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Chiral copper–bipyridine complexes: Synthesis, characterization and mechanistic studies on asymmetric cyclopropanation

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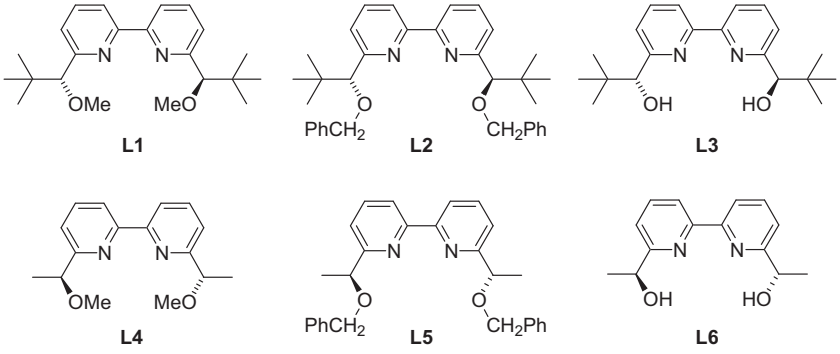
ABSTRACT

Chiral bipyridine ligands of different steric properties when reacted with $CuCl_2$ formed orange, yellow or green solids of new copper(II) complexes, [Cu(**L**)Cl_2] (**L** = **L2**–**6**), in good yield. Together with [Cu(**L1**)Cl_2], these complexes were characterized in solution by UV–Vis spectroscopy and cyclic voltammetry. The complexes give *d*–*d* transitions between 860 and 970 nm, and exhibit one quasi-reversible Cu(II)/Cu(I) couple between +0.405 V and +0.516 V versus NHE. Two of the copper(II) complexes, [Cu(**L5**)Cl_2] and [Cu(**L6**)Cl_2], and a copper(I) complex of **L1**, [Cu(**L1**)Cl], were characterized by X-ray crystallography. The triflate derivatives of both the Cu(I) and Cu(II) complexes are active catalysts towards the cyclopropanation of ethyl diazoacetate with styrene. The asymmetric induction suffers when the size difference between the alkyl and alkoxyl groups was minimized. The mechanism of the cyclopropanation was studied with kinetic and competition experiments. The rate is first order in catalyst and ethyl diazoacetate, inverse order with styrene and is strongly affected by the counterion.

1. Introduction

Copper–diimine complexes have been of great interest in a number of research areas, such as photochemistry [1,2], supramolecular chemistry [3,4] electrochemistry [5,6] and catalysis [7–9]. In enantioselective reactions, chiral versions of the complexes have also been used successfully in catalysis that involved cyclopropanation [10–13] and allylic oxidation [14–16]. The results led us to systematically investigate a family of chiral copper(II) complexes with ligands having different steric properties. Herein, we report the synthesis, spectroscopic characterisation and redox behaviours of a series of copper(II)–bipyridine complexes, as well as their use in the asymmetric cyclopropanation of styrene with ethyl diazoacetate (EDA). X-ray crystal structures for [Cu(**L5**)Cl_2] and [Cu(**L6**)Cl_2] and a copper(I) complex, [Cu(**L1**)Cl], are described. The results of mechanistic studies and kinetic studies under pseudo-first order conditions on the asymmetric cyclopropanation catalysts are also presented.



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2. Experimental

2.1. General methods

Toluene was distilled under N_2 over sodium. Dichloromethane and acetonitrile were distilled over calcium hydride. Diethyl ether and THF were distilled under N_2 over sodium/benzophenone. Chemicals were of reagent-grade quality and were obtained commercially. Infrared spectra in the range 500–4000 cm^{-1} using a Nujol matrix or KBr plates were recorded on a Perkin–Elmer Model FTIR-1600 spectrometer. The electronic absorption spectra were measured on a Perkin–Elmer Lambda 19 double-beam UV–Vis-NIR spectrophotometer. ^1H and ^{13}C NMR spectra were recorded on a Varian 300 MHz Mercury instrument. Positive ion FAB mass spectra as a 3-nitrobenzylalcohol matrix were recorded on a Finnagin MAT 95 spectrometer. ESI-MS were taken by a PE SCIEX API 365 mass spectrometer. Electron ionization mass spectra were recorded on a Hewlett–Packard 5890II GC instrument coupled with a 5970 mass selective detector. Elemental analyses were performed on a Vario EL elemental analyzer. Optical rotations were measured by a JASCO DIP-370 digital polarimeter. Melting points were measured by an electrothermal digital apparatus. The chiral bromopyridine intermediates and bipyridines L1, L3 and L6 were prepared according to the literature procedures [17]. [Cu(**L1**)Cl_2] and [Cu(**L1**)Cl] were synthesized according to our previously reported procedure [11].

2.2. Synthesis of bipyridines *L2*, *L4* and *L5*

At 70 °C and under N_2, to $NiCl_2{\cdot}6H_2O$ (6 mmol, 1.43 g) in degassed DMF (30 ml), triphenylphosphine (24 mmol, 6.30 g) was added to give a blue solution. Zinc powder (13 mmol, 0.87 g) was then added and the resulting mixture was stirred for 1 h, resulting in the formation of a dark-brown mixture. The suitable bromopyridine (5 mmol) in degassed DMF (5 ml) was added slowly and the mixture was stirred for another 3 h. The mixture was then allowed to cool to room temperature and 5% aqueous NH_3 (50 ml) was added. The layers were separated, and the aqueous layer was extracted three times with CH_2Cl_2 (70 ml × 3). The combined organic layers were washed three times with water (50 ml × 3) and once with brine (50 ml). Drying with Na_2SO_4 and removal of the solvent under reduced pressure yielded a pale yellow solid. This was purified by column chromatography (petroleum ether–ethyl acetate) to give a white solid.

2.2.1. Bipyridine *L2*

Yield: 0.66 g (52%); ^1H NMR ($CDCl_3$): δ 1.02 (s, 18H), 4.33 (s, 2H), 4.32–4.50 (m, 4H), 7.27–7.35 (m, 10H), 7.47 (d, 2H, J = 7.5 Hz), 7.81 (t, 2H, J = 7.5 Hz), 8.29 (d, 2H, J = 7.5 Hz); ^{13}C NMR ($CDCl_3$): δ 26.3, 26.3, 26.4, 35.7, 71.3, 90.4, 119.4, 121.6, 121.6, 127.1, 128.0, 136.5, 138.7, 154.8, 159.6. *Anal.* Calc. for $C_{34}H_{40}O_2N_2$: C, 80.28; H, 7.93; N, 5.51. Found: C, 80.48; H, 7.70; N, 5.24%.

2.2.2. Bipyridine *L4*

Yield: 0.38 g (56%); ^1H NMR ($CDCl_3$): δ 1.53 (d, 6H, J = 6.6 Hz), 3.36 (s, 6H), 4.50–4.56 (m, 2H), 7.43 (d, 2H, J = 7.8 Hz), 7.83 (t, 2H, J = 7.8 Hz), 8.33 (d, 2H, J = 7.5 Hz); ^{13}C NMR ($CDCl_3$): δ 22.3, 56.8, 80.8, 119.5, 119.6, 137.3, 155.3, 162.2. *Anal.* Calc. for $C_{16}H_{20}O_2N_2$: C, 70.56; H, 7.40; N, 10.29. Found: C, 70.70; H, 7.38; N, 9.99%.

2.2.3. Bipyridine *L5*

Yield: 0.52 g (49%); ^1H NMR ($CDCl_3$): δ 1.59 (d, 6H, J = 6.6 Hz), 4.47–4.58 (m, 4H), 4.72–4.79 (m, 2H), 7.30–7.37 (m, 10H), 7.54 (d, 2H, J = 7.5 Hz), 7.84 (t, 2H, J = 7.8 Hz), 8.35 (d, 2H, J = 7.5 Hz); ^{13}C NMR ($CDCl_3$): δ 22.7, 70.9, 78.8, 78.9, 119.7, 127.5, 127.6, 128.3, 137.5, 138.3, 155.3, 162.6. *Anal.* Calc. for $C_{28}H_{28}O_2N_2$: C, 79.22; H, 6.65; N, 6.60. Found: C, 79.29; H, 6.54; N, 6.34%.

2.3. Procedure for the preparation of [Cu(*L*)Cl_2]

Chiral bipyridine **L** (0.4 mmol) in CH_2Cl_2 (5 ml) was added drop-by-drop to a solution of $CuCl_2{\cdot}2H_2O$ (0.4 mmol, 0.068 g) in absolute ethanol (5 ml). The mixture was refluxed for a few hours. Addition of ether to the cooled reaction mixture led to the formation of a microcrystalline solid. The mixture was placed in the refrigerator overnight and the microcrystalline solid was filtered and washed with ether.

2.3.1. [Cu(*L2*)Cl_2]

Recrystallization from CH_2Cl_2/EtOH/Et_2O gave 0.136 g (53%) of an orange solid: *Anal.* Calc. for $CuN_2Cl_2C_{34}H_{40}O_2$: C, 63.49; H, 6.22; N, 4.36. Found: C, 64.10; H, 6.12; N, 4.48%. UV–Vis-NIR spectrum (CH_2Cl_2), λ_{max} (nm) (ε/M^{-1} cm^{-1}): 245 (16 000), 311 (15 000), 390 sh (852), 887 (150); MS (+FAB): 607(M^+−Cl) and 572 (M^+−2Cl).

2.3.2. [Cu(*L3*)Cl_2]

Recrystallization from CH_2Cl_2/EtOH/Et_2O gave 0.152 g (83%) of a green solid: IR (KBr, cm^{-1}): 3268 s; *Anal.* Calc. for $CuN_2Cl_2{\cdot}C_{20}H_{28}O_2{\cdot}(H_2O)$: C, 49.94; H, 6.24; N, 5.83. Found: C, 49.98; H, 6.27; N, 5.79%. UV–Vis-NIR spectrum (MeOH), λ_{max} (nm) (ε/M^{-1} cm^{-1}): 304 (11 400), 246 (10 700), 257 (9300), 871 (70); MS (API): 390 (M^+−HCl−Cl).

2.3.3. [Cu(*L4*)Cl_2]

Recrystallization from CH_2Cl_2/EtOH/Et_2O gave 0.109 g (67%) of a yellow solid: *Anal.* Calc. for $CuN_2Cl_2C_{16}H_{20}O_2$: C, 47.23; H, 4.92; N, 6.89. Found: 47.57; H, 4.83; N, 7.01%. UV–Vis-NIR spectrum (CH_2Cl_2), λ_{max} (nm) (ε/M^{-1} cm^{-1}): 315 (15 400), 301 (14 500), 246 (12 600), 366 sh (770), 996 (110); MS (+FAB): 370 (M^+−Cl) and 335 (M^+−2Cl).

2.3.4. [Cu(*L5*)Cl_2]

Recrystallization from CH_2Cl_2/EtOH/Et_2O gave 0.132 g (59%) of a yellow solid: *Anal.* Calc. for $CuN_2Cl_2C_{28}H_{28}O_2$: C, 60.16; H, 5.01; N, 5.01. Found: 61.13; H, 4.91; N, 5.11%. UV–Vis-NIR spectrum (CH_2Cl_2), λ_{max} (nm) (ε/M^{-1} cm^{-1}): 307 (16 000), 317 (14 900), 246 sh (11 000), 377 sh (738), 980 (130); MS (+FAB): 522 (M^+−Cl) and 587 (M^+−2Cl).

2.3.5. [Cu(*L6*)Cl_2]

Recrystallization from MeOH/Et_2O gave 0.064 g (42%) of a green solid: IR (KBr, cm^{-1}): 3534 versus; *Anal.* Calc. for $CuN_2Cl_2C_{14}H_{16}O_2$: C, 44.39; H, 4.23; N, 7.40. Found: 44.44; H, 4.15; N, 7.49%. UV–Vis-NIR spectrum (MeOH), λ_{max} (nm) (ε/M^{-1} cm^{-1}): 308 (10 300), 258 (12 000), 318 (7900), 438 (100), 860 (70); MS (+FAB): 342 (M^+−Cl).

2.4. X-ray crystallography analysis for [Cu(*L5*)Cl_2], [Cu(*L6*)Cl_2] and [Cu(*L1*)Cl]

For [Cu(**L5**)Cl_2] and [Cu(**L1**)Cl], diffraction data were obtained on a Rigaku AFC7R diffractometer at 296 and 301 K, respectively. Absorption corrections based on the PSI scans technique were applied on both of these complexes. The structures were solved by using direct methods (SHELXS97) and refined on F^2 against all reflections. The absolute configurations of [Cu(**L1**)Cl] at C11 and C17 were found to be *R*, as confirmed by the Flack parameter of 0.000(14). For [Cu(**L6**)Cl_2], diffraction data were obtained on a Burker SMART 1000 CCD diffractometer at 298 K. The multi-scan method was applied for absorption correction. The structure was