

One-Step Synthesis of 4,4'-Dicyano-2,2'-bipyridine and Its Bis(4,4'-di-*tert*-butyl-2,2'-bipyridine)ruthenium(II) Complex

Sebastian Losse,^[a] Helmar Görls,^[a] Robert Groarke,^[b] Johannes G. Vos,^[b] and Sven Rau,^{*[a]}

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This report describes a new route for the fast, economical and effective one-step synthesis and facile workup procedure of 4,4'-dicyano-2,2'-bipyridine (dnbpy) and its corresponding ruthenium complexes. The complex [(tbbpy)₂Ru(dnbpy)](PF₆)₂ was prepared for the first time (tbbpy = 4,4'-di-*tert*-butyl-2,2'-bipyridine) and the solid-state molecular structure was investigated with the help of a single-crystal X-ray analysis. The influence of the dnbpy ligand on the metal-to-

ligand charge-transfer (MLCT) processes of the complex was studied. The compound shows two absorption maxima in the MLCT region of the UV/Vis spectrum at 418 and 510 nm and the emission is 116 nm redshifted in comparison to that of [(tbbpy)₃Ru](PF₆)₂.

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Introduction

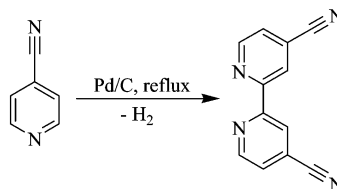
The preparation of 4,4'-dicyano-2,2'-bipyridine (dnbpy) is a known multistep synthesis with a low overall yield.^[1,2] The compound, which is used as a functional ligand for transition metal complexes,^[3] is an important intermediate for the preparation of potential anticancer agents^[2] and acts as a precursor in ligand design for several luminescent ruthenium(II) bipyridine-calix[4]arene complexes.^[4] The cyano function itself can be used for several reactions, e.g. to synthesise carboxylic acids, amines or amidines. Moreover, this function can also be utilised for the synthesis of compounds like 2-aryl-4,6-bis(2-pyridyl)-s-triazine.^[5] It has also been shown that the cyano function may serve as a donor site for the formation of heterooligonuclear metal complexes.^[6] Cyano moieties have been introduced by modification of appropriately substituted bipyridines with the help of Pd-catalysed reactions.^[7,8] Considering the possible applications and the potential of further reactions at the cyano group, the multistep low-yield synthesis represents a serious drawback for further investigations. The electronic structure of the 4,4'-dicyano-2,2'-bipyridine will most likely differ from that of the normal bipyridine as the substituents will lower the energy of the LUMO (π^*). This fact might be exploited for the tuning of photophysical properties in metal complexes featuring metal-to-ligand charge-transfer (MLCT) excitation and emission. The simplified synthetic

route, a one-step synthesis of the ligand, presented here is a fast, economical and effective approach to this synthon. In order to investigate the effect of the cyano substituent on the reactivity of the bipyridine ligand, we prepared the corresponding ruthenium(II) complex [(tbbpy)₂Ru(dnbpy)](PF₆)₂ (**1**) (tbbpy is 4,4'-di-*tert*-butyl-2,2'-bipyridine). The formation of **1** has been verified by NMR spectroscopy and high-resolution mass spectrometry. Moreover, for the first time the solid-state molecular structure of a dnbpy-containing compound has been investigated by single-crystal X-ray analysis. The absorption and emission measurements of **1** were recorded to investigate MLCT processes which are correlated with the homoleptic ruthenium(II) complex [(tbbpy)₃Ru](PF₆)₂ (**2**).

Results and Discussion

Synthesis of dnbpy and [(tbbpy)₂Ru(dnbpy)](PF₆)₂

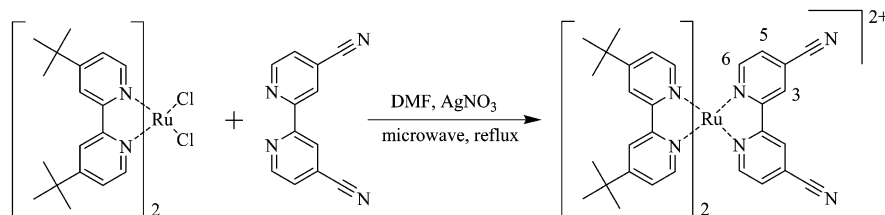
The coupling reaction of 4-cyanopyridine in the presence of 10% Pd/C as a catalyst under reflux conditions lead to the formation of dnbpy (Scheme 1). Working under exclusion of oxygen was essential in this reaction.



Scheme 1. Coupling reaction of 4-cyanopyridine.

[a] Friedrich-Schiller-Universität Jena, Institut für Anorganische und Analytische Chemie, August-Bebel-Straße 2, 07743 Jena, Germany
Fax: +49-3641-948102
E-mail: sven.rau@uni-jena.de

[b] Dublin City University, SFI Strategic Research Cluster for Solar Energy Conversion, School of Chemical Sciences, Dublin 9, Ireland



Scheme 2. Complexation reaction for the synthesis of **1**, numbering scheme is the same as that used in Figure 1.

When the reaction was performed under aerobic conditions no conversion was observed. The modest yield of 20% was more than compensated by a facile workup procedure which consists of a simple recrystallisation from chloroform. In addition, the starting materials, especially the catalyst, could be reused in further preparations. In contrast to the reaction of *tert*-butylpyridine with Pd/C where large quantities of the corresponding 4,4',4''-tri-*tert*-butyl-2,2':6',2''-terpyridine derivative may be obtained,^[9] no cyano-substituted terpyridine could be observed under these conditions. The reaction of the dnbpy ligand with a suitable ruthenium precursor, (tbbpy)₂Ru(Cl)₂, was performed in order to assess the reactivity of this ligand in the formation of transition metal complexes. Complex **1** could be obtained in the presence of AgNO₃ in dried dmf and under microwave irradiation in more than 70% yield (Scheme 2). However, it could not be isolated when the reaction was attempted under standard conditions,^[10] i.e. reflux in ethanol–water mixtures. These observations suggest that the chelating nitrogen functionalities are deactivated because of the strong electron-withdrawing effect of the cyano groups. The ¹H NMR spectrum of **1** shows the typical signals for a ruthenium(II) bipyridine complex (Figure 1). The singlet at $\delta = 8.79$ ppm (H3) and the two doublets at $\delta = 7.95$ and 7.70 ppm (H6 and H5, respectively) are low-field shifted compared to the tbbpy signals and can be assigned to dnbpy on the basis of two-dimensional NMR experiments. The number and position of all signals in the NMR spectrum suggest a symmetrical binding of the dnbpy to the ruthenium centre.

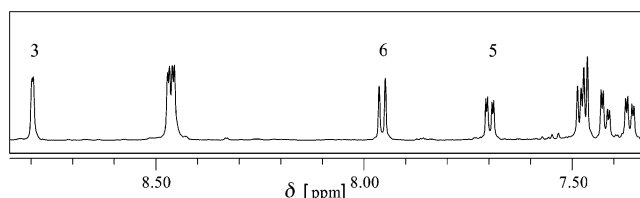


Figure 1. 400 MHz ¹H NMR spectrum of **1** in CD₃CN; aromatic region, dnbpy signals are labelled, all other signals can be assigned to the two tbbpy ligands.

The recording of a high-resolution mass spectrum (see Experimental Section) confirms the formation of **1** and the molecular structure was further verified by a single-crystal X-ray analysis (Figure 2).

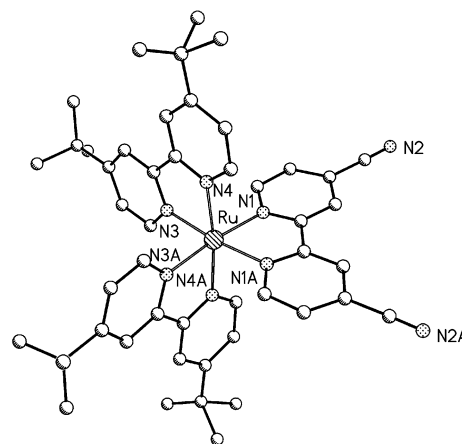


Figure 2. Solid-state molecular structure of the ruthenium(II) complex **1** containing dnbpy.

The ruthenium centre is surrounded by the three bipyridine ligands in a distorted octahedral coordination geometry. The six Ru–N distances fall in the range of 2.044(5)–2.054(5) Å with bite angles of the ligands of 78.24(18)° for tbbpy and 79.3(3)° for dnbpy. These values are similar to those reported for the [(tbbpy)₃Ru]²⁺ complex.^[11]

Complex **1** exhibits a horizontal mirror plane which explains the symmetrical NMR spectra observed. Selected bond lengths and angles are reported in Table 1. Complex **2** was prepared under standard conditions as described in the literature.^[10,11]

Table 1. Selected bond lengths [Å] and angles [°] for **1**.

Ru–N1	2.044(5)	Ru–N1A	2.044(5)
Ru–N4	2.045(5)	Ru–N3	2.054(5)
Ru–N3A	2.054(5)	Ru–N4A	2.045(5)
N2–C6	1.151(11)	C3–C6	1.440(11)
N1–Ru–N1A	79.3(3)	N4–Ru–N3	78.25(18)
N4A–Ru–N3	78.24(18)	N1A–Ru–N4A	87.95(18)
N3A–Ru–N3	88.5(3)	N1–Ru–N4	87.95(18)

Absorption and Emission Spectra

The UV/Vis and emission data of **1** and **2** in acetonitrile and dichloromethane are presented in Table 2. The excited-state lifetimes of **1** and **2** at different temperatures and in different solvents are given in Table 3. The absorption spectra of both complexes **1** and **2** in acetonitrile exhibit UV

transitions corresponding to intraligand transitions at 210 nm and 288 nm. For the homoleptic tbbpy complex **2** a single maximum at 460 nm was observed in the visible range (Figure 3) and has been assigned as a $^1\text{MLCT}$ transition. The ruthenium complex **1** exhibits two maxima at 418 nm and 510 nm which are indicative of two different $^1\text{MLCT}$ transitions. Relative to the energy of the $^1\text{MLCT}$ band of **2**, the lowest-energy $^1\text{MLCT}$ band is redshifted by 50 nm and the high-energy MLCT band, presumably Ru–tbbpy-based, is hypsochromically shifted by 42 nm (Figure 3). These observations are similar to the values observed for the heteroleptic ruthenium complexes with dicarboxylic esters of 2,2'-bipyridine.^[11,12] Recently, we synthesised a ruthenium complex with carboxylic methylester groups $[(\text{tbbpy})\text{Ru}(\text{dmcb})]^{2+}$ whose absorption spectrum shows two MLCT maxima as well (dmcb = 4,4'-dimethoxycarbonyl-2,2'-bipyridine). In an acetonitrile solution the first MLCT band occurs at 426 nm and the second at 492 nm, which implies a hypsochromic shift of 34 nm and a bathochromic shift of 32 nm compared with **2**. In this compound we have assigned the transition at 492 nm to the Ru–dmcb $^1\text{MLCT}$ using resonance Raman spectroscopy. These comparisons support the assumption that the dicyanologand is a stronger π -acceptor than tbbpy because of a stronger –M-effect. So the two distinct maxima of the heteroleptic complex **1** may be assigned as d– π^* (dnbpy) for the low-energy maximum at 510 nm and d– π^* (tbbpy) for the high-energy maximum at 418 nm. This interpretation is further supported by electrochemical data. For **1** in acetonitrile the metal-based oxidation is observed at 1.34 V vs. SCE, while three quasi-reversible ligand-based reductions are observed at –0.86, –1.44 and –1.73 V. The rather positive first reduction process, about 400 mV more positive than observed for **2**, can be explained by the strong π -acceptor properties of the dnbpy ligand.

Table 2. UV/Vis and emission data of **1** in acetonitrile and dichloromethane.

Sample	Solvent	λ_{max} [nm]	Emission [nm]
1	CH ₃ CN	285, 312, sh. 395, 418, 510	730
1	CH ₂ Cl ₂	285, 312, sh. 395, 418, 512	730

Table 3. Excited-state lifetime of **1** and **2** in aerated dichloromethane (DCM) and acetonitrile (ACN) at room temperature and in a 4:5 mixture of propionitrile (PCN)/butyronitrile (BuCN) at 77 K.

Sample	Solvent	Temperature	Lifetime [ns]
1	DCM	room temperature	200
1	ACN	room temperature	134
1	4:5 PCN/BuCN	77 K	3580
2	DCM	room temperature	264
2	ACN	room temperature	105
2	4:5 PCN/BuCN	77 K	5697

While the emission spectrum of **2** has a maximum at 614 nm in acetonitrile (Figure 4), for **1** a maximum is observed at 730 nm. This represents a bathochromic shift of 116 nm compared to **2**. The complex $[(\text{tbbpy})\text{Ru}(\text{dmcb})]^{2+}$

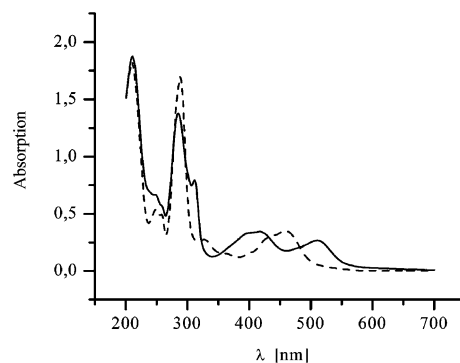


Figure 3. Absorption spectra in acetonitrile for $[(\text{tbbpy})_2\text{Ru}(\text{dnbpy})]^{2+}$ (**1**) (solid) and $[(\text{tbbpy})_3\text{Ru}]^{2+}$ (**2**) (dashed).

shows an emission wavelength of 691 nm in acetonitrile which is 77 nm redshifted compared to **2**. On the basis of the absorption and electrochemical data we propose that the emission of **1** occurs exclusively from the lowest-energy $^3\text{MLCT}$ state localised on the dnbpy ligand. Ruthenium complexes emitting in the red are known in the literature.^[13,14] Most of these compounds are difficult to synthesise because large π -systems are used to generate the red emission which makes it a complicated and often multistep preparation. The presented dnbpy-containing ruthenium complex is emissive in the red at room temperature and in fluids without further substituents and can be obtained easily. The lifetimes obtained at lower temperature correlate well with the energy gap law with lower lifetimes for **1** (emission at 730 nm) in comparison with **2** (emission at 613 nm).

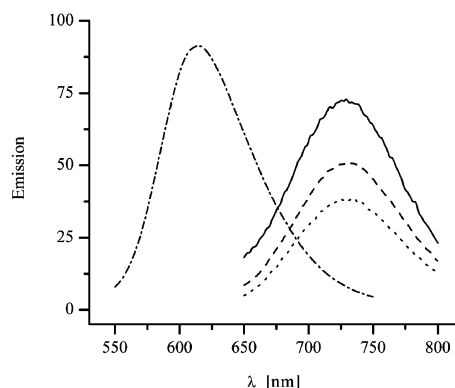


Figure 4. Emission spectra in acetonitrile of $[(\text{tbbpy})_2\text{Ru}(\text{dnbpy})]^{2+}$ (**1**) with an excitation wavelength of 280 nm (solid), 410 nm (dashed) and 510 nm (dotted); $[(\text{tbbpy})_3\text{Ru}]^{2+}$ (**2**) at 460 nm (dashed-dotted); uncorrected at room temperature.

Conclusions

The ligand dnbpy was prepared in a one-step synthesis for the first time. The bipyridine derivative can easily be obtained by a fast and facile workup procedure. The complexation reaction of dnbpy on the ruthenium(II) fragment $(\text{tbbpy})_2\text{Ru}(\text{Cl})_2$ resulting in the corresponding complex **1** is only possible under microwave irradiation in DMF with the

addition of AgNO_3 . All analytical data confirm the formation of **1**. The solid-state structure of **1** has been investigated and the obtained bond lengths and angles lie in the expected range. The electrochemical, absorption and emission data of the ruthenium complex **1** lead to the conclusion that dnbpy has a lower-energy π^* -state than tbbpy and dmcbbpy. With the now established one-step synthesis of dnbpy, larger amounts of this important building block can be isolated faster and much more economically. The application for the manipulation of MLCT processes in ruthenium(II) complexes was demonstrated.

Experimental Section

General: ^1H and ^{13}C NMR spectra were recorded with a Bruker 400 MHz/200 MHz spectrophotometer, and UV/Vis spectra were obtained with a Analytic Jena SPECORD® S 600. The mass spectra were recorded with a SSQ 170, Finnigan Mat spectrometer. Electrospray mass spectra were recorded with a Finnigan MAT, MAT 95 XL. The high-resolution mass spectrum peak for **1** is given for the ^{96}Ru isotope. All other values quoted for m/z are for the most-intense peak of the isotope pattern. Emission spectra were recorded with a Perkin–Elmer LS50B spectrometer equipped with a Hamamatsu R928 red-sensitive detector. Electrochemical experiments were carried out using a CHI750C electrochemical bipotentiostat. Cyclic voltammograms and differential pulse voltammograms were recorded against a saturated calomel reference electrode (SCE). Glassy carbon (GC) and platinum (Pt) macro electrodes were used as the working electrodes and a platinum wire was employed as the counter electrode. A solution of 0.1 M TBA PF_6 (Fluka, electrochemical grade) in acetonitrile (Aldrich, anhydrous, 99.8%) was used. Luminescence lifetime measurements were obtained using an Edinburgh Analytical Instruments (EAI) time-correlated single-photon-counting apparatus (TCSPC) comprised of two model J-yA monochromators (emission and excitation), a single-photon photomultiplier detection system model 5300 and a F900 nanosecond flashlamp (nitrogen-filled at 1.1 atm pressure, 40 kHz or 0.3 atm pressure, 20 kHz) interfaced with a personal computer by a Norland MCA card. A 410 nm cut-off filter was used in emission to attenuate scatter of the excitation light (337 nm); luminescence was monitored at the λ_{max} of the emission.

Data correlation and manipulation was carried out using EAI F900 software version 6.24. Emission lifetimes were calculated using a single-exponential fitting function, Levenberg–Marquardt algorithm with iterative deconvolution (Edinburgh instruments F900 software). The reduced χ^2 and residual plots were used to judge the quality of the fits. Lifetimes are $\pm 5\%$.

4-Cyanopyridine and 10% Pd/C were used as purchased from Fluka and $[(\text{tbbpy})_3\text{Ru}](\text{PF}_6)_2$ (**2**) was prepared according to a literature procedure.^[10,11]

Preparations

4,4'-Dicyano-2,2'-bipyridine (dnbpy): The reaction was carried out under argon to prevent oxygen at all times. 4-Cyanopyridine (30 g, 0.29 mol) and 10% Pd/C (900 mg) were placed into a 500 mL round-bottomed flask and heated to reflux for 24 h. After cooling to room temperature, chloroform was added (250 mL). The dark black suspension was filtered through a frit to give a pale yellow solution under removal of the catalyst Pd/C. Chloroform was evaporated until the product started to crystallise. Pentane (50 mL) was added and the concentrated solution was stored in a fridge for 5 h.

The pale yellow precipitate was collected on a frit, washed with ethanol and dried in vacuo. Yield: 6.2 g (20%). MS (DE): m/z (%) = 206 (100), 179 (20), 103 (20). ^1H NMR (400 MHz, CDCl_3): δ = 8.85 (d, J = 5.2 Hz, 2 H), 8.69 (s, 2 H), 7.58 (d, J = 4.8 Hz, 2 H) ppm. ^{13}C NMR (50 MHz, CDCl_3): δ = 116.32, 121.82, 123.1, 125.8, 150.3, 155.4 ppm.

$[(\text{tbbpy})_2\text{Ru}(\text{dnbpy})](\text{PF}_6)_2$ (1**):** $\text{Ru}(\text{tbbpy})_2\text{Cl}_2$ (200 mg, 0.28 mmol), dnbpy (58.2 mg, 0.28 mmol) and AgNO_3 (96 mg, 0.56 mmol) were dissolved in DMF (100 mL). The reaction mixture was heated to reflux under microwave irradiation for 2 h at 200 W. After cooling to room temperature, filtration and evaporation of the solvent, ethanol was added to give a clear solution from which the product could be precipitated by adding an aqueous solution of NH_4PF_6 . The solid was isolated, washed with diethyl ether and dried in vacuo. The crude product was purified by column chromatography on silica with acetonitrile as eluent. Crystals suitable for the X-ray diffraction were obtained from a methanol/water solution. Yield: 236 mg (74%). MS (ESI in acetonitrile and methanol): m/z (%) = 989 (100) $[\text{M} - \text{PF}_6]^+$, 422 (10) $[(\text{M} - 2\text{PF}_6)/2]^{2+}$. MS (HR-ESI in methanol): m/z = 983.3189 $[\text{M} - \text{PF}_6]^+$, calcd. ($\text{C}_{48}\text{H}_{54}\text{F}_6\text{N}_8\text{P}_6\text{Ru}$) 983.3189. ^1H NMR (400 MHz, CD_3CN): δ = 8.79 (s, J = 1.2 Hz, 2 H), 8.47 (d, J = 2 Hz, 2 H), 8.45 (d, J = 2.0 Hz, 2 H), 7.95 (d, J = 6.0 Hz, 2 H), 7.7 (dd, J = 1.6 and 6.0 Hz, 2 H), 7.47 (m, 4 H), 7.41 (dd, J = 2.0 and 10 Hz, 2 H), 7.36 (dd, J = 2.0 and 10 Hz, 2 H), 1.39 (s, 36 H) ppm. ^{13}C NMR (100 MHz, CD_3CN): δ = 30.4, 36.4, 116.5, 120.9, 122.7, 125.8, 126.0, 127.9, 130.3, 151.6, 152.2, 154.0, 157.2, 157.4, 158.5, 164.4, 164.5 ppm.

Crystal Structure Determination: The intensity data for the compound was collected on a Nonius Kappa CCD diffractometer using graphite-monochromated Mo-K_α radiation. Data were corrected for Lorentz-polarisation effects, but not for absorption effects.^[15–16] The structure was solved by direct methods (SHELXS^[17]) and refined by full-matrix least-squares techniques against F_o^2 (SHELXL-97).^[18] The hydrogen atoms were included at calculated positions with fixed thermal parameters. All non-hydrogen atoms were refined anisotropically.^[18] XP (SIEMENS Analytical X-ray Instruments, Inc.) was used for structure representations.

CCDC-667619 (for **1**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/datarequest/cif.

Acknowledgments

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