Dalton Transactions

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: P. A. Benavides, T. A. Matias and K. Araki, *Dalton Trans.*, 2017, DOI: 10.1039/C7DT03658B.

This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the author guidelines.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard Terms & Conditions and the ethical guidelines, outlined in our author and reviewer resource centre, still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.

ROYAL SOCIETY OF CHEMISTRY

rsc.li/dalton

View Article Online
DOI: 10.1039/C7DT03658B

Journal Name

ARTICLE

Unexpected lability of the [Ru^{III}(phtpy)Cl$_3$] complex

Paola A. Benavides,[a] Tiago A. Matias[a] and Koiti Araki*[a]

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Ruthenium(III) complexes are known for their high stability and inertness. To the best of out knowledge, the only well characterized example of labile Ru(III) complex is [Ru^{III}(edta)(H$_2$O)] as consequence of an intramolecular hydrogen bonding leading to the formation of a large opening in the molecule front, thus changing the mechanism from dissociative to associative. Compeling experimental evidences are presented demonstrating that the [Ru^{III}(phtpy)Cl$_3$] complex is labile also indicating that the Ru(III)-phtpy bond is much weaker than expected, in contrast with the strongly π-back-bonding stabilized Ru(II)-phtpy bond. .

Introduction

The concept of lability/inertness and thermodynamic stability of transition metal complexes are fundamental in coordination chemistry, particularly when considering the catalytic/electrocatalytic activity of such compounds, since the binding of a molecular substrate to the active site followed by the reaction and release of the product are the key steps controlling their efficiency.[1,2] Accordingly, the mechanism and rate of substitution reactions in transition metal complexes were extensively studied in the last century and are well established.[3,4] For example, it is known that representative elements cations and first row transition metal elements in 2+ oxidation state tend to generate labile coordination compounds with high ionic character metal-ligand bonds. The covalent character and stability of those complexes are enhanced in the 3+ oxidation state species, but the ligand exchange continue to be fast except for the Cr(III) and Co(III) complexes in which the ligand field stabilization energy is maximized.[5–9] Nevertheless, the covalent character and stability of second row transition metal complexes are much larger and are all low spin and quite inert,[10–13] particularly in the case of Ru(II) d^6 complexes with π-acceptor polypyridyl ligands and respective Ru(III) complexes.[14–16] Hence, except for the [Ru^{III}(edta)(H$_2$O)]$^-$ complex in which the aqua ligand can be easily substituted by associative or interchange mechanism,[17–19] the complexes are inert and the ligand exchange by dissociation mechanism tend to be slow.

Recently, we showed the enhancement by 20 times of the catalytic activity for water oxidation of the weakly coupled binuclear complex [{Ru^{II}(bpy)(H$_2$O)}$_2$(tpy$_2$ph)](PF$_6$)$_4$ (where bpy is 2,2'-bipyridine and tpy$_2$ph is 1,3-bis(4'-2,2':6',2''-terpyridin-4-yl)benzene), when compared with the mononuclear counterpart [Ru^{II}(phtpy)(H$_2$O)(bpy)](PF$_6$)$_2$ (where phtpy is 4'-phenyl-2,2':6',2''-terpyridine) evidencing significant synergic effects involving the metal sites.[20] This fact has encouraged us to investigate binuclear complexes for catalytic water oxidation such as the [{Ru^{II}(phtpy)(H$_2$O)}$_2$(dpimbH$_2$)]$^{4+}$ complex, where dpimbH$_2$ is the bis(2-pyridyl)benzodiimidazole ligand. However, unexpected difficulties were faced in the preparation of the respective chloro complex precursor [{Ru^{II}(phtpy)Cl}$_2$(dpimbH$_2$)]$^{2+}$ based on the well-established reaction of [Ru^{III}(phtpy)Cl$_3$] (**1**) complex with bidentated ligands in the presence of a weak reducing agent.[20] Surprisingly, the main reaction product was always the [Ru^{II}(phtpy)$_2$]$^{2+}$ complex suggesting that the terdentated N-heterocyclic ligand phtpy is actually dissociating from that Ru(III) complex and reacting with reduced [Ru^{II}(phtpy)Cl$_3$] species.

Interestingly enough, such mind bogging result was reproducible even when changing reaction parameters such as solvent, reaction time, and temperature, as well as in the presence of weak reducing species, precluding the preparation of the desired [Ru^{II}(phtpy)(LL)(H$_2$O)]$^{2+}$ complexes, where LL= dpimbH$_2$ and bpy, with suitable yields. Accordingly, we decided to carefully investigate that reaction, in order to shed light on the possible reasons for the formation of the [Ru^{II}(phtpy)$_2$]$^{2+}$ complex as main product. Therefore, herein described are the experimental evidences demonstrating the lability of the [Ru^{III}(phtpy)Cl$_3$] complex while reporting the attempts to solve such an improbable synthetic problem.

Results and discussion

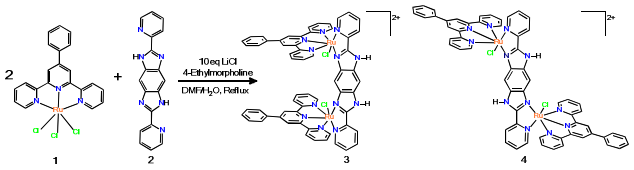
In a typical reaction, dpimbH$_2$ ligand, [Ru^{III}(phtpy)Cl$_3$] (2 equiv.) and LiCl (10 equiv.) were added to a DMF/H$_2$O 3:1 (v/v) mixture in a two-necked round bottom flask (Scheme 1). Then

[a] Department of Chemistry, Institute of Chemistry, University of São Paulo, Av. Lineu Prestes 748, Butantã, São Paulo, SP 05508-000, Brazil.
E-mail: koiaraki@iq.usp.br
Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

View Article Online
DOI: 10.1039/C7DT03658B

4-ethylmorpholine (NEM) was added and the reaction mixture refluxed for 3 h while monitoring by UV-vis spectroscopy and thin layer chromatography (TLC). NEM is added to facilitate the reduction of the final substitution product, or the reduction of the $[Ru^{III}(phtpy)Cl_3]$ complex to the respective Ru(II) complex, thus facilitating the dissociation of chloro ligands and the binding of $dpimbH_2$, whereas LiCl assures the formation of the desired monochloro complexes 3 and 4 (Scheme 1).

The UV-Vis spectrum of the reaction mixture after 3 h of reflux in DMF (Fig. 1a), showed that the phtpy ligand absorption bands were bathochromically shifted respectively from 253 and 290 nm (free ligand) to 290 and 320 nm, whereas the bands of the free $dpimbH_2$ bridging ligand were shifted from 351 and 368 nm to 382 and 406 nm. In addition, the ruthenium complex generated in the reaction exhibited broad overlapping bands spanning the whole visible range, that can be attributed to metal-to-ligand charge-transfer transitions characteristic of ruthenium(II) polypyridine species.[20]



Scheme 1. Reaction scheme for the synthesis of the binuclear $[\{Ru^{II}(phtpy)(Cl)\}_2(dpimbH_2)]^{2+}$ species (two of 6 possible isomers are shown) from the $[Ru^{III}(phtpy)Cl_3]$ complex and $dpimbH_2$ ligand.

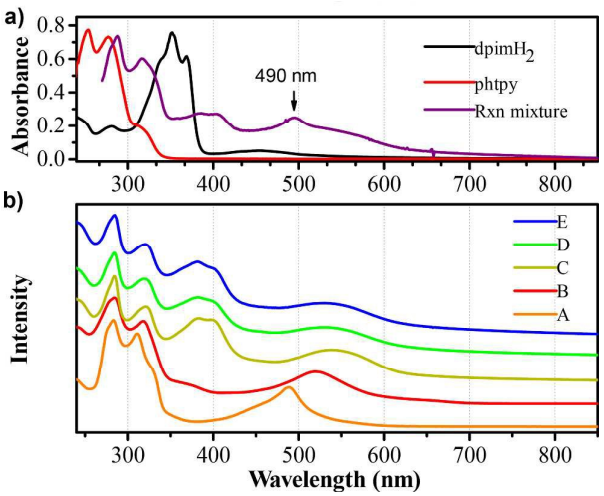


Figure 1. a) UV-Vis spectra of the crude reaction mixture of $[Ru^{III}(phtpy)Cl_3]$ with $dpimbH_2$ ligand after 3 h reflux in DMF, compared with the authentic free $dpimbH_2$ and phtpy ligands in MeOH and b) UV-Vis spectrum of the five representative fractions isolated by silica gel column chromatography.

As shown in Figure 1b, the spectroscopic profiles of fractions C, D and E obtained by column chromatography are very similar, exhibiting the phtpy and $dpimH_2$ intraligand bands as well as the metal-to-ligand charge-transfer (MLCT) bands in the visible region, as expected for the $[\{Ru^{II}(phtpy)Cl\}_2(dpimH_2)]^{2+}$ complex. However, the main fraction labelled as A, corresponding to 54% yield, displayed a contrasting spectral profile characterized by the absence of the band belonging to the bridging ligand and the presence of a strong MLCT band centred at 490 nm. Analysis of this fraction by UV-Vis and ^{1}H-NMR spectroscopy (see SI Fig. S2) showed that, under these experimental conditions, the major reaction product is the $[Ru^{II}(phtpy)_2]^{2+}$ complex. This outcome was completely unexpected since $dpimbH_2$ is a strong σ-donor and π-acceptor bis-bidentated bridging ligand, known to stabilize binuclear complexes generated upon reaction with two equivalents of $[Co(bpy)_2Cl_2]$, $[Rh(bpy)_2Cl_2]$, and $[Ru(bpy)_2Cl_2]$ complexes.[21,22]

Similar results were obtained in reactions carried out in ethanol and methanol even in the absence of NEM. Thus, the possible reduction of Ru(III) to Ru(II) in methanol solution was confirmed by dispersing solid $[Ru^{III}(phtpy)Cl_3]$ in MeOH at 50 °C under stirring, monitoring the spectral evolution as a function of time (Fig. 2a), and then reacting with hydrogen peroxide (Fig. 2b). The absorption at 440 nm decayed with the concomitant rise of the bands at 379, 490 and 573 nm, while the colour changed from pale brown to purple and the scattering contribution decreased, as confirmed visually by the decrease of turbidity. Such spectroscopic behaviour was attributed to the formation of soluble reduced $[Ru^{II}(phtpy)L_1L_2L_3]$ derivatives (where L_n = solvent or Cl^-) and the $[Ru^{II}(phtpy)_2]^{2+}$ complex. In order to confirm this hypothesis, diluted hydrogen peroxide was added into the purple solution and the mixture monitored spectrophotometrically. The bands at 379 and 573 nm disappeared rapidly after the addition of H_2O_2 concomitantly with the rise of the band at 440 nm, suggesting the regeneration of the initial Ru(III) species (Fig. 2b). Interestingly, the final spectrum of the solution, except for the absorption at 440 nm, matched that of the bis-terpyridine complex indicating that the redox potential of $[Ru^{II}(phtpy)_2]^{2+}$ is more positive than that of H_2O_2, thus remaining unchanged in solution.

In a parallel experiment, $[Ru^{III}(phtpy)Cl_3]$ was reduced with zinc almagam, Zn(Hg), (see SI Fig. S3a) a strong reducing agent, in MeOH at 50 °C under N_2 atmosphere, in order to evaluate the stability of the Ru(II)-phtpy complex and its eventual contribution to the formation of the bis-phtpy complex. After addition of Zn(Hg) into the solution, strong absorption bands, characteristic of the MLCT bands of reduced $[Ru^{II}(phtpy)L_1L_2L_3]$ species, started to appear in the 450 to 750 nm range as the band of $[Ru^{III}(phtpy)Cl_3]$ at 440 nm fade. After 30 min, the reduction reaction and consequent solubilisation process was complete. The Zn(Hg) was removed and the solution monitored spectrophotometrically for up to 2.5 h with no significant spectral change. Then H_2O_2 was added leading to the immediate disappearance of the MLCT bands and regeneration of the spectral pattern of the Ru(III) complex, with no evidence of formation of the $[Ru(phtpy)_2]^{2+}$ species

View Article Online
DOI: 10.1039/C7DT03658B

exhibiting a sharp MLCT band at 490 nm (Fig. S3b). This result clearly indicates that phtpy ligand does not dissociate from the reduced ruthenium complex, in agreement with the behaviour reported for cis/trans-$[Ru^{II}(DMSO)_4Cl_2]$ that promptly react with tpy generating the respective cis/trans-$[Ru^{II}(tpy)(DMSO)Cl_2]$ (tpy= 2,2':6',2''-terpyridine) complexes in high yields (>95%) without formation of $[Ru^{II}(tpy)_2]^{2+}$ species, as expected for the high stability of Ru^{II}-tpy bond.[23]

Considering that there is no significant amount of free phtpy ligand as impurity of complex 1 (as shown below by ^{1}H-NMR) to explain the formation of $[Ru^{II}(phtpy)_2]^{2+}$ complex as major product, the reaction conditions (solvents, temperature and stoichiometry of reagents) were varied in an attempt to avoid the formation of that complex (see SI Table 1). However, since all reactions gave similar results, we accepted the possibility that the $[Ru^{III}(phtpy)Cl_3]$ precursor complex is in fact releasing the coordinated phtpy ligand to generate the homoleptic complex, as well as solvated $RuCl_3$.

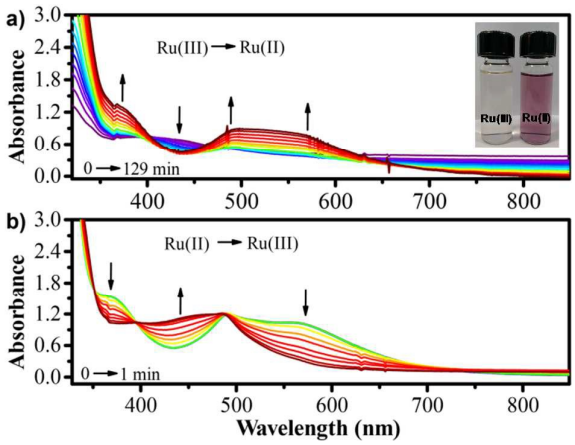


Figure 2. a) Evolution of the UV-Vis spectrum of a $[Ru^{III}(phtpy)Cl_3]$ complex suspension in methanol at 50 °C, under stirring, as a function of time up to 129 min; and photo of the initial solution and final solution; b) spectroscopic behaviour of the final purple solution as a function of time after addition of diluted H_2O_2 solution, at room temperature.

Similar experimental fact was previously reported by Ziegler et. al.[24] for a Ru^{III} complex containing a more sterically hindered 'pineno'-fused terpyridyl (L1) ligand which dissociates releasing Ru^{III} and free L1 in dilute solutions of polar solvents, that in the presence of terpyridine ligand yielded statistical mixtures of hetero and homoleptic ruthenium complexes.[25] Although the authors did not give additional evidences to confirm that behaviour, it is supportive of the fact that the terdentated terpyridine ligand may be dissociating from our precursor leading to the formation of $[Ru^{II}(phtpy)_2]^{2+}$, a quite unusual hypothesis considering the well-known high stability of chelate species and the supposed inertness of ruthenium(III) complexes.

In an effort to get stronger evidences, the supernatant solution of a $[Ru^{III}(phtpy)Cl_3]$ complex suspension in methanol, under stirring at room temperature, was monitored by transmission UV-Vis and by TLC as a function of time. In this case, the evolution of the reaction was monitored by UV-Vis reflectance spectroscopy directly at the spots in the chromatoplates (Fig. 3). The spectral profile of the supernatant solution changed continuously, as seen by the rise of the absorption bands at 390 and 490 nm, suggesting the build-up of $[Ru(phtpy)_2]^{2+}$ complex in solution. However, although the absorption band at 490 nm increased in the first 15 min, the formation of that homoleptic species was confirmed only after 2 h at room temperature (Fig. 3a). In fact, the spot in the chromatoplate with spectrum matching the authentic compound increased in size for longer reaction times, indicating that phtpy ligand is dissociating from **1** at room temperature and possibly reacting with $[Ru^{II}(phtpy)Cl_3]$ complex or solvated derivatives.

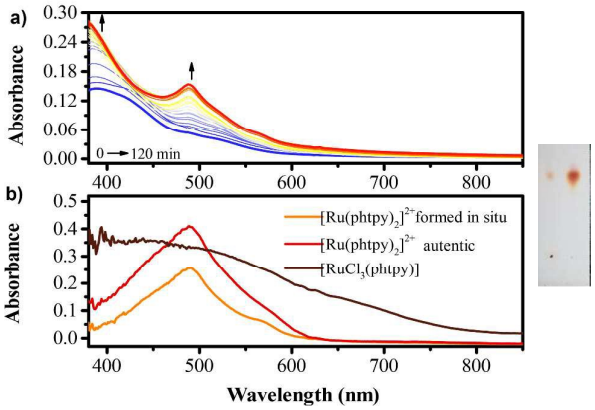


Figure 3. a) Series of UV-Vis spectra collected while monitoring a suspension of $[Ru^{III}(phtpy)Cl_3]$ complex in MeOH as a function of time for up to 2 h. Note that there is almost no $[Ru^{II}(phtpy)_2]^{2+}$ complex MLCT band at 490 nm at t = 0 min. b) UV-Vis reflectance spectrum of solid $[Ru^{III}(phtpy)Cl_3]$ precursor (brown line), of authentic $[Ru^{II}(phtpy)_2]^{2+}$ complex (red line), and the spots in the chromatoplate after TLC analysis of the supernatant solution of a $[Ru^{III}(phtpy)Cl_3]$ complex suspension in MeOH after 2 h (orange line).

Considering the well stablished inertness and stability of ruthenium(III) terpyridine derivatives, the only other possible explanation for the results described above was the presence of significant amounts of free phtpy ligand as impurity of complex **1**, thus leading to the formation of $[Ru^{II}(phtpy)_2]^{2+}$ as major product. To verify this hypothesis, we performed a careful characterization of the $[Ru^{III}(phtpy)Cl_3]$ complex used as precursor by ^{1}H-NMR spectroscopy in search of organic impurities, particularly free phtpy ligand.

The ^{1}H-RMN spectrum of complex **1** in DMSO-d_6 is characterized by the presence of signals spanning from -37 ppm to 10 ppm (see SI Fig. S4). All signals in the high field region below 1 ppm, and at 7.31 ppm and 9.70 ppm were assigned to the $[Ru^{III}(phtpy)Cl_3]$ complex, whereas the five peaks indicated with stars can be attributed to the respective reduced Ru(II) species. As expected, the paramagnetic effect

View Article Online
DOI: 10.1039/C7DT03658B

due to the presence of S=1/2 low spin Ru(III) ion is changing the local magnetic field and strongly shifting most of the phtpy ligand signals to higher fields. It is also evident the broadening of the peaks corresponding to the oxidized species such as the peaks at 7.31 ppm and -35.81 ppm, respectively attributed to the $H_{3'}$ and H_6 (see Figure S4), as expected for the shortening of the nuclear spin relaxation time of the coordinated ligand protons[26]. Notice also the presence of four signals in the 7.5-9.0 ppm range (labelled with dots) assigned to the phtpy ligand coordinated to a diamagnetic center.[23]

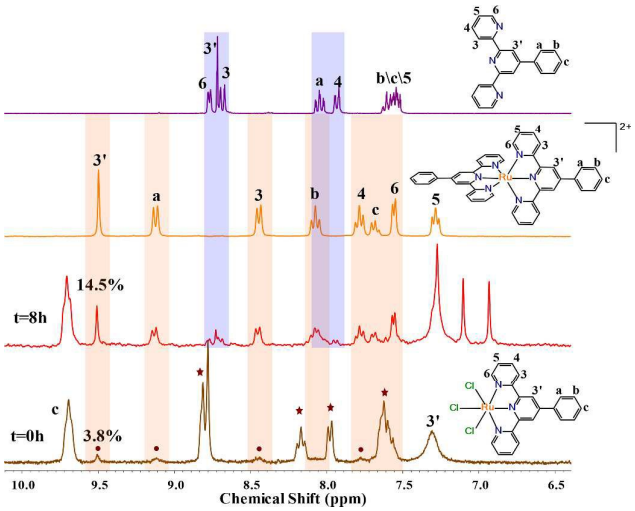


Figure 4. ^{1}H-RMN in DMSO-d_6 of the $[Ru^{III}(phtpy)Cl_3]$ complex contaminated with the respective reduced species (t=0h, brown line), the $[Ru^{II}(phtpy)_2]^{2+}$ complex (orange line), free phtpy ligand (purple line) and the solution obtained after heating a suspension of 1 in EtOH for 8 h (red line).

Accordingly, a typical sample of the $[Ru(phtpy)Cl_3]$ complex used as precursor in the preparation of ruthenium terpyridine derivatives is a mixture of the Ru(III) and Ru(II) species formed during its preparation, where the solvent methanol acts as a weak reducing agent.[25,27] The weak signals labelled with dots perfectly matched the spectrum of $[Ru^{II}(phtpy)_2]^{2+}$, a complex formed as byproduct in the synthesis of $[Ru^{III}(phtpy)Cl_3]$.[26,28] It is important to remember that the amount of this impurity (about 4%) is much smaller than that found after reaction of $[Ru(phtpy)Cl_3]$ complex with the $dpimbH_2$ ligand (can reach up to 54% under conditions shown in scheme 1), thus not being enough to explain its presence as major reaction product.

Finally, a dispersion of 1 in methanol under stirring for eight hours at 60 °C was dried in a flash evaporator, and its ^{1}H-NMR spectrum in DMSO-d_6 (Figure 4) compared with the spectrum of phtpy ligand, the $[Ru^{II}(phtpy)_2]^{2+}$ and freshly prepared solution of the $[Ru^{III}(phtpy)Cl_3]$ complex. This was found to contain a mixture of **1** and its respective reduced species, as well as a small amount of $[Ru^{II}(phtpy)_2]^{2+}$ complex as impurity, as discussed above. After 8 h at 60°C in methanol, however, the amount of this homoleptic species increased to 14.5% and the signals assigned to the reduced $[Ru^{III}(phtpy)Cl_3]$ species decreased, while the weak signals of the free phtpy ligand (indicated in light purple) increased concomitantly.

This result clearly demonstrates that the oxidized species dissociates releasing free phtpy ligand, which in turn is reacting with reduced $[Ru^{II}(phtpy)L_1L_2L_3]$ species generating the homoleptic complex, while more compound **1** reduced species is slowly generated in solution. Notice that there is no significant amount of reduced ruthenium precursor left, yet the peaks of initially absent free phtpy ligand can now be observed in the spectrum of the solution after 8 h (Fig. 4), strongly indicating that chelating ligand is in fact dissociating from the $[Ru^{III}(phtpy)Cl_3]$ complex. This seems to be the driving force pushing the reaction towards the formation of $[Ru^{II}(phtpy)_2]^{2+}$ as the major reaction product. In fact, reactions of the bis-bidentated ligand $dpimbH_2$ with the $[Ru^{II}(phtpy)Cl_3]$ complex, prepared by previous reduction of **1** with zinc amalgam, successfully lead to the formation of the desired binuclear complexes in high yield, indicating that the back-bonding interactions in the reduced species strengthen the Ru^{II}-phtpy bonds and weakens the Ru^{II}-Cl bonds facilitating the chloro ligand substitution reactions. The expected binuclear complex was also obtained upon reaction of $dpimbH_2$ with $[Ru(bpy)_2Cl_2]$ in suitable conditions. This behaviour seems to parallel that of Fe(III/II) complexes with bidentated polypyridyl ligands such as bpy, phen and tpy,[29,30] whose Fe(II) complex formation constants are significantly much larger than that of the respective Fe(III) complex because of the major contribution of π-backbonding. Thus, Ru(III)-phtpy bond should have much higher ionic character than expected and suggest to be weaker than Ru(III)-Cl bonds because of the favourable electrostatic contribution absent in the first one, despite of its low spin nature, in contrast with the highly covalent Ru(II)-phtpy bond. In fact, the bidentated polypyridyl ligands of the $[Ru^{II}(bpy)_2Cl_2]$ and $[Ru^{II}(phen)_2Cl_2]$ complexes have no tendency to dissociate, in contrast with the chloro ligands that tend to dissociate more promptly.

Conclusions

Summarizing, the improbable dissociation of the phtpy ligand from the $[Ru^{III}(phtpy)Cl_3]$ complex was demonstrated by the espontaneous formation of the $[Ru(phtpy)_2]^{2+}$ complex in methanol, ethanol and DMF solution, as confirmed by UV-vis and ^{1}H-NMR spectroscopy, as well as by TLC and column chromatography. In fact, its reduction with a strong reducing agent (zinc amalgam) completely shut down that process indicating that the Ru(II)-tpy bond is highly stabilized by π-back-bonding, whilst the Ru(III)-tpy bond has much higher than expected ionic character and lower bond strength as confirmed by the unexpected lability of that terdentated polypyridyl ligand from a Ru(III) complex.

Experimental

Instrumentation and methods.

View Article Online
DOI: 10.1039/C7DT03658B

The ^{1}H-NMR spectra were acquired in a Bruker AIII 300 MHz spectrometer using samples dissolved in pure deuterated solvents or mixtures of deuterated solvents, in order to generate 2-3 mg/500 µL solutions, using TMS as internal reference. ESI-MS spectra were recorded in a Bruker Daltonics Esquire 3000 plus mass spectrometer using samples dissolved in *N,N*-dimethylformamide diluted in methanol just before injection, setting the capillary voltage to 4 kV. Elemental analyses of the samples were recorded in a Perkin Elmer 2400 series II elemental analyzer equipped with a thermal conductivity detector. The electronic spectra of the compounds in the UV-Vis region (190 nm to 1100 nm) were recorded in a Hewlett Packard 8453A spectrophotometer. The UV-vis absorption and reflectance spectra were registered respectively in a HP8453A diode-array spectrophotometer (190-1100 nm range), employing 1.00 cm optical path length quartz cuvettes, and in a FieldSpect 3 fiber optic spectroradiometer from Analytical Spectral Devices (350-2500 nm range). Thin layer chromatography was carried out using silica gel 60 F_{254} TLC chromatoplates employing acetone:methanol:KNO_3(saturated solution) 3:2:1 as eluent mixture.

The percentage yields calculations by ^{1}H-NMR were realized by comparing the peak areas normalized with respect to the H_3' proton peak, which has a integration value corresponding to 2 protons in the phtpy complexes, to determine their relative amounts in the mixtures. The experiment shown in figure 2 were carried out using a solution of 1 mg of [Ru(phtpy)Cl_3] dispersed in 25 mL of MeOH, whereas the experiments shown in figure 3 used a suspension of 2 mg of [Ru(phtpy)Cl_3] in 4 mL of MeOH.

Synthetic Details

All solvents and reactants were of analytical grade and employed as received, without further purification.

4-phenyl-2,2':6',2''-terpyridine (phtpy) ligand. This polypyridyl ligand was prepared by following a modified Kröhnke reaction for the synthesis of substituted terpyridines.[20, 31] 1g (9.4 mmol) of benzaldehyde was transferred to a 250 mL round-bottom flask containing 40 mL of a 0.3 M KOH solution in ethanol. After 10 minutes of stirring at room temperature, 2.2 g (19 mmol) of 4-acetylpyridine and 27 mL of NH_4OH 28% were added into. Four hours later the precipitate dispersed in a yellow-green solution was collected, washed with ethanol and water, and dried under vacuum to obtain a greenish solid, which yielded a white solid after two times recrystallization from ethanol. Yield: 60%. CHN Analysis %found (%calc) for $C_{21}H_{15}N_3 \cdot 4H_2O$: C 81.76 (81.53); H 4.99 (4.89); N 13.53 (13.58).

[Ru^{III}(phtpy)Cl_3] precursor complex.[20] 0.27 g (1 mmol) of $RuCl_3 \cdot 3H_2O$ was transferred into a two-necked round-bottom flask of 100 mL and dissolved with 70 mL of ethanol. Then, a saturated solution of the phtpy ligand in chloroform was slowly added into the ruthenium complex solution employing an addition funnel, while keeping the temperature constant at 70 °C. After three hours of reflux, the reaction mixture was cooled to room temperature and the brown precipitate filtered out and washed with water and ethanol. The solid was dispersed in hot ethanol, filtered and washed with hot ethanol to get the final product. Yield 60%. CHN Analysis %found (%calc) for $C_{21}H_{15}Cl_3N_3 \cdot 4H_2O$: C 45.00 (45.62); H 3.25 (3.46); N 7.28 (7.60).

Reduction of the [Ru^{III}(phtpy) Cl_3] complex with Zn amalgam. Zinc amalgam was prepared by transferring granulated Zn pellets into a 250 mL erlenmeyer, activating them by washing tree times with a 50% v/v aqueous HCl solution, and reacting with $HgCl_2$ powder under manual shaking for five minutes. The bright amalgamated Zn pellets were carefully washed with distilled water, then with methanol, and immediately added into a suspension of the [Ru^{III}(phtpy)Cl_3] complex in methanol, previously purged with nitrogen gas. The solution color changed from brown to bluish-violet and no precipitate remained after 30 min, indicating the complete reduction of the ruthenium(III) complex, as confirmed spectrophotometrically (no further spectral change). The pellets were removed while N_2 gas was continuously bubbled in the solution to keep an inert atmosphere, thus avoiding re-oxidation by O_2 in air.

Conflicts of interest

There are no conflicts to declare

Acknowledgements

Authors gratefully acknowledge the financial support by the Brazilian Agencies Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq 302368/2010-8 and 133876/2015-2), and Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP 2013/24725-4). PAB thanks Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES) for the fellowship.

Notes and references

1 C. K. Prier, D. A. Rankic and D. W. C. MacMillan, *Chem. Rev.*, 2013, **113**, 5322–5363.
2 K. C. Gupta and A. K. Sutar, *Coord. Chem. Rev.*, 2008, **252**, 1420–1450.
3 R. G. Wilkins, in *Kinetics and Mechanism of Reactions of Transition Metal Complexes*, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, FRG, 2nd edn., 2003, pp. 199–256.
4 D. T. Richens, *Chem. Rev.*, 2005, **105**, 1961–2002.
5 J. E. Barclay, S. C. Davies, D. J. Evans, S. A. Fairhurst, C. Fowler, R. A. Henderson, D. L. Hughes and K. E. Oglieve, *Transit. Met. Chem.*, 1998, **23**, 701–713.
6 G. W. Luther, D. T. Rickard, S. Theberge and A. Olroyd, *Environ. Sci. Technol.*, 1996, **30**, 671–679.
7 H. Ma, C. Wan and A. H. Zewail, *Proc. Natl. Acad. Sci. U. S. A.*, 2008, **105**, 12754–7.
8 S. V. Wegner and J. P. Spatz, *Angew. Chemie Int. Ed.*, 2013,

View Article Online
DOI: 10.1039/C7DT03658B

52, 7593–7596.
9 H. Irving and R. J. P. Williams, *J. Chem. Soc.*, 1953, **0**, 3192.
10 J. R. Khusnutdinova, N. P. Rath and L. M. Mirica, *J. Am. Chem. Soc.*, 2010, **132**, 7303–7305.
11 M. Bröring, C. D. Brandt, A. F. Volpe and V. Lynch, *Chem. Commun.*, 2003, **11**, 2156–2157.
12 H.-L. Jiang, D. Feng, K. Wang, Z.-Y. Gu, Z. Wei, Y.-P. Chen and H.-C. Zhou, *J. Am. Chem. Soc.*, 2013, **135**, 13934–13938.
13 C. Gomes Silva, I. Luz, F. X. Llabrés i Xamena, A. Corma and H. García, *Chem. - A Eur. J.*, 2010, **16**, 11133–11138.
14 M. D. Kärkäs, O. Verho, E. V Johnston and B. Åkermark, *Chem. Rev.*, 2014, **114**, 11863–2001.
15 A. S. Goldstein, R. H. Beer and R. S. Drago, *J. Am. Chem. Soc.*, 1994, **116**, 2424–2429.
16 R. E. White and T. P. Hanusa, in *Encyclopedia of Inorganic Chemistry*, John Wiley & Sons, Ltd, Chichester, UK, 2006.
17 T. Matsubara and C. Creutz, *J. Am. Chem. Soc.*, 1978, **100**, 6255–6257.
18 R. C. Rocha, K. Araki and H. E. Toma, *Transit. Met. Chem.*, 1997, **23**, 13–16.
19 K. Araki, F. N. Rein, S. G. Camera and H. E. Toma, *Transit. Met. Chem.*, 1992, **17**, 535–538.
20 T. A. Matias, A. P. Mangoni, S. H. Toma, F. N. Rein, R. C. Rocha, H. E. Toma and K. Araki, *Eur. J. Inorg. Chem.*, 2016, **2016**, 5547–5556.
21 T. Ohno, K. Nozaki and M. Haga, *Inorg. Chem.*, 1992, **31**, 4256–4261.
22 M. Haga, T. Matsumura-Inoue and S. Yamabe, *Inorg. Chem.*, 1987, **26**, 4148–4154.
23 R. Ziessel, V. Grosshenny, M. Hissler and C. Stroh, *Inorg. Chem.*, 2004, **43**, 4262–4271.
24 M. Ziegler, V. Monney, H. Stoeckli-Evans, A. Von Zelewsky, I. Sasaki, G. Dupic, J.-C. Daran and G. G. A. Balavoine, *J. Chem. Soc. Dalt. Trans.*, 1999, **109**, 667–676.
25 U. Schubert, H. Hofmeier and G. R. Newkome, *Modern terpyridine chemistry*, Wiley-VCH, 2006, pp. 44-45.
26 M. P. Santoni, A. K. Pal, G. S. Hanan, A. Proust and B. Hasenknopf, *Inorg. Chem. Commun.*, 2011, **14**, 399–402.
27 E. D. Dikio, *E-Journal Chem.*, 2011, **8**, 1006–1013.
28 A. K. Pal, N. Zaccheroni, S. Campagna and G. S. Hanan, *Chem. Commun. (Camb).*, 2014, **50**, 6846–9.
29 S. H. Toma, J. J. Santos, R. G. Velho, M. Nakamura, H. E. Toma and K. Araki, *Electrochim. Acta*, 2012, **66**, 287–294.
30 J. J. Santos, S. H. Toma, P. M. Lalli, M. F. Riccio, M. N. Eberlin, H. E. Toma and K. Araki, *Analyst*, 2012, **137**, 4045.
31 A. M. W. Cargill Thompson, *Coord. Chem. Rev.*, 1997, **160**, 1–52.