

A singly stranded, helical di-ruthenium(II) complex of a novel 6,6-ethynyl-linked bis(terpyridine) ligand. Distortion of the ethyne linkage and inversion of helicity

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Received 2nd March 1999, Accepted 12th March 1999

The new, ethynyl-bridged ditopic ligand, 1,2-bis[4'-(4-methylphenyl)-2,2':6'2"-terpyridin-6-yl]ethyne (**L**) was prepared and used in the formation of the helical dinuclear complex $[L\{Ru(ttpy)\}_2][PF_6]_4$ ($ttpy = 4'-(4\text{-methylphenyl})\text{-}2,2':6',2''\text{-terpyridine}$), whose crystal structure exhibits pronounced bending of the central ethynyl bridge and whose solution NMR spectra indicate a rapid inversion of helicity at 335 K.

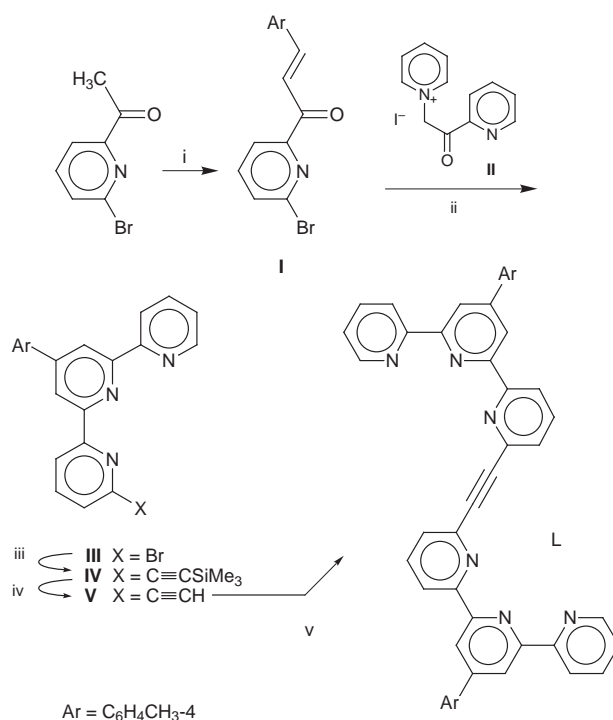
Multinuclear complexes of Ru(II) have been built with a number of bridging ligands¹ but helical complexes based on terpyridine (tpy) units are few.²⁻⁵ Helicating ditopic ligands can be built by coupling monotopic, unsymmetrically substituted terpyridines, which are available by Kröhnke synthesis.⁶ Linkages through the 6 position can lead to strong inter-ligand congestion but alkynyl substituents are relatively sterically undemanding. We report herein the successful preparation and structural characterization of a helical, singly stranded dinuclear Ru(II) complex of the first ditopic ligand assembled from two tpy units joined at the 6 position through an ethynyl bridge. This is the first structurally characterized complex of this type. The electronic character of the bridge was also of interest as ethyne substituents are electron-withdrawing groups and, like these,⁷ can dramatically enhance triplet lifetimes and luminescence yields over those of $Ru(tpy)_2$.^{2+, 8}

The starting material **I** was obtained in near quantitative yield from the condensation of 2-acetyl-6-bromopyridine⁹ with *p*-tolualdehyde (Scheme 1).[†] The reaction of **I** with pyridinium salt **II**¹⁰ produced the 6-bromoterpyridine **III** in $\approx 90\%$ yield. This was coupled with trimethylsilylacetylene to afford the protected 6-ethynylterpyridine **IV**, which was then deprotected to give the terminal alkyne **V** in $\approx 75\%$ overall yield. The ditopic ligand **L** was assembled by Sonogashira coupling¹¹ of **III** and **V** in 98% yield ($\approx 66\%$ overall from 2-acetyl-6-bromopyridine).

The direct reaction of **L** with $Ru(tpy)Cl_3$ ¹² failed to proceed. However, the dinuclear complex $[L\{Ru(ttpy)\}_2][PF_6]_4$ **1** was obtained after activation of $Ru(tpy)Cl_3$ ($AgBF_4$, acetone, reflux, 0.5 h) and heating with 0.5 equivalent of **L** (dmf, reflux, 8 h), followed by precipitation with aqueous NH_4PF_6 , chromatography (silica, 14:2:1 CH_3CN -saturated KNO_3-H_2O), reprecipitation (NH_4PF_6) and recrystallization, in 65% isolated yield.[†]

There are only two possible conformations for **1**: the flat, fully conjugated (and achiral) form, or the non-conjugated, helical (and chiral) form in which both metals have the same absolute configurations. The ¹H NMR spectrum of **1** showed considerable complexity but, with the help of COSY spectra, revealed one set of signals for two *symmetrical* monotopic ttpy units. The outer pyridines of these units gave broad signals which sharpened upon heating to 335 K. This symmetrization implies an interconversion in solution between the enantiomers of the helical form. In contrast, NMR suggested that the only other comparable, singly-stranded Ru(II) helicate, bearing a 6,6-linked *m*-phenylene bridge, was rigid at room temperature.²

The crystal and molecular structure of **1** at 150 K is shown in Fig. 1.[‡] This clearly revealed the cation to be helical, with a



Scheme 1 *i*, $CH_3C_6H_4CHO-4$, KOH in 80% MeOH; *ii*, excess NH_4OAc in AcOH, reflux, 4 h; *iii*, 6 mol% $Pd(PPh_3)_4$, 12 mol% CuI, iPr_2NH , room temp., 8 h; *iv*, KF, MeOH, room temp., 1 h; *v*, 10 mol% $Pd(PPh_3)_4$, iPr_2NH , room temp., 8 h.

123.8° dihedral angle about the triple bond. There appears to be considerable distortion at the ethynyl linkage, which is bent out of linearity, and in the linked ttpy units, which are bowed such that the least-squares planes of the inner pyridines (ring 1) are 16° out of planarity with the outer pyridines (ring 3) and form the longest bonds (2.107 Å) to the Ru. The other Ru–N distances are normal and the two N_3 binding planes are nearly orthogonal to one another (88.3°). Another notable feature is the twisting by 33.4° of the tolyl ring on the ttpy ligand (ring 8) to become almost parallel (4.4°) with the nearest pyridine (ring 1A) of the ethynyl-linked ttpy unit at the neighbouring metal, thus enabling π – π interactions at a 3.6–3.8 Å inter-planar distance, whereas the tolyl groups on **L** (ring 4) are more coplanar (inter-planar angle 7.8°) with the attached pyridines (ring 2).

The cyclic voltammogram of **1** showed one reversible $Ru^{3+/2+}$ couple (1.42 V vs. SCE) and several reduction waves. The two least negative reduction waves (-1.07 and -1.16 V) were both more positive than the first reductions of $Ru(tpy)_2^{2+}$ (-1.24 V).¹³ Reductions of both **L** and ttpy ligands in **1** are expected to be easier than in $Ru(tpy)_2^{2+}$, on the one hand because of the electron-withdrawing effect of the ethyne group combined with the presence of a second metal and, on the other hand, because the loss of conjugation between the tolyl and terpyridine portions of the ttpy ligand in **1** (see above) amounts

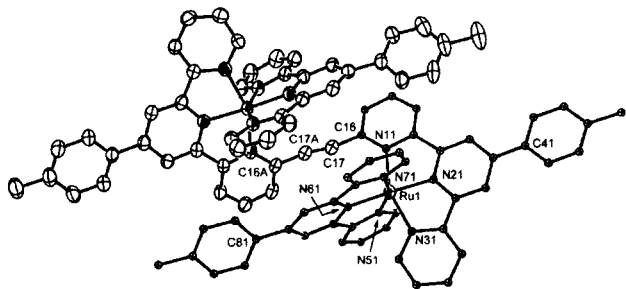


Fig. 1 ORTEP¹⁶ diagram of the complex cation of **1**·10.5CH₃COCH₃ with H atoms omitted for clarity. The unlabelled portion is the symmetry equivalent of the labelled portion and is drawn with 50% probability thermal ellipsoids. The first digit of a ring atom label is the ring number. Selected bond lengths (Å) and angles (°): Ru1–N11 2.107(3), Ru1–N21, 1.986(3), Ru1–N31 2.060(3), Ru1–N51 2.069(3), Ru1–N61 1.976(3), Ru1–N71 2.066(3), C17–C17A 1.215(8), C16–C17–C17A 167.8(5), C15–C16–C17 118.7(3), N11–C16–C17 119.5(3), C16–C17–C17A–C16A 123.8.

to a loss of an electron-donating group, relative to the conjugated ttpy in Ru(tppy)₂²⁺. In any case, the potentials here indicate significant stabilizations of both metal-centred HOMO and ligand-centred LUMO to equal extents (170 mV), when compared with Ru(tppy)₂²⁺,¹³ unlike the effects of other electron-withdrawing groups on terpyridine complexes.⁷ There resulted the same HOMO–LUMO gap ($E_i^{3+/2+} - E_i^{2+/+}$) and similar MLCT band λ_{\max} values [494 nm, ϵ 35 800 M⁻¹ cm⁻¹, with a shoulder at 454 nm, vs. 490 nm, ϵ 15 500 M⁻¹ cm⁻¹ for Ru(tppy)₂²⁺]. This contrasts with the 4',4'-ethyne-bridged analogue,¹⁴ where the bridge and the second metal centre act as more typical electron-withdrawing groups, *i.e.* affecting mostly the LUMO and red-shifting the MLCT λ_{\max} . Our case is reminiscent of the 6-vinylterpyridine complex¹⁵ in which similar effects were observed and attributed to a weaker binding typical of 6-substituted terpyridines. The long Ru–N bond measured here would support such an explanation in the present case. On the other hand, data from the singly stranded, 6,6-linked *m*-phenylene-bridged² and quinquepyridine³ helicates indicate that these linkages behaved as e⁻-donating groups. A doubly stranded, 5,5-ethanyl linked helicate showed unsurprisingly weak effects.⁴ Whether linked at positions 6, 5 or 4', all cases except the unsymmetrical quinquepyridine helicate³ showed single Ru^{3+/2+} couples, implying weak electronic communication between the metals.

Notes and references

† All new compounds were fully characterized by ¹H NMR, ¹³C-NMR, and EI- or FAB-mass spectra, and by elemental analysis.

‡ Crystal data: C_{121.5}H₁₂₉F₂₄O_{10.5}P₄Ru₂, $M = 2707.39$, monoclinic, space group *C2/c* (no. 15), $a = 25.6950(7)$, $b = 14.0790(4)$, $c = 35.4180(9)$ Å, $\beta = 100.370(2)^\circ$, $U = 12603.5(6)$ Å³, $Z = 4$, $D_c = 1.427$ Mg m⁻³, $\mu(\text{Mo-K}\alpha) = 0.388$ mm⁻¹, $F(000) = 5560$, $T = 150.0(1)$ K. Of 41,430 reflections collected, the final R indices were, for all data, $R = 0.0834$ and $R_w = 0.1850$ and for the 9463 reflections where $I > 2\sigma(I)$, $R = 0.0603$ and $R_w = 0.1652$. CCDC reference number 186/1381. See <http://www.rsc.org/suppdata/dt/1999/1373> for crystallographic files in .cif format.

§ In CH₃CN with 0.1 M ⁿBu₄NPF₆ at 298 K; values were ± 0.02 V and peak-to-peak separations were all 50–75 mV.

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Communication 9/01696A