ChemComm

RSCPublishing

COMMUNICATION

Isolated facial and meridional tris(bipyridine)Ru(II) for STM studies on Au(111)†

Cite this: *Chem. Commun.*, 2013, **49**, 1076

Received 31st October 2012,
Accepted 12th December 2012

DOI: 10.1039/c2cc37904j

www.rsc.org/chemcomm

Alexandrina Schramm,[a] Christophe Stroh,*[a] Kerrin Dössel,[ab] Maya Lukas,[ab] Olaf Fuhr,[ab] Hilbert v. Löhneysen[abc] and Marcel Mayor*[abd]

Tripodal facial and meridional Ru(II) complexes comprising three conjugated legs with acetyl-protected thiol end groups are designed, synthesized and isolated for investigation on a gold surface. Preliminary ultrahigh vacuum scanning tunnelling microscopy (UHV STM) measurements of a monolayer of facial isomer deposited on Au(111) are presented.

The class of Ru(II)–polypyridine complexes have been extensively studied due to their cumulative charge-transfer characteristics, chemical stability, photophysical and redox properties.[1] They have found widespread applications in photoinduced electron-transfer processes,[2] artificial photosynthesis[3] and dye-sensitized solar cells.[4] Moreover, all these properties make them attractive for nanotechnology as potential photon-induced switches[5] and for molecular machines and devices.[6] To understand the specific way of surface arrangement on the molecular level is a challenge which in the case of Ru–polypyridine complexes has been tackled by STM in few reports only.[7,8]

For better stability and control of molecular spacing on the surface a few groups designed tripodal to multipodal structures based on polypyridine systems.[9] Recently we reported a differently functionalized tripodal Ga(III) complex and its single molecule detection on Au(111) by UHV STM.[10] The structure was intended to stand by itself upright on the surface, a structural concept which also led to the design of a tris(bipyridine)Ru(II) complex presented here.

In a pseudo-octahedral ligand field unsymmetrical bidentate ligands, *e.g.* 2,2′-bipyridine (*bipy*), adopt two geometric forms in trishomoleptic complexes: facial (***fac***) and meridional (***mer***) stereoisomers, each of them appearing in a subset of Δ and Λ enantiomers.[11–13] The isolation of the isomers is challenging and less well established which prevents the widespread use of such compounds and their applications in science.[14] Few reports characterized and compared the two geometrical isomers with each other,[11] which is of primary importance for the attachment and the geometrical control on the metallic surfaces. Furthermore, to our knowledge a single isomer of the ***fac*** or ***mer*** complex on metal surfaces has not been reported for STM studies so far.

Our synthetic strategy is based on the functionalization of a conjugated 2,2′-*bipy* ligand, equipped with thioacetyl protection end-groups, which after coordination forms the two ***fac*** and ***mer*** isomers (Fig. 1). The different spatial geometry of the two isomers provides distinguishable polarities between them which allows for separation by standard column chromatography.

Both isomers form rigid tripodal structures, where the conjugated ligands enclose the Ru(II) ion. In the ***fac*** species all three legs are prearranged on one side. In the ***mer*** isomer one ligand is turned to the opposite direction which defines a pronounced geometry difference to the facial arrangement. Of particular interest will be the behaviour of the ***fac*** stereoisomer on a gold substrate. The three thiol groups define a plane and should in principle enable

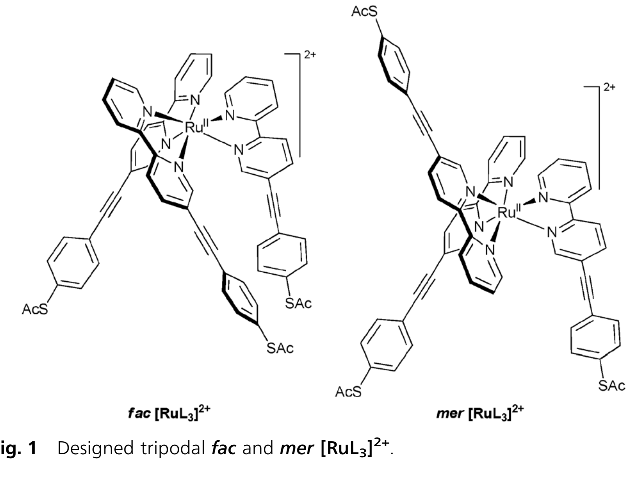
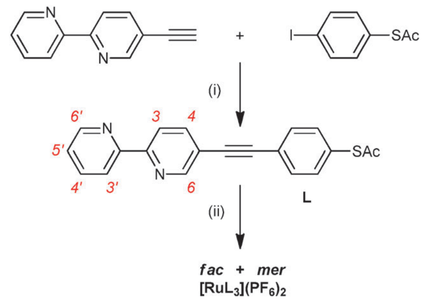


Fig. 1 Designed tripodal ***fac*** and ***mer*** $[RuL_3]^{2+}$.

---

[a] Institute of Nanotechnology, Karlsruhe Institute of Technology (KIT), P.O. Box 3640, D-76021 Karlsruhe, Germany
[b] DFG Center for Functional Nanostructures (CFN), Karlsruhe Institute of Technology (KIT), D-76049 Karlsruhe, Germany
[c] Physics Institute and Institute of Solid State Physics, Karlsruhe Institute of Technology (KIT), P.O. Box 3640, D-76021 Karlsruhe, Germany
[d] Department of Chemistry, University of Basel, CH-4003 Basel, Switzerland. E-mail: marcel.mayor@unibas.ch; Fax: +41 61 267 1016; Tel: +41 61 267 1006

† Electronic supplementary information (ESI) available: Experimental procedures, compounds characterization and X-ray crystallographic data for the ***fac*** isomer. CCDC 813446. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2cc37904j



Scheme 1 Synthesis of ***fac*** and ***mer*** **[RuL$_3$](PF$_6$)$_2$**. (i) PdCl$_2$(PPh$_3$)$_2$, CuI, THF anh./DIEA anh., N$_2$, rt, 50%; (ii) (a) Ru(DMSO)$_4$Cl$_2$, EtOH, Ar, reflux; (b) KPF$_6$ aq., MeCN, rt, 26% *fac*, 10% *mer*.

interactions of all three anchor groups with a plane substrate. In the present case however, the three thiol groups remain protected preventing the formation of direct gold–thiol bonds. In addition, on an atomically flat substrate the match of distances and orientations between the thiol groups with the periodicity of the surface atoms might become important as well. Finally, the superior photophysical properties of Ru(II)tris(bipyridine) derivatives motivated the investigation of the ***fac*** isomer on metallic surfaces.

The thioacetyl terminated ligand **L** was obtained by a *Sonogashira* cross-coupling reaction (Scheme 1) between 5-ethynyl-2,2′-bipyridine[15] and 4-(thioacetyl)-iodobenzene.[16] The reaction of 3 eq. of **L** with Ru(DMSO)$_4$Cl$_2$[17] resulted in both ***fac*** and ***mer*** **[RuL$_3$]$^{2+}$** isomers. The isolation of each of the two isomers was achieved by silica flash column chromatography eluted with an aqueous solution of KNO$_3$. After separation, anion metathesis was carried out by application of excess of KPF$_6$ aq.

The ligand **L** and its ***fac*** and ***mer*** Ru(II) complexes were fully characterized by NMR, electrospray ionization mass spectrometry, IR, UV-vis spectroscopy and elemental analysis. The molecular structure of the ***fac*** Ru(II) isomer was determined by single crystal X-ray diffraction. All obtained data confirm the formation and separation of the two stereoisomers.

As observed by ^{1}H NMR (Fig. 2b) the ***fac*** complex exhibits in solution a C_3-symmetry, expressed in a clearly resolved spectrum with all three legs being chemically equivalent. The ***mer*** isomer is not symmetric, which leads to a more complex spectrum (Fig. 2c), where the signals appear as broad complex multiplets. This results from the non-equivalent interaction of each proton with the electron density of the neighbouring ligands. Integration of these signals corresponds to the formulated structure, considering accordant assignment to the ***fac*** isomer. Our ^{1}H NMR shift resulting from the changes in electron densities after chelation of the ligands (Fig. 2a) is comparable with reported values.[13,18] A closer analysis of the ^{1}H NMR spectra, electrospray-ionisation mass spectra, IR and elemental analysis is discussed in the ESI.†

Additional evidence for the distinction of the two isomers can be gained from ^{13}C NMR analyses.† The higher symmetric ***fac*** species resolves 18 carbon signals, while the ***mer***-species exhibits several sets of closely pitched signals representing the chemically similar but symmetrically different carbon atoms of the three ligand moieties.

The UV-vis spectrum in MeCN of the ligand presents a broad absorption peak at 320 nm with a red-sided shoulder at 336 nm, which is usually observed for n–π* or π–π* transitions.† Excitation into these wavelengths yielded a strong fluorescence signal at 376 nm.

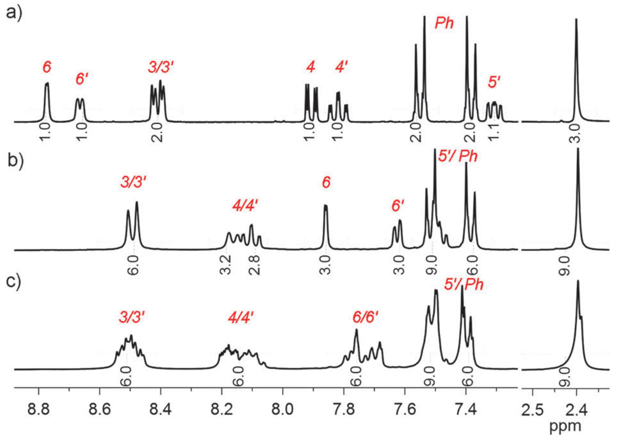


Fig. 2 ^{1}H NMR spectra of: (a) **L** in CDCl$_3$; (b) ***fac*** **[RuL$_3$](PF$_6$)$_2$**; (c) ***mer*** **[RuL$_3$](PF$_6$)$_2$** in CD$_2$Cl$_2$; the assignment of protons is declared in Scheme 1 above.

The photophysical investigation of both ***fac*** and ***mer*** isomers in MeCN indicates no significant difference between two structural forms as reported for similar structures.[11] There, transitions of the ligand-centered (^{1}LC) and metal-to-ligand-charge-transfer (^{1}MLCT) character dominate the spectrum. The features of ligand based transitions are found at 325–335 nm (broad) which is very close to the absorption of the free ligand. The ^{1}MLCT based peak at 471 nm experiences a bathochromic shift in comparison to the reported values of the [Ru(bipy)$_3$](PF$_6$)$_2$ (452 nm ^{1}MLCT, 286 nm ^{1}LC)[19] which is caused by the extended conjugated π-electron system on the ligand.[8] A strong ^{3}MLCT emission band at 635 nm was observed after excitation into the 471 nm ^{1}MLCT maximum. The MLCT character of the emissive species is supported by the emission–excitation spectrum (maximum peak at 471 nm) which complies well with the UV-vis absorption spectrum.

The molecular structure of the Λ isomer of ***fac*** **[RuL$_3$]$^{2+}$** is shown in Fig. 3.‡ The metal ion is coordinated by six nitrogen atoms of the three bidentate *bipy* ligands in a distorted octahedral arrangement. In the solid state the three *bipy* ligands are positioned in a pseudo C_3-symmetry around the central metal. The *cis*-arrangement of each of the three ligand legs confirms the ^{1}H NMR studies described before. The values of the Ru–N bond lengths are between 2.058(6) Å and 2.066(5) Å, and N–Ru–N angles are between 78.6(2)° and 174.4(2)°, similar to that found in comparable [Ru(bipy)$_3$]$^{2+}$ structures.[12] The distance between the plane formed by three sulphur atoms and the upper 5′-*bipy* carbon atoms is 12.6 Å, while that from the Ru ion to the same plane of sulphur atoms is 9.5 Å. The distances between the sulphur atoms are on the average 13 Å. The complex crystallizes as a racemate in the triclinic space group $P\bar{1}$ with two formula units and three additional solvate molecules (MeCN) per unit cell. The unit cell contains the two enantiomers, one Δ and the other Λ, positioned head to head.† The crystal packing presents intermolecular π···π stacking interactions (3.86 Å centroid–centroid) between the pyridine and phenyl rings of two very closely positioned neighbouring molecules.†

Molecules of the ***fac*** isomer were deposited on Au(111) from MeCN solution (for details see ESI†). Fig. 4 shows an STM image of such a sample at monolayer coverage. In contrast to the previously reported tripodal molecules,[10] the ***fac*** Ru complex forms islands of dimers which exhibit a medium range order. The intermolecular

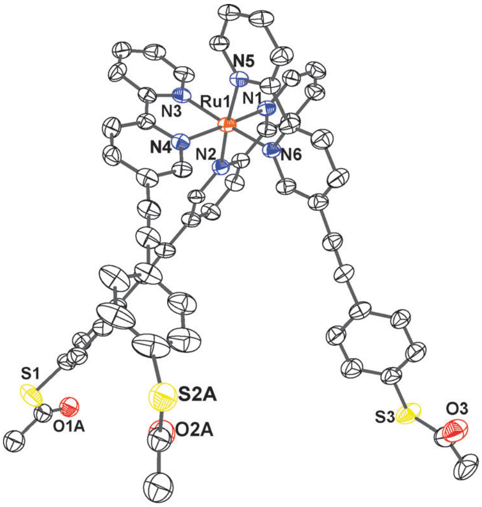


Fig. 3 Solid state structure of ***fac*** $[\mathbf{RuL_3}]^{2+}$ determined by single crystal X-ray diffraction (Λ isomer). The hydrogen atoms were omitted for clarity (ellipsoid plot at the 50% probability level).

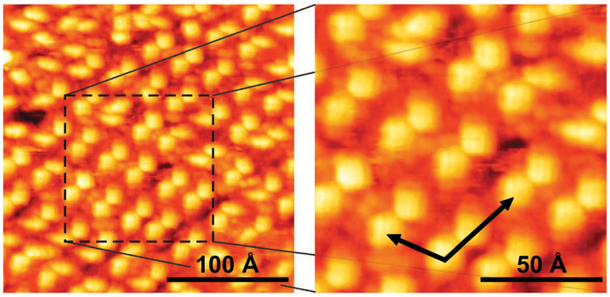


Fig. 4 STM image of island of ***fac*** dimers with medium range order. The arrows indicate the unit cell of the structure with 38 Å × 24 Å, $V_{\text{gap}} = -1.5$ V, $I_{\text{set}} = 140$ pA.

spacing within the dimer is 13 Å, the lattice of dimers has a unit cell of approx. 38 Å × 24 Å. Interestingly, this surface arrangement bears some similarities to the packing in the solid state (ESI,† Fig. S19). Tight dimers of enantiomers were found in the single crystal structure of ***fac*** $[\mathbf{RuL_3}](\mathbf{PF_6})_2$. The distance between both enantiomers of a dimer in the solid state of about 10 Å is comparable to the spacing observed between both molecules of a dimer on the surface. It is thus tempting to postulate that the dimers observed on Au(111) consist of pairs of enantiomers as well. However, as the STM resolution did not allow resolving the molecule's chirality, this remains a working hypothesis. The lateral spacing of the pairs on the substrate (38 Å × 24 Å) is larger than their distances in the solid state, which suggests that surface–pair interactions on Au(111) exceed the interpair interactions in the crystal.

In conclusion, the synthetic development of an unsymmetrical bipyridine ligand terminated with thiol anchoring groups was achieved. Subsequent coordination of Ru(II) led to the formation of tripodal ***fac*** and ***mer*** isomers which were separated by column chromatography. Both stereoisomeric forms were fully characterized. Single crystal diffraction data of the ***fac*** form corroborate the spatial arrangement of all three thiol termini located on the same side of the complex. We are currently investigating wet deposition techniques in order to immobilize the ***fac*** isomer by covalent bonds of the thiol anchor groups to metal substrates.

Financial support from the KIT is gratefully acknowledged. We thank Dr Frank Schramm and Matthias Fischer for providing chemical reagents.

Notes and references

‡ Crystal data: ***fac*** $[\mathbf{RuL_3}](\mathbf{PF_6})_2\cdot\mathbf{1.5(CH_3CN)}$, CCDC 813446, $C_{63}H_{46.5}F_{12}N_{7.5}O_3P_2RuS_3$, $M = 1443.77$, triclinic, space group $P\bar{1}$, $a = 13.081(5)$ Å, $b = 15.083(6)$ Å, $c = 18.470(8)$ Å, $\alpha = 95.06(3)^\circ$, $\beta = 108.12(3)^\circ$, $\gamma = 104.55(3)^\circ$, $V = 3297(2)$ Å^3, $T = 143(2)$ K, $Z = 2$, $\mu(\text{MoK}\alpha) = 0.465$ mm^{-1}, 18 404 reflections measured, 10 343 unique ($R_{\text{int}} = 0.0693$); 7058 with $I > 2\sigma(I)$; 820 parameters, 2 restraints, GOF = 1.020; final R_1 values for refl. with $I > 2\sigma(I)$: $R_1 = 0.0775$, w$R(F^2) = 0.1940$; for all data: final $R_1 = 0.1148$, w$R(F^2) = 0.2169$. Crystals of the ***fac*** isomer were grown by slow diffusion of Et_2O into a MeCN solution of the complex, yielding red needles suitable for single crystal X-ray investigation. Two thioacetyl groups and one hexafluorophosphate anion were refined disordered.

1 V. Balzani, A. Juris, M. Venturi, S. Campagna and S. Serroni, *Chem. Rev.*, 1996, **96**, 759.
2 K. Ohkubo, T. Hamada and H. Ishida, *J. Chem. Soc., Chem. Commun.*, 1993, 1423; T. J. Meyer, *Nature*, 2008, **451**, 778.
3 M. Chen, K. P. Ghiggino, S. H. Thang and G. J. Wilson, *Angew. Chem., Int. Ed.*, 2005, **44**, 4368; T. J. Meyer, *Acc. Chem. Res.*, 1989, **22**, 163.
4 A. Hagfeldt and M. Grätzel, *Acc. Chem. Res.*, 2000, **33**, 269; M. K. Nazeeruddin, S. M. Zakeeruddin, J. J. Lagref, P. Liska, P. Comte, C. Barolo, G. Viscardi, K. Schenk and M. Graetzel, *Coord. Chem. Rev.*, 2004, **248**, 1317; M. K. Nazeeruddin, C. Klein, P. Liska and M. Graetzel, *Coord. Chem. Rev.*, 2005, **249**, 1460.
5 V. Balzani, G. Bergamini, F. Marchioni and P. Ceroni, *Coord. Chem. Rev.*, 2006, **250**, 1254.
6 V. Balzani, A. Credi, S. Silvi and M. Venturi, *Chem. Soc. Rev.*, 2006, **35**, 1135; V. Balzani, M. Clemente-León, A. Credi, B. Ferrer, M. Venturi, A. H. Flood and J. F. Stoddart, *Proc. Natl. Acad. Sci. U. S. A.*, 2006, **103**, 1178.
7 K. Seo, A. V. Konchenko, J. Lee, G. S. Bang and H. Lee, *J. Am. Chem. Soc.*, 2008, **130**, 2553; E. Figgemeier, L. Merz, B. A. Hermann, Y. C. Zimmermann, C. E. Housecroft, H. J. Guentherodt and E. C. Constable, *J. Phys. Chem. B*, 2003, **107**, 1157; P. Salvatore, A. G. Hansen, K. Moth-Poulsen, T. Bjørnholm, R. J. Nichols and J. Ulstrup, *Phys. Chem. Chem. Phys.*, 2011, **13**, 14394; A. Sasahara, C. L. Pang and H. Onishi, *J. Phys. Chem. B*, 2006, **110**, 4751.
8 J. Otsuki, H. Kameda, S. Tomihira, H. Sakaguchi and T. Takido, *Chem. Lett.*, 2002, **31**, 610.
9 E. Galoppini, W. Guo, W. Zhang, P. G. Hoertz, P. Qu and G. J. Meyer, *J. Am. Chem. Soc.*, 2002, **124**, 7801; K. Terada, K. Kobayashi and M.-a. Haga, *Dalton Trans.*, 2008, 4846; S. Ramachandra, K. C. Schuermann, F. Edafe, P. Belser, C. A. Nijhuis, W. F. Reus, G. M. Whitesides and L. De Cola, *Inorg. Chem.*, 2011, **50**, 1581.
10 A. Schramm, C. Stroh, K. Dössel, M. Lukas, M. Fischer, F. Schramm, O. Fuhr, H. v. Löhneysen and M. Mayor, *Eur. J. Inorg. Chem.*, 2012, DOI: 10.1002/ejic.201200928; M. Lukas, *et al.*, unpublished work, 2012.
11 E. A. P. Armstrong, R. T. Brown, M. S. Sekwale, N. C. Fletcher, X.-Q. Gong and P. Hu, *Inorg. Chem.*, 2004, **43**, 1714; N. C. A. Baker, N. McGaughey, N. C. Fletcher, A. V. Chernikov, P. N. Horton and M. B. Hursthouse, *Dalton Trans.*, 2009, 965; M. Kyakuno, S. Oishi and H. Ishida, *Inorg. Chem.*, 2006, **45**, 3756.
12 R. T. Brown, N. C. Fletcher, M. Nieuwenhuyzen and T. E. Keyes, *Inorg. Chim. Acta*, 2005, **358**, 1079; N. C. Fletcher, M. Niewenhuyzen, R. Prabarahan and A. Wilson, *Chem. Commun.*, 2002, 1188.
13 N. C. Fletcher, M. Nieuwenhuyzen and S. Rainey, *J. Chem. Soc., Dalton Trans.*, 2001, 2641; T. J. Rutherford, D. A. Reitsma and F. R. Keene, *J. Chem. Soc., Dalton Trans.*, 1994, 3659.
14 M. H. Filby, J. Muldoon, S. Dabb, N. C. Fletcher, A. E. Ashcroft and A. J. Wilson, *Chem. Commun.*, 2011, **47**, 559.
15 V. Grosshenny, F. M. Romero and R. Ziessel, *J. Org. Chem.*, 1997, **62**, 1491.
16 D. T. Gryko, C. Clausen, K. M. Roth, N. Dontha, D. F. Bocian, W. G. Kuhr and J. S. Lindsey, *J. Org. Chem.*, 2000, **65**, 7345.
17 E. Dulière, M. Devillers and J. Marchand-Brynaert, *Organometallics*, 2003, **22**, 805.
18 G. Orellana, C. A. Ibarra and J. Santoro, *Inorg. Chem.*, 1988, **27**, 1025.
19 P. A. Anderson, G. B. Deacon, K. H. Haarmann, F. R. Keene, T. J. Meyer, D. A. Reitsma, B. W. Skelton, G. F. Strouse, N. C. Thomas, J. A. Treadway and A. H. White, *Inorg. Chem.*, 1995, **34**, 6145.