Letter

A stable chiral diolefin complex of Cu^I with predetermined configuration at the metal centre

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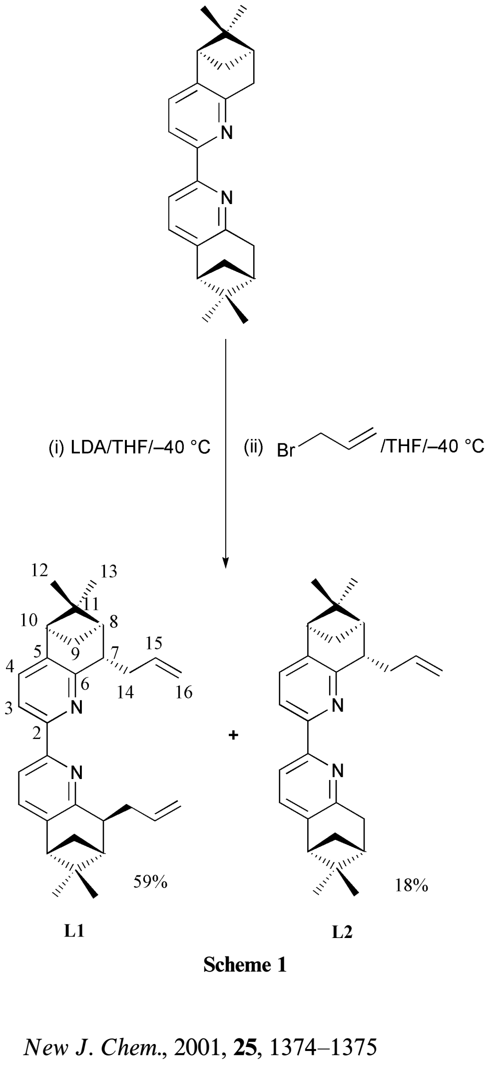
A derivative of (*S*,*S*)-bis(pinene)bipyridine, which contains two terminal olefin groups, forms a mononuclear complex with Cu^I; X-ray crystallography shows the predetermination of configuration around the metal centre.

Ring closing metathesis (RCM) has been successfully applied in order to obtain large macrocycles appearing in catenanes and molecular knots by the group of Sauvage.[1] We prepared diolefin derivatives of chiral bipyridine ligands with the aim of fabricating macrocycles with predetermined configurations.† Ligand **L1** is easily accessible from bis(5,6-pinene)bipyridine[2] through stereoselective reaction[3] with 3-bromopropene after deprotonation of the CH_2 group in the pinene moiety (Scheme 1). When it was reacted with Cu^I in acetonitrile–CH_2Cl_2 solution, complex formation took place spontaneously, to yield a solid *air-stable* product, which could be recrystallised from ethanol as the PF_6^- salt. The cationic complex represents, to the best of our knowledge, the first *chiral diolefin* species reported for Cu^I. One report on a chiral Cu^I mono-olefin complex has recently been published.[4]



Scheme 1

X-Ray analysis shows the cation $Cu(\mathbf{L1})^+$ in which both olefin groups are coordinated to the metal centre (Fig. 1). The overall symmetry is approximately C_2. The first coordination sphere is thus formed by the two bipyridine N donor atoms and the two terminal olefin groups. The chirality at the metal centre can be assigned in the Δ,Λ scheme by considering the lines defined by the two N atoms of the bipyridine moiety, and either of those formed by the two C=C groups (C14/15, C34/35), respectively. In this way, the absolute configuration is classified as Λ. An alternative description of the chirality is the assignment of a helix of configuration *M*, if the complex is viewed along the approximate C_2 axis. While the Cu–N bond lengths correspond to normal values,[5,6] the Cu–C distances are rather long, as compared with most of the Cu^I–olefin complexes reported in the literature.[5,6] Only a few cases of diolefin adducts of Cu^I have been described hitherto.[7,8] The most closely related species is Cu(COD)(2,2′-bipyridine)$^+$, where the Cu–C bond lengths are comparable to the present case.[8] The high overall stability of $Cu(\mathbf{L1})^+$ is undoubtedly due to the predisposed geometry of the ligand, which accomodates the Cu^+ in a pocket formed by the two N donor atoms of the bipyridine moiety and the two olefinic groups.

π-Backdonation from Cu^I to the olefin ligands seems to be rather weak. The C=C vibration frequency is only slightly influenced by complex formation $\{\nu(\mathbf{L1}) = 1640\ cm^{-1}; \nu[Cu(\mathbf{L1})^+] = 1637\ cm^{-1}\}$. The UV spectrum of the complex features a band at 332 nm that is not present in the ligand. It is attributed to a MLCT (metal-to-ligand charged transfer) transition to the bpy moiety. Interestingly, $Cu(\mathbf{L1})^+$ has been obtained quantitatively, even in the presence of an excess of

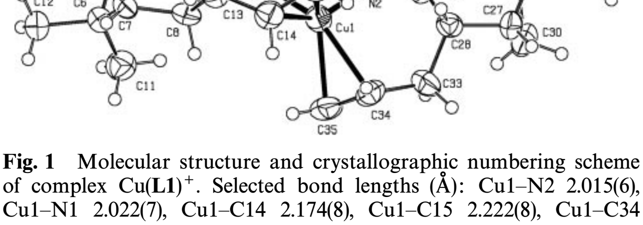


Fig. 1 Molecular structure and crystallographic numbering scheme of complex $Cu(\mathbf{L1})^+$. Selected bond lengths (Å): Cu1–N2 2.015(6), Cu1–N1 2.022(7), Cu1–C14 2.174(8), Cu1–C15 2.222(8), Cu1–C34 2.259(8), Cu1–C35 2.262(8), C14–C15 1.359(12), C34–C35 1.349(11).

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ligand **L1**. ES-MS measurement, as well as the NMR data (^{1}H, ^{13}C) indicate that the same complex Cu(**L1**)$^+$ is also by far the dominant species in solution. Cu(**L1**)$_2{}^+$ appears in very minor concentrations (≈0.02%) in Cu$^+$: **L1** = 1 : 1 mixtures. Finally, we tested the possibility of obtaining a macrocycle from Cu(**L1**)$^+$ by attempting a ring closure metathesis reaction.[1] The recovery of the starting complex was a clear indication that in our case, RCM is prevented by the coordination of the olefins to the atom of Cu$^{\mathrm{I}}$.

In conclusion, we present an example of a ligand carrying two chirally anchored olefin groups that are put in a neighbouring skew line orientation through complex formation with Cu$^{\mathrm{I}}$.

Experimental

Synthesis

Bipyridines L1 and L2. To a Schlenk flask containing 2.17 mmol of freshly prepared LDA in 5 ml of dry THF at −40 °C, were added 250 mg (0.72 mmol) of bis(5,6-pinene)bipyridine in 5 ml of dry THF. After stirring the deep blue solution at −40 °C for 2 h, 500 mg (4.35 mmol) of 3-bromopropene in 5 ml of dry THF were added dropwise and the mixture was allowed to warm up to room temperature overnight. The reaction was then quenched with water (5 ml), THF was removed and the mixture was extracted with CH_2Cl_2 (50 ml). After drying of the organic phase over $MgSO_4$ and removal of the solvent, the residue was purified by column chromatography (SiO_2, hexane–ethyl acetate 95 : 5). Yield: 59% (179 mg) of **1** and 18% (49 mg) of **2**.

L1. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.03 (d, J 7.6 Hz, 2H, H$_3$), 7.30 (d, J 7.6 Hz, 2H, H$_4$), 6.01–5.92 (m, 2H, H$_{15}$), 5.09–5.03 (m, 4H, H$_{16\,cis}$, H$_{16\,trans}$), 3.23 (d, J 13.9 Hz, 2H, H$_{14a}$), 3.15 (d, J 10.5 Hz, 2H, H$_7$), 2.81–2.75 (m, 2H, H$_{10}$), 2.56–2.50 (m, 2H, H$_{9b}$), 2.33–2.27 (m, 2H, H$_8$), 2.23 (d, J 13.9 Hz, 2H, H$_{14b}$), 1.40 (s, 6H, H$_{13}$), 1.32 (d, J 9.8 Hz, 2H, H$_{9a}$), 0.61 (s, 6H, H$_{12}$); ^{13}C-NMR (400 MHz, $CDCl_3$) δ 158.59–154.16 (C$_2$, C$_6$), 141.64 (C$_5$), 138.0 (C$_{15}$), 133.68 (C$_4$), 117.82 (C$_3$), 115.84 (C$_{16}$), 46.80 (C$_{10}$), 44.04 (C$_7$), 43.02 (C$_8$), 41.18 (C$_{11}$), 37.11 (C$_{14}$), 28.39 (C$_9$), 26.37 (C$_{13}$), 20.88 (C$_{12}$); FAB MS (m/z) 425 (M + 1)$^+$ 100%; Anal. calc. for $C_{30}H_{36}N_2$: C 84.86, H 8.55, N 6.60; found: C 84.38, H 8.91, N 6.27%.

L2: ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.04 (d, J 7.6 Hz, 1H, H$_3$), 7.99 (d, J 8.0 Hz, 1H, H$_{3'}$), 7.28 (d, J 7.6 Hz, 1H, H$_4$), 7.27 (d, J 7.6 Hz, 1H, H$_{4'}$), 6.01–5.92 (m, 1H, H$_{15}$), 5.09–5.03 (m, 2H, H$_{16\,cis}$, H$_{16\,trans}$), 3.23 (d, J 14.1 Hz, 1H, H$_{14a}$), 3.16 (m, 3H, H$_{7'}$, H$_7$), 2.79–2.75 (m, 2H, H$_{10}$, H$_{10'}$), 2.70–2.65 (m, 1H, H$_{9'b}$), 2.55–2.50 (m, 1H, H$_{9b}$), 2.35–2.39 (m, 1H, H$_{8'}$), 2.33–2.27 (m, 1H, H$_8$), 2.23 (d, J 13.9, 1H, H$_{14b}$), 1.40 (s, 3H, H$_{13}$), 1.39 (s, 3H, H$_{13'}$), 1.33–1.24 (m, 2H, H$_{9a}$, H$_{9'a}$), 0.63 (s, 3H, H$_{12'}$), 0.62 (s, 3H, H$_{12}$); ^{13}C-NMR (400 MHz, $CDCl_3$) δ 157.57, 154.37 (C$_2$, C$_6$), 156.27, 154.06 (C$_{2'}$, C$_{6'}$), 141.56, 141.51 (C$_5$, C$_{5'}$), 117.73, 117.67 (C$_3$, C$_{3'}$), 115.84 (C$_{16}$), 46.81 (C$_{10}$), 46.46 (C$_{10'}$), 44.06 (C$_7$), 43.04 (C$_8$), 41.16 (C$_{11}$), 40.31 (C$_{8'}$), 39.61 (C$_{11'}$), 37.11 (C$_{14}$), 36.74 (C$_{7'}$), 31.98 (C$_{9'}$), 28.41 (C$_9$), 26.39 (C$_{13}$), 26.10 (C$_{13'}$), 21.26 (C$_{12'}$), 20.91 (C$_{12}$); FAB MS (m/z) 385 (M + 1)$^+$ 100%; Anal. calc. for $C_{27}H_{32}N_2 \cdot 0.25EtOAc$: C 82.76, H 8.37, N 6.89; found: C 83.12, H 8.85, N 6.06%.

Complex Cu(L1)$^+$. To a degassed solution of **L1** (179 mg, 0.42 mmol) in CH_2Cl_2 (5 ml) were added $Cu(MeCN)_4PF_6$ in MeCN (5 ml). The orange–yellow solution was stirred overnight and the solvent was evaporated. Complex Cu(**L1**)$^+$ was redissolved in a minimum of CH_2Cl_2 and precipitated as a $PF_6{}^-$ salt by addition of Et_2O. Yield 88%. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.04 (d, J 7.6 Hz, 2H, H$_3$), 7.66 (d, J 7.6 Hz, 2H, H$_4$), 6.09–5.99 (m, 2H, H$_{15}$), 5.16 (d, J 9.1 Hz, H$_{16}$), 4.40 (d, J 16.2 Hz, 2H, H$_7$), 3.18 (d, J 10.6 Hz, 2H, H$_{14a}$), 2.97–2.94 (m, 2H, H$_{10}$), 2.71–2.66 (m, 2H, H$_{9b}$), 2.52 (d, J 10.1 Hz, 2H, H$_{14b}$), 2.41–2.38 (m, 2H, H$_8$), 1.47 (s, 6H, H$_{13}$), 1.34 (d, J 11.1 Hz, 2H, H$_{9a}$), 0.74 (s, 6H, H$_{12}$); ^{13}C-NMR (400 MHz, $CDCl_3$) δ 159.95, 149,22 (C$_2$, C$_6$), 144.76 (C$_5$), 136.90 (C$_4$), 122.11 (C$_{15}$), 119.53 (C$_3$), 96.40 (C$_{16}$), 46.97 (C$_{10}$), 46.88 (C$_7$), 45.25 (C$_{11}$), 42.94 (C$_8$), 38.82 (C$_{14}$), 29.10 (C$_9$), 26.26 (C$_{13}$), 21.10 (C$_{12}$); ES MS (m/z) 487 [Cu(**L1**)$^+$ 100%], 911 [Cu(**L1**)$_2$]$^+$, 0.025%); Anal. calc. for $C_{30}H_{36}N_2 \cdot CuPF_6 \cdot Et_2O$: C 57.74, H 6.56, N 3.96; found: C 58.29, H 6.11, N 3.78%; UV-Vis [MeCN, λ/nm (ε/l mol^{-1} cm^{-1})] 263 (12 237), 270 (11 918), 314 (11 120), 331 (9097); CD [MeCN, λ/nm ($\Delta\varepsilon$)] 220 (4.4), 242 (0.7), 266 (−5.1), 300 (−3.9), 334 (1.5), 370 (0.7).

X-Ray crystallography

$C_{36}H_{54}CuF_6N_2O_3P$, $M = 771.32$, orthorombic, $a = 12.8728(11)$, $b = 15.8948(12)$, $c = 18.2031(14)$ Å, $U = 3724.5(5)$ Å^3, $T = 153$ K, space group $P2_12_12_1$, $Z = 4$, μ(Mo-Kα) = 0.696 mm^{-1}, 29366 reflections measured, 7281 unique ($R_{\mathrm{int}} = 0.1784$), which were used in all calculations. The final wR (F^2) was 0.0567 [obs. data, $I > 2\sigma(I)$]. The structure was solved by direct methods using the programme SHELXS-97[9] The refinement and all further calculations were carried out using SHELXL-97.[10] The H atoms were included in calculated positions and treated as riding atoms using SHELXL default parameters. The non-H atoms were refined anisotropically, using weighted full-matrix least-squares on F^2. The crystal did not diffract significantly beyond 40° in 2θ and the R_{int} value is rather high, despite the application of an empirical absorption correction (reduced from 0.21 to 0.17); transmission factors $T_{\mathrm{min}}/T_{\mathrm{max}} = 0.412/0.801$. Complex Cu(**L1**)$^+$ crystallises with three molecules of ethanol per molecule of complex. The atomic coordinates correspond to the abolute structure of the molecule in the crystal.

CCDC reference number 170401. See http://www/rsc.org/suppdata/nj/b1/b105870n/ for crystallographic data in CIF or other electronic format.

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