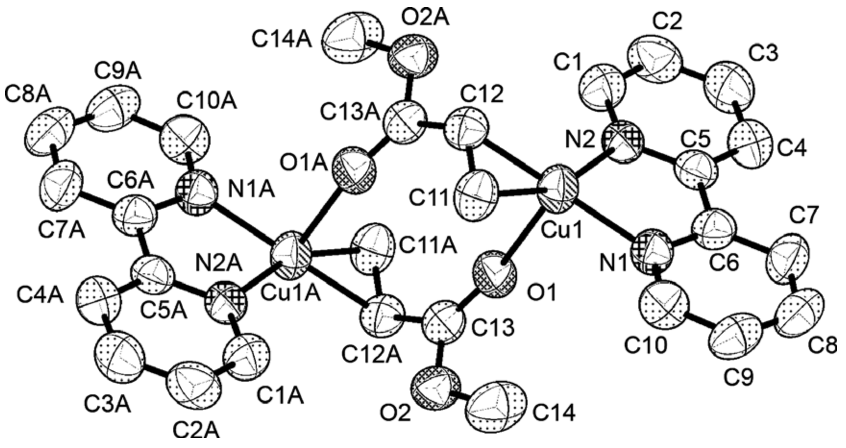


Fig. 3. Molecular structure of $[Cu^{I}(bpy)(\pi\text{-MA})]^{2+}$ cation with thermal ellipsoids at 50% probability. Hydrogen atoms have been omitted for clarity. Symmetry transformations used to generate equivalent atoms: $-x + 2$, $-y + 1$, $-z + 1$.

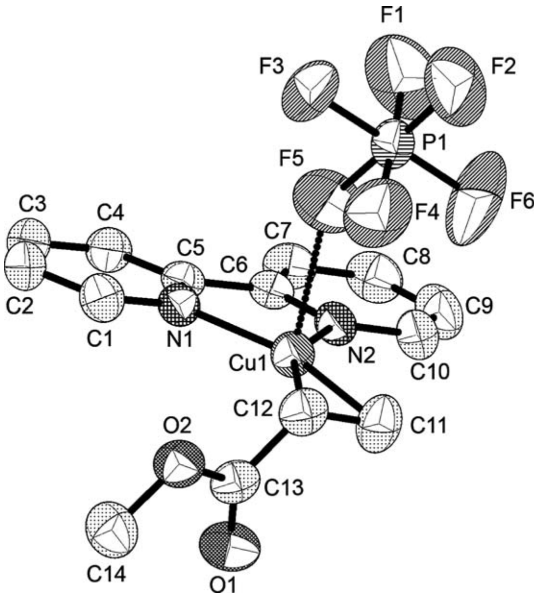


Fig. 4. Molecular structure of **3** with thermal ellipsoids at 50% probability. Hydrogen atoms have been omitted for clarity.

of oxygen atom from the carbonyl group of methyl acrylate to the copper(I) center does not significantly change C=O bond distance (1.215(6) vs. 1.193(6) and 1.205(2) Å for **1** and **3**, respectively).

Shown in Fig. 4 is the molecular structure of **3**. Similarly to **1**, complex **3** is trigonal pyramidal. Copper(I) atom is coordinated by two nitrogen atoms of bpy ligand, two carbon atoms of methyl acrylate moiety, and a fluorine atom of PF_6^- anion. Relatively long Cu^{I}–$F(PF_5)$ distance (2.609(2) Å) indicates that counterion in this complex is weakly coordinated to the copper(I) center. The Cu^{I}–N and C=C bond lengths (Cu(1)–N(1) = 1.9767(16) Å, Cu(1)–N(2) = 1.9678(16) Å, C(11)–C(12) = 1.379(3) Å) in **1** are similar to those found in **2** and **3**. The dihedral angle between Cu(1)–C(12)–C(11) and Cu(1)–N(1)–N(2) planes in **3** is 7.97(3)°, which is much smaller than 19.54(2)° and 14.94(4)° observed in **1** and **2**, respectively. This result indicates that $Cu^{I}(bpy)(\pi\text{–}CH_2CHCOOCH_3)^+$ moiety in **3** is more trigonal planar in geometry than in **1** and **2**.

Complexes **1**–**3** are very stable in the solid state even in the presence of air. However, they disproportionate in CD_3OD, $(CD_3)_2CO$ and CD_2Cl_2 within 10 min at room temperature. This limited our use of NMR spectroscopy to ^1H only. The spectra of **1**–**3** in CD_2Cl_2 (Section 2) indicated 1:1 ratio between 2,2′-bipyridine and methyl acrylate. However, only four resonances for bpy ligand were observed for all compounds which is not consistent with solid state structures. This is most likely induced by the rapid exchange on the NMR time scale between free and complexed methyl acrylate or rotation about the alkene-copper(I) bond. Chemical shifts of complexed methyl acrylate are summarized in Table 3 and compared to those of free methyl acrylate. For **1**–**3**, very strong shielding of vinyl protons was observed which indicates π-backbonding donation from Cu^{I}, although with different magnitudes. The shielding effect is the weakest with α-carbon, which is also further away from Cu^{I} than is the β-carbon. Similar findings were reported previously for $[Cu^{I}(bpy)(\pi\text{-styrene})][ClO_4]$ [14]. The π-nature of C=C of methyl acrylate is further supported by a decrease in the IR stretching frequency of C=C by approximately 30 cm^{-1} upon coordination. Larger decrease in the stretching frequency of C=O in **2** (31 cm^{-1}), as compared to **1** (19 cm^{-1}) and **3** (20 cm^{-1}) is consistent with the solid state structure in which the O atom from C=O of methyl acrylate is weakly coordinated to the Cu^{I}.

In summary, novel copper(I)/2,2-bipyridine complexes with π-coordinated methyl acrylate have been synthesized and characterized. These complexes are used as catalysts in copper(I) mediated cyclopropanation and aziridination reactions and represent the first class of trigonal pyramidal copper(I) complexes with electron poor olefins. In **1** and **3**, weak coordination of the counterion was observed. In complex **2**, the ClO_4^- anion was noncoordinating and dimerization occurred in the solid state with the oxygen atoms of the carbonyl moieties in methyl acrylate bridging

Table 3
^{1}H NMR chemical shifts (400 MHz, CD_2Cl_2, RT) of olefinic protons and C=C and C=O stretching frequencies (cm^{-1}) for **1**–**3**

	1	**2**	**3**
$\delta H_\alpha(\delta\Delta H_\alpha)$[a]	5.65(0.47)	5.63(0.49)	5.56(0.56)
$\delta H_\beta^{trans}(\delta\Delta H_\beta^{trans})$	5.30(1.07)	5.21(1.16)	5.27(1.10)
$\delta H_\beta^{cis}(\delta\Delta H_\beta^{cis})$	5.05(0.77)	5.01(0.81)	4.95(0.87)
ν(C=C)($\delta\Delta\nu$)[b]	1706(19)	1694(31)	1705(20)
ν (C=O)($\delta\Delta\nu$)	1603(31)	1608(26)	1601(33)

[a] $\delta\Delta H_\alpha = \delta H_\alpha$(free MA) - δH_α(observed), ppm ($-RCH_\alpha = CH_\beta^{trans}CH_\beta^{cis}$).

[b] $\delta\Delta\nu = \nu$(free MA) - ν(observed), cm^{-1}.

two copper(I) centers. We are presently exploring π-coordination with other polar monomers and conducting detailed kinetic measurements to more precisely determine the effect of counterion on reactivity and stereoselectivity in copper(I) mediated cyclopropanation and aziridination reactions.

4. Supporting information available

Crystallographic data for **1**–**3** have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 606230, 606231, and 606232, respectively, in CIF format. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44 1223 336033; email: deposit@ccdc.cam.ac.uk).

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