

Pd-catalyzed diarylation of aniline—a way to a non-linear bis(terpyridyl) ligand providing increased electronic communication†

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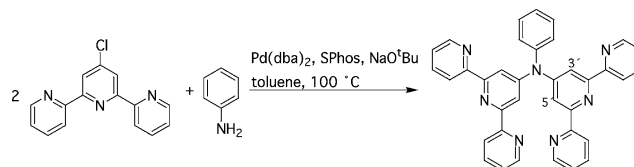
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An amine-linked bis(terpyridyl) ligand, prepared via Pd-catalyzed diarylation of aniline, mediates unusually strong metal–metal interaction in its Ru₂ polypyridyl complex.

Bridging bis-2,2':6',2''-terpyridyl (tpy) ligands continue to be of wide interest in many research fields. In particular the ruthenium(II) complexes of “back-to-back” ligands have been thoroughly investigated as light- and redox-active terminals in molecular electronic devices and energy conversion schemes.¹ In view of such applications, the degree of electronic communication² between two metal centers mediated by the ligands is of crucial importance. Non-linear bis-tpy ligands on the other hand have often been used in the synthesis of metallodendrimers³ and self-assembly of metallomacrocycles.⁴ However, even the simplest non-linear bis-tpy ligand, bis(4'-(2,2':6',2''-terpyridyl))ether, where an oxygen atom bridges two tpy units provides only poor electronic communication between two Ru polypyridyl units.⁵ Here we present an alternative non-linear amine-linked bis-tpy ligand prepared via Pd-catalyzed diarylation of aniline, and show that this bridging motif provides strong metal–metal interaction in a dinuclear Ru polypyridyl complex.

The synthesis of bis-tpy derivatives⁶ usually relies on condensation methodologies,⁷ C–C coupling strategies of preformed terpyridyl moieties,⁸ or 4'-position substitution reactions on commercially available 4'-chloro-2,2':6',2''-terpyridine.^{9,10} We recently reported a strategy for amine substitutions at the 4'-position involving Pd-catalyzed C–N bond formation that avoid the harsh conditions typically needed with amine nucleophiles.¹¹ The use of aniline derivatives as nucleophilic components in palladium catalyzed amination of nitrogen heterocycles has been successfully accomplished,¹² and we anticipated that this strategy could be successful also in the preparation of an amine-linked bis-tpy ligand by diarylation of aniline. Using Pd(dba)₂/SPhos (dba = dibenzylideneacetone, SPhos = 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl), the bis-tpy ligand **L** was prepared in one step from commercially available starting materials (Scheme 1).[‡] The ligand was typically obtained in 60–65% yield using 1% Pd at 100 °C for 18 h in toluene, and the remaining 4'-chloro-2,2':6',2''-terpyridine and the intermediate phenyl(4'-(2,2':6',2''-terpyridyl))amine were removed by washing the obtained solid with CH₃CN.¹³



Scheme 1

In the ¹H NMR of **L** (CDCl₃), a characteristic singlet that integrates to four protons was observed at 8.20 ppm (3',5'-tpyH) and mass peaks (ESI-MS) were detected at *m/z* 556.7 (M + H)⁺ and *m/z* 1133.2 (2M + Na)⁺ which confirmed the structure of **L**.

Single crystals for X-ray diffraction analysis were obtained by recrystallization from CH₃CN–toluene.[‡] The structure (Fig. 1) shows a 123.60° angle between the two terpyridyl units, and exhibits a dihedral angle of 40.5° between the terpyridyl least square planes. The pyridine rings of the terpyridyl moieties adopt the all-*trans* conformation typical for such compounds with NCCN torsional angles in the range 159.57(16)–177.21(16)°.

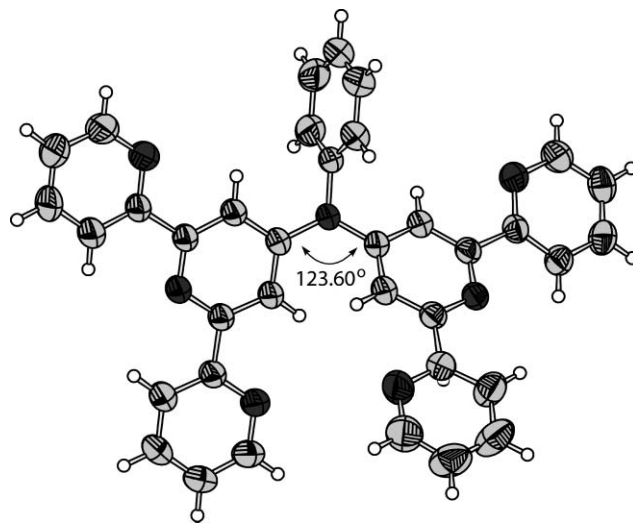


Fig. 1 ORTEP view of **L** at 50% probability level.

To illustrate the potential of **L** as a bridging ligand in dinuclear assemblies, the corresponding ruthenium(II) polypyridyl complex was prepared. Heating the ligand with two equivalents of Ru(tpy)Cl₃ (tpy is 4'-tolyl-2,2':6',2''-terpyridine) and *N*-ethylmorpholine in ethylene glycol at 196 °C using microwave irradiation gave 'Ru(**L**)Ru' (Fig. 2) in 67% isolated yield after column chromatography (silica, KNO₃ (sat'd) in CH₃CN–H₂O (8 : 1)) and recrystallisation.[§] The ¹H NMR spectrum (CD₃CN) showed two singlets at 8.68 and 9.01 ppm each integrating to

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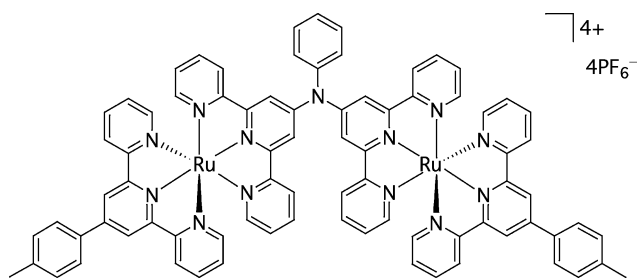


Fig. 2 Structure of 'Ru(L)Ru'.

four protons ($3',5'$ -tpyH protons of **L** and the two ttpy ligands) in agreement with the proposed structure. All molecular ions from sequential loss of the four PF_6^- counterions (at m/z 1840.3, 847.5, 516.7, and 351.3) were detected by mass spectrometry (ESI-MS).

The electrochemical properties of 'Ru(L)Ru' were studied by differential pulse voltammetry and cyclic voltammetry in CH_3CN solution. In the cyclic voltammogram (Fig. 3), two reversible oxidation processes are observed at $E_{1/2}(1) = 0.71$ V (vs. Fc) and at $E_{1/2}(2) = 0.90$ V that arise from the $\text{Ru}^{\text{II/III}}$ couples of the two metal centers. The magnitude of their separation ($\Delta E_{1/2} = 190$ mV) indicates considerable stability of the mixed-valence state with a comproportionation constant of $K_c = \exp(\Delta E_{1/2} F/RT) = 1.63 \times 10^3$ (at 298 K) and a free energy of stabilization due to metal–metal interaction of $\Delta G = \frac{1}{2} RT \ln(K_c/4) = 7.45$ kJ mol $^{-1}$.¹⁴ Interestingly, no separation between the metal-centered redox processes was reported for the directly linked "back-to-back" dinuclear Ru complex^{1c} or for the O-linked bis(terpyridyl)ether analogue.⁵ In contrast, strong metal–metal interaction was reported for triruthenium complexes with N-linked tri(4-ethynylphenyl)amine bridges.¹⁵ Also in a series of diruthenium complexes with bis(4-pyridyl)-type bridging ligands the maximum metal–metal interaction was observed with the bis(4-pyridyl)amine ligand and it has been suggested that the electrons in the lone pair of the amine N are responsible for the efficient electronic coupling of the aromatic ring systems.¹⁶

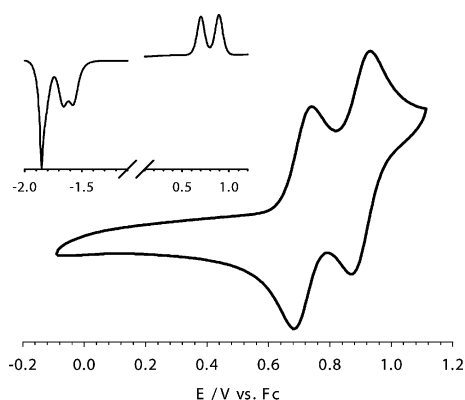


Fig. 3 Cyclic voltammogram of 'Ru(L)Ru' at 0.1 V s $^{-1}$ (CH_3CN , 1 mM, 0.1 M TBAPF_6). Inset: differential pulse voltammetry.

On the reductive side differential pulse voltammograms (inset, Fig. 3) resolve two close lying peaks at -1.58 V and -1.66 V. These arise presumably from the one electron reductions of the two peripheral ttpy ligands and the small separation would be consistent with a minor interaction between the ligand radicals as compared to the metal centers.

The electronic absorption spectrum of 'Ru(L)Ru' is characterized by an intense metal-to-ligand charge transfer (MLCT) band peaking at 513 nm ($19\,508$ cm $^{-1}$, 58×10^3 M $^{-1}$ cm $^{-1}$) that is partly bleached upon oxidation to the $\text{Ru}^{\text{II}}\text{Ru}^{\text{III}}$ state. In the mixed-valence state the peak of the MLCT band shifts to 493 nm ($20\,292$ cm $^{-1}$, 36.5×10^3 M $^{-1}$ cm $^{-1}$) and additional absorption bands in the red and near infrared are observed. The band at 768 nm ($13\,024$ cm $^{-1}$, 5.4×10^3 M $^{-1}$ cm $^{-1}$) can be attributed to a ligand-to-metal charge transfer (LMCT) transition from the amine substituted bridging ligand to the Ru^{III} center while the 1517 nm band ($6\,592$ cm $^{-1}$, 5.8×10^3 M $^{-1}$ cm $^{-1}$) is assigned to an intervalence charge transfer (IVCT) transition. These assignments are corroborated by the spectrum of the isoivalent Ru_2^{III} complex that lacks the IVCT band and features instead a more intense LMCT band at 858 nm ($11\,655$ cm $^{-1}$, 11.5×10^3 M $^{-1}$ cm $^{-1}$).

The IVCT band has a Gaussian profile (inset Fig. 4) and, as for most valence localized systems (class II), is somewhat broader ($\Delta\tilde{\nu}_{1/2} = 4.6 \times 10^3$ cm $^{-1}$) than estimated with eqn (1)

$$(\Delta\tilde{\nu}_{1/2})^2 = 16k_{\text{B}}T\lambda\ln 2 = 2.31 \times 10^3(E_{\text{IVCT}} - \Delta G^\circ) \quad (\text{at } 298 \text{ K in cm}^{-1}) \quad (1)$$

within the limits of Hush's classical model (3.9×10^3 cm $^{-1}$).¹⁷ Here E_{IVCT} is the energy of the IVCT transition ($\tilde{\nu}_{\text{max}}$) that equals the reorganization energy λ for the intramolecular electron transfer in a symmetric mixed-valence system ($\Delta G^\circ = 0$).

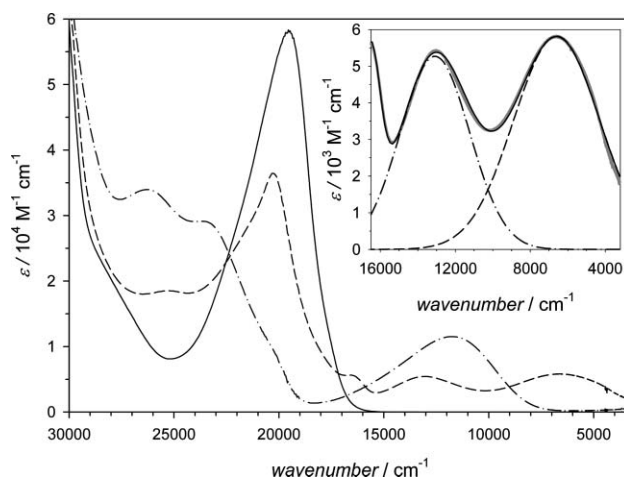


Fig. 4 Absorption spectrum of 'Ru(L)Ru' (Ru_2^{II} , —) and spectra after oxidation at 0.81 V ($\text{Ru}^{\text{II}}\text{Ru}^{\text{III}}$, ---) and 1.12 V (Ru_2^{III} , -·-) (CH_3CN , 0.1 M TBAPF_6). Inset: Near infrared range of the spectrum of the mixed valence complex (—) and its representation (—) by Gaussian bands for the LMCT (---) and IVCT (---) transition.

Within the same theoretical framework the magnitude of electronic coupling H_{ab} between the Ru centers is given by eqn (2)

$$H_{\text{ab}} (\text{cm}^{-1}) = [(4.2 \times 10^{-4})\epsilon\Delta\tilde{\nu}_{1/2}E_{\text{IVCT}}]^{1/2}/d \quad (2)$$

where ϵ is the extinction coefficient at the band maximum and d is the electron transfer distance in Å.

From the structure of the ligand a Ru–Ru distance of 11 Å can be inferred that results in a value of $H_{\text{ab}} = 7.8 \times 10^2$ cm $^{-1}$ for the mixed-valence complex. Comparison to the electrochemical data shows that resonance exchange with $\Delta G_{\text{r}} = H_{\text{ab}}^2/\lambda = 1.1$ kJ mol $^{-1}$ makes a significant, but not dominating, contribution to the metal–metal interaction. Since electrostatic effects cannot

be expected to differ substantially between 'Ru(L)Ru' and *e.g.* its ether analogue these results suggest that L is not only an efficient mediator for resonance exchange but also for inductive effects.

In summary, the non-linear amine-linked bis-tpy ligand described herein can be employed as a bridging ligand in dinuclear or polynuclear complexes. Compared to similar bis-tpy bridging ligands 'Ru(L)Ru' features substantially stronger metal–metal interaction in the mixed-valence state. From the $\sim 120^\circ$ angle observed in the X-ray crystal structure, it is intriguing to consider its potential use in the self-assembly of hexagonal metallomacrocycles with pronounced metal–metal interactions.

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Notes and references

† The reaction was typically performed in a sealed vial on a 0.4 mmol scale (Cl-tpy) in 3 mL argon-degassed toluene. Analytical data for bis(4'-(2,2':6',2''-terpyridyl))phenylamine (L): ^1H NMR (CDCl_3): δ 7.22–7.28 (m, 5H), 7.33 (m, 2H), 7.42 (m, 2H), 7.81 (dt, $J = 7.7, 1.5$ Hz, 4H), 8.20 (s, 4H), 8.55 (m, 4H), 8.59 (d, $J = 8.0$ Hz, 4H). ^{13}C (CDCl_3): δ 114.9, 121.4, 123.8, 126.2, 127.1, 130.3, 136.8, 144.9, 149.1, 155.4, 156.1, 157.1. ESI-MS: $m/z = 556.7$ ($\text{M} + \text{H}^+$), 1133.2 ($2\text{M} + \text{Na}^+$). X-Ray crystallography experimental data for L: $\text{C}_{36}\text{H}_{25}\text{N}_7$, monoclinic, space group $C2/c$ (no. 15), $a = 30.670(3)$ Å, $b = 8.4665(12)$ Å, $c = 22.428(2)$ Å, $\alpha = 90^\circ$, $\beta = 94.063(12)^\circ$, $\gamma = 90^\circ$, $V = 5809.4(11)$ Å³, $D_{\text{calc}} = 1.271$ g cm⁻³, $T = 293(2)$ K, $Z = 8$, $R_{\text{int}} = 0.0623$, $R = 0.0430$ for 2998 observed unique reflections. § Analytical data for Ru(L)Ru: ^1H NMR (CD_3CN): δ 2.54 (s, 6H), 7.16 (m, 4H), 7.32 (m, 4H), 7.44 (m, 4H), 7.59 (d, $J = 8.0$ Hz, 4H), 7.63 (m, 1H), 7.69 (m, 4H), 7.79 (t, $J = 7.7$ Hz, 2H), 7.85 (dt, $J = 7.7, 1.5$ Hz, 4H), 7.91 (m, 2H), 7.99 (dt, $J = 7.7, 1.5$ Hz, 4H), 8.12 (d, $J = 8.1$ Hz, 4H), 8.39 (d, $J = 7.7$ Hz, 4H), 8.67 (d, $J = 7.7$ Hz, 4H), 8.68 (s, 4H), 9.01 (s, 4H). ESI-MS $m/z = 1840.3$ ($\text{M} - \text{PF}_6$)⁺, 847.5 ($\text{M} - 2\text{PF}_6$)²⁺, 516.7 ($\text{M} - 3\text{PF}_6$)³⁺, 351.3 ($\text{M} - 4\text{PF}_6$)⁴⁺. Anal. Calcd for $\text{C}_{80}\text{H}_{59}\text{N}_{13}\text{Ru}_2\text{P}_4\text{F}_{24}$: C 48.42, H 3.00, N 9.18. Found: C 48.19, H 3.22, N 9.17%.

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