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

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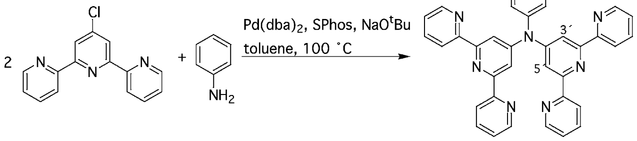
An amine-linked bis(terpyridyl) ligand, prepared *via* Pd-catalyzed diarylation of aniline, mediates unusually strong metal–metal interaction in its Ru_2 polypyridyl complex.

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 communication[2] 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 metallodendrimers[3] 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 derivatives[6] 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 CH_3CN.[13]



Scheme 1

In the ^1H NMR of **L** ($CDCl_3$), a characteristic singlet that integrates to four protons was observed at 8.20 ppm (3′,5′-tpy*H*) 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 CH_3CN–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)°.

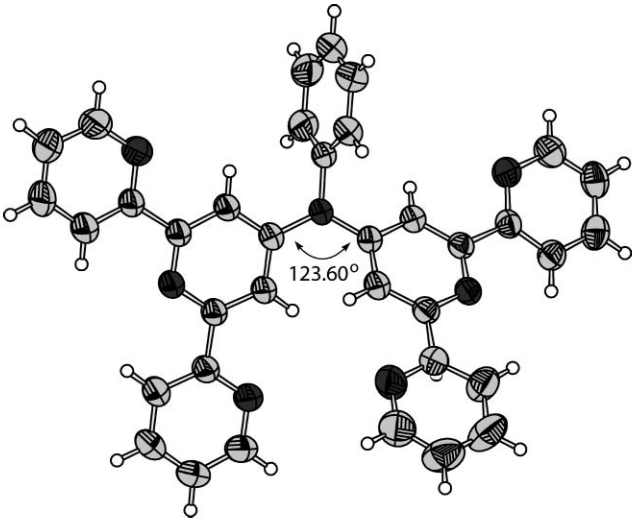


Fig. 1 ORTEP view of **L** at 50% probability level.

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(ttpy)Cl_3 (ttpy 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, KNO_3 (sat'd) in CH_3CN–H_2O (8 : 1)) and recrystallisation.§ The ^1H NMR spectrum (CD_3CN) showed two singlets at 8.68 and 9.01 ppm each integrating to

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† CCDC reference number 677273. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b804461a

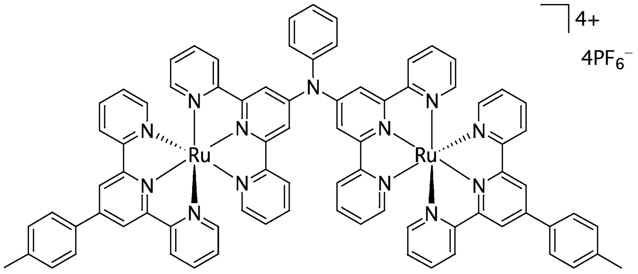

Fig. 2 Structure of 'Ru(**L**)Ru'.

four protons (3′,5′-tpy*H* 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 $E_{\frac{1}{2}}(1) = 0.71$ V (*vs.* Fc) and at $E_{\frac{1}{2}}(2) = 0.90$ V that arise from the $Ru^{III/II}$ couples of the two metal centers. The magnitude of their separation ($\Delta E_{\frac{1}{2}} = 190$ mV) indicates considerable stability of the mixed-valence state with a comproportionation constant of $K_c = \exp(\Delta E_{\frac{1}{2}} F/RT) = 1.63 \times 10^3$ (at 298 K) and a free energy of stabiliztion 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]

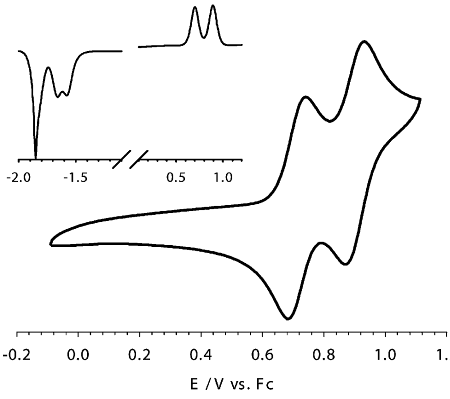

Fig. 3 Cyclic voltammogram of 'Ru(**L**)Ru' at 0.1 V s^{-1} (CH_3CN, 1 mM, 0.1 M $TBAPF_6$). Inset: differential pulse voltammetry.

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 $Ru^{II}Ru^{III}$ 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 (6592 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 isovalent 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).

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)

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

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 ($\tilde{\nu}_{max}$) that equals the reorganization energy λ for the intramolecular electron transfer in a symmetric mixed-valence system ($\Delta G^\circ = 0$).

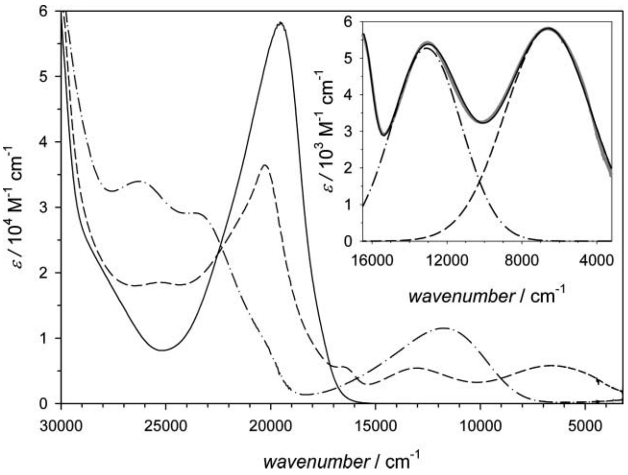

Fig. 4 Absorption spectrum of 'Ru(**L**)Ru' (Ru_2^{II}, —) and spectra after oxidation at 0.81 V ($Ru^{II}Ru^{III}$, ---) and 1.12 V (Ru_2^{III}, -·-) (CH_3CN, 0.1 M $TBAPF_6$). Inset: Near infrared range of the spectrum of the mixed valence complex (━) and its representation (—) by Gaussian bands for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

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

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 $H_{ab} = 7.8 \times 10^2$ cm^{-1} for the mixed-valence complex. Comparison to the electrochemical data shows that resonance exchange with $\Delta G_r = H_{ab}{}^2/\lambda = 1.1$ 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 ~120° 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**): ^{1}H 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 ($M + H^+$), 1133.2 ($2M + Na^+$). X-Ray crystallography experimental data for **L**: $C_{36}H_{25}N_7$, monoclinic, space group $C2/c$ (no. 15), $a = 30.670(3)$ Å, $b = 8.4665(12)$ Å, $c = 22.428(2)$ Å, $\alpha = 90°$, $\beta = 94.063(12)°$, $\gamma = 90°$, $V = 5809.4(11)$ Å^3, $D_{calc} = 1.271$ g cm^{-3}, $T = 293(2)$ K, $Z = 8$, $R_{int} = 0.0623$, $R = 0.0430$ for 2998 observed unique reflections.

§ Analytical data for Ru(**L**)Ru: ^{1}H 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 $(M - PF_6)^+$, 847.5 $(M - 2PF_6)^{2+}$, 516.7 $(M - 3PF_6)^{3+}$, 351.3 $(M - 4PF_6)^{4+}$. Anal. Calcd for $C_{80}H_{59}N_{13}Ru_2P_4F_{24}$: C 48.42, H 3.00, N 9.18. Found: C 48.19, H 3.22, N 9.17%.

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