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Inorganic Chemistry Communications 6 (2003) 1400–1405
INORGANIC CHEMISTRY COMMUNICATIONS
www.elsevier.com/locate/inoche

(Terpyridine)(acetylacetonate)ruthenium(II) complex with a zwitterionic form of phosphoniophenylcyanamide ligand

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Received 5 June 2003; accepted 21 August 2003
Published online: 28 September 2003

Abstract

The complex [Ru(tpy)(acac)(PPh_4cyd)][PF_6] (where tpy: 2,2′:6′,2″-terpyridine, acac: acetylacetone and PPh_4cyd: 4-triphenylphosphoniophenylcyanamide) has been synthesized. It contains the zwitterionic form of the phosphoniophenylcyanamide ligand. Characterizations were carried out using IR, ES-MS, UV–Vis, electrochemistry and ^1H, ^{13}C and ^{31}P NMR spectroscopy.

Keywords: Ruthenium(II) complex; Cyanamide; NMR; Zwitterion; Phosphonium

1. Introduction

Our previous work led to the synthesis of [Ru(tpy)(bpy)Ipcyd)]$^+$ (where Ipcyd: 4-Iodophenylcyanamide anion) [1]. The strategy was to find good candidates giving a strong interaction between distant paramagnetic sites following the building blocks approach [2]. Unfortunately, the desired paramagnetic form of the complex (Ru(III) state) could not be reached because of the proximity in energy of the ruthenium and cyanamide orbitals making the ruthenium impossible to oxidize. In the present work, we have replaced the bipyridine ligand with a better donor group such as acetylacetone which has shown its capacity to tune the redox potential of ruthenium complexes [3]. The Iodophenylcyanamide ligand was chosen for two reasons: firstly, because of the NCN's efficiency to mediate electronic or magnetic interactions [4] and secondly, because iodide has proven to be an efficient reaction center for further metal-catalyzed coupling reactions [5]. Here, we show the successful synthesis of a new neutral building block [Ru(tpy)(acac)Ipcyd)] and an unexpected result, the obtaining of [Ru(tpy)(acac)(PPh_4cyd)]$^+$ which contains a zwitterionic form of the phosphoniophenylcyanamide ligand. This last is shown in Scheme 1.

As well as the synthetic work, we also present here the characterization of the complex through a series of procedures including, UV–Vis spectroscopy, mass spectrometry, electrochemistry and detailed NMR.

2. Experimental

2.1. Materials

All chemicals and solvents were reagent grade or better. [Ru(tpy)Cl_3] [6] and 4-Iodophenylcyanamide (IpcydH) [1] were prepared according to literature procedures. Weakly acidic Brockmann I type alumina (Aldrich) was used. All manipulations were carried out under an atmosphere of dry Ar.

2.2. Physical measurements

Electrospray spectra (positive mode) were obtained with a Perkin–Elmer Sciex (Nermag R10-R10). IR were

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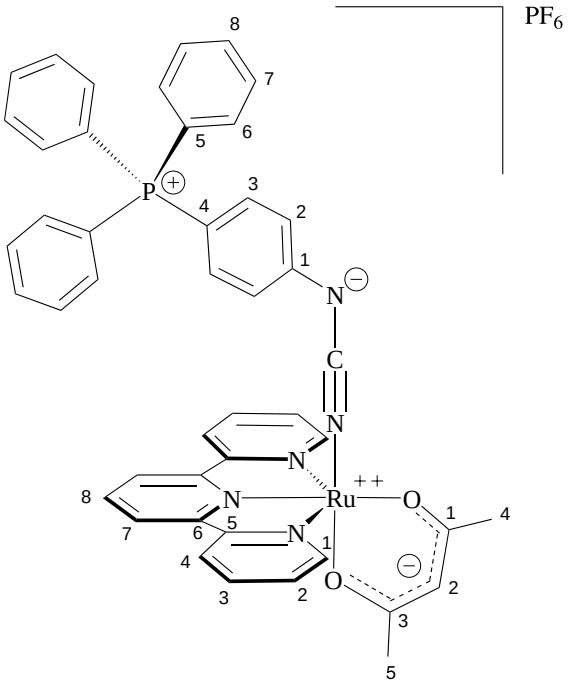
doi:10.1016/j.inoche.2003.08.016



Scheme 1. Schematic drawing of $[Ru(tpy)(acac)(PPh_4cyd)]^+$.

recorded in KBr pellets on a Perkin–Elmer FT-IR 1725. UV–Vis electronic spectra were obtained with a Shimadzu UV-3100. Cyclic voltammograms were obtained with an Autolab system (PGSTAT100) (0.1 M tetrabutylammonium hexafluorophosphate, TBAH as supporting electrolyte) at 25 °C. A three electrode cell was used comprising a 1 mm Pt-disk working electrode, a Pt wire auxiliary electrode, and an aqueous saturated calomel (SCE) reference electrode. NMR spectra were recorded on a Bruker AMX400 spectrometer equipped with a 5 mm triple resonance inverse probe with dedicated ^{31}P channel operating at 400.13 MHz for ^{1}H, 161.97 MHz for ^{31}P and 100.61 MHz for ^{13}C. All chemical shifts for ^{1}H and ^{13}C are relative to TMS using ^{1}H (residual) or ^{13}C chemical shifts of the solvent as a secondary standard. ^{1}H, ^{13}C $\{^{1}H\}$, ^{13}C $\{^{1}H, ^{31}P\}$ and ^{31}P $\{^{1}H\}$ spectra were recorded at 293 K in CD_2Cl_2.

Signal assignments were made with the aid of gradient-enhanced ^{1}H COSY45. ^{1}H–^{13}C correlation spectra using a gradient-enhanced HMQC sequence (delay was optimized for $^{1}J_{CH}$ of 140 Hz) was obtained with 40 scans per increment. A gradient-enhanced HMBC experiment was performed allowing 62.5 ms for long-range coupling evolution (176 scans were accumulated). All 2D experiments were realized with phosphorus selective decoupling. Typically, 2048 t_2 data points were collected for 256 t_1 increments. The FID along t_1 was zero-filled to 512 points prior to Fourier transformation.

1D selective DPFGSE-NOE [7] were obtained with a mixing time of 800 ms. Gradients were sine shaped in all experiments with durations of 1 or 1.7 ms. The selective pulse used were all gaussians truncated at the 1% level. Durations of the shaped pulses were kept as short as possible.

2.3. Syntheses of complexes

2.3.1. [*Ru*(*tpy*)(*acac*)*Cl*] (**1**) (*blue grey*)

The synthesis was adapted from a literature procedure [3]. Ethanol (150 ml) was added to $Ru(tpy)Cl_3$ (440 mg, 1.0 mmol). The apparatus was flushed with Ar, then triethylamine (1.5 ml, 11 mmol) and acetylacetone (acac) (0.5 ml, 5 mmol) were added using a plastic syringe. Upon addition, the dark brown solution turned a deep red. The solution was heated under reflux for 4 h. The resulting violet solution was evaporated to dryness to leave a dark green solid. Dichloromethane (100 ml) was added and the solution was then stirred under Ar for 10 min, before being filtered through Celite and washed with dichloromethane until the filtrate was clear. The solution was concentrated (~30 ml) and hexane (50 ml) was added to it to precipitate the final product of [Ru(tpy)(acac)Cl] which was then filtered and washed consecutively with hexane, water and diethyl ether before being air dried (0.289 g, 61.6%). NMR ^{1}H (CD_2Cl_2 $\delta = 5.35$): 8.72 (2H, d, 5.6 Hz), 8.16 (2H, d, 8.1 Hz), 8.09 (2H, d, 7.9 Hz), 7.84 (2H, ddd, 7.5, 6.3 and 1.7 Hz), 7.53–7.54 (2H, dd, 5.6 and 1.4 Hz and 1H, dd, 7.5 and 8.1 Hz), 5.40 (1H, s), 2.49 (3H, s), 1.27 (3H, s). Anal. Calcd. (%) for $C_{20}H_{18}ClN_3O_2Ru \cdot 1/2(CH_2Cl_2)$: C, 48.1; H, 3.6; N, 8.5. Found: C, 48.7; H, 3.6; N, 8.5.

2.3.2. [*Ru*(*tpy*)(*acac*)*Ipcyd*] (**2**) (*dark blue*)

An ethanol/water mixture (200:40 ml) was added to **1** (393 mg, 0.83 mmol), and the blue solution was then degassed for 10 min, before $AgBF_4$ (486 mg, 2.5 mmol) was added, at which the solution turned green. The solution was left at reflux for 4 h. The solution was allowed to cool down before being filtered through Celite and washed with ethanol. The solution was then concentrated before being degassed. IpcydH (1.68 g, 6.88 mmol) was added to the solution, and it was then left under Ar at 40 °C for 48 h, after which the solution was then allowed to cool before being evaporated to dryness. This was then dissolved in dichloromethane and was purified using column chromatography (acidic alumina, solvent: dichloromethane, eluent: 1% ethanol:dichloromethane). The column produced nine bands, the first was a pale yellow, corresponding to the free ligand, the second was a pale violet/pink, followed by a white band. After this was a dark blue band, then another white band followed by a violet band, a dark blue, a pale blue and a red band. The first dark blue band was collected and then evaporated to dryness to yield a lacquer of **2** (120 mg, 25%). NMR ^{1}H (CD_2Cl_2 $\delta = 5.35$): 8.70 (2H, d, 5.6 Hz), 8.15 (2H, d, 8.1 Hz), 8.08 (2H, d, 8.1 Hz), 7.90 (2H, ddd, 8.1, 7.5 and 1.5 Hz), 7.60–7.52 (2H, dd,

7.5 and 5.6 Hz and 1H, t, 8.1 Hz), 7.06 (2H, d, 8.7 Hz), 5.88 (2H, d, 8.7 Hz), 5.37 (1H, s), 2.52 (3H, s), 1.37 (3H, s). MS (ES, CH_3CN): $[M + H^+]^+ = 678.1$; calcd. 677.99. $[Ru(tpy)(acac)(HCN) + H^+]^+ = 462.0$. IR: $\nu_{NCN} = 2176$ cm^{-1}. Anal. Calcd. (%) for $C_{27}H_{22}IN_5O_2Ru$: C, 47.9; H, 3.3; N, 10.4. Found: C, 47.3; H, 2.5; N, 9.8.

2.3.3. [*Ru*(*tpy*)(*acac*)(*PPh*$_4$*cyd*)][PF_6] (**3**) (*violet*)

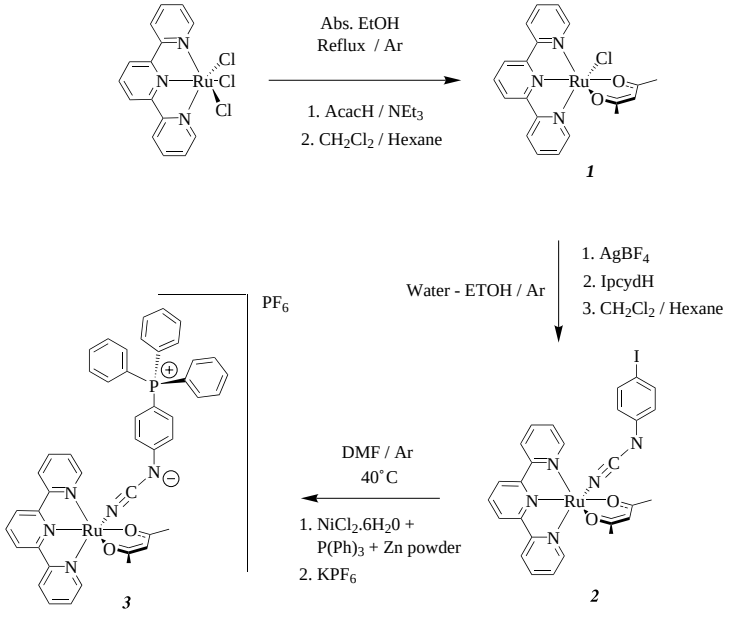
Dimethylformamide (5 ml) was added to $NiCl_2 \cdot 6H_2O$ (43 mg, 0.18 mmol) and triphenyl phosphine (191 mg, 0.71 mmol), which caused the solution to turn blue. The solution was degassed before activated zinc (80 mg, 1.24 mmol) was added to the solution, which immediately turned green. The solution was then left for 90 min, during which time the solution changed color from green, through yellow and orange, to orange/red before it was heated to 40 °C, and after 30 min of heating the solution had turned brick red. **2** (120 mg, 0.18 mmol) was then dissolved in dimethylformamide, degassed, and added to the brick red solution, which turned dark blue. The reaction was then left overnight. A saturated solution of KPF_6 (15 ml) was added to the solution to form a precipitate, which was filtered through a sinter and left to air dry. The precipitate was redissolved in dichloromethane and purified using column chromatography (acidic alumina, solvent: dichloromethane, eluent: 1% ethanol:dichloromethane). At first there were two separate bands on the column, but the second band merged with the first to yield an impure product. This was then recrystalized using dichloromethane/ether to leave a powder corresponding to the title complex **3** (86 mg, 50%), which was filtered through a sinter and left to air dry. IR (KBr pellet, cm^{-1}): $\nu_{NCN} = 2181.4$ cm^{-1}, $\nu_{PF_6} = 847.0$ cm^{-1}. MS (ES) *m*/*z*: calcd. for $C_{45}H_{37}N_5O_2PRu$ $(M–PF_6)^+$ 812.17. Found 812.3. Anal. Calcd. (%) for $C_{45}H_{37}F_6N_5O_2P_2Ru$: C, 56.5; H, 3.9,; N, 7.3. Found: C, 55.3; H, 3.7; N, 7.1.

3. Results and discussion

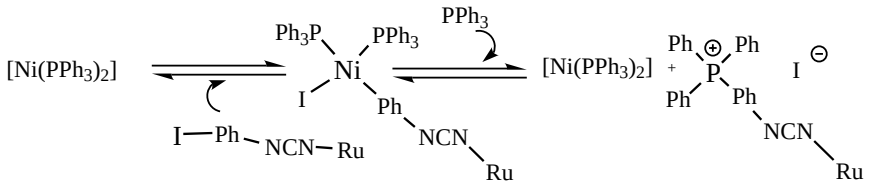
3.1. Synthesis

The synthesis of [Ru(tpy)(acac)Cl] (**1**) and [Ru(tpy)(acac)Ipcyd] (**2**) were adapted from literature procedure [1,3]. A general scheme is shown in Scheme 2.

[Ru(tpy)(acac)Cl] (**1**) was prepared from the appropriate $Ru(tpy)Cl_3$ and the appropriate β-diketone. $Ru(tpy)Cl_3$ was placed in ethanol with a 5-fold excess of β-diketone and an 11-fold excess of triethylamine, and heated at reflux for 4 h. The triethylamine serves as a reducing agent toward the $Ru(tpy)Cl_2$ and possibly as a deprotonating agent for the β-diketone. The solvent was removed, and the residual solid was reprecipitated from methylene chloride and hexane. Product purity was evaluated by cyclic voltammetry and thin layer chromatography. The chloride ligand on Ru(tpy)(acac)Cl is easily displaced in refluxing ethanol/water by adding $AgBF_4$, permitting the synthesis of [Ru(tpy)(acac)L], where L is an anionic ligand such as 4-Iodophenylcyanamide (or Ipcyd). This ligand is of particular interest since it can serve as precursor to bimetallic complexes [8]. The utility of the [Ru(tpy)(acac)Ipcyd] complex as starting material is illustrated here by its capability to form [Ru(tpy)(acac)(PPh_4cyd)][PF_6] (**3**) in the presence of stoechiometric amount of Ni(II)Cl_2, triphenylphosphine



Scheme 2. General scheme of synthesis.



Scheme 3. Mechanism of formation of the phosphonium salt, Ru being the abbreviation for Ru(tpy)(acac).

and zinc powder in DMF. The mechanism of the reaction seems to involve oxidative addition of the aryl halide to a nickel(0)–phosphane complex, followed by the reductive elimination of the phosphonium ion and a loss of the halide ion from the metal center as it is shown on Scheme 3 [9].

Initially, under these conditions, we expected to get the homometallic dimer [10] and in this aspect, it did not lead to the formation of the desired complex. Instead of that, at the homocoupling step the complex appears to have reacted with the PPh_3 to give a phosphine compound. One possible explanation is that the electron rich environment around the metal and the cyanamide group were helping to stabilize the positive charge on the phosphorus thus stabilizing the phosphine compound **3**.

3.2. NMR spectroscopy

In the present study, ^1H, ^{13}C and ^{31}P NMR spectroscopy were used for the characterization of the [Ru(tpy)(acac)(PPh_4cyd)][PF_6] complex. This study was performed at 293 K, a temperature at which it was clear that rotation around all the phosphorus phenyl bonds was rapid on the NMR time scale. All the ^1H and ^{13}C signals were unambiguously assigned on the basis of chemical shifts, spin–spin coupling constants, splitting patterns and signal intensities, and by using ^1H–^1H COSY, ^1H–^{13}C HMQC and ^1H–^{13}C HMBC experiments. The ^1H and ^{13}C chemical shifts as well as proton–proton, proton–phosphorus and carbon–phosphorus coupling constants are given in supplementary materials. The ^{31}P NMR spectrum of the complex displayed a singlet at 24.4 ppm.

For the triphenylphosphoniophenylcyanamide unit, the ^1H NMR spectrum (Fig. 1) shows a typical AA′MM′NX spin system pattern for the triphenylphosphine protons (A = H_{PHOS6}, M = H_{PHOS7}, N = H_{PHOS8}, X = P) with $^3J_{AM} = {}^3J_{A'M'} = 7.2$ Hz, $^3J_{MN} = {}^3J_{M'N'} = 7.5$ Hz, $^4J_{AN} = {}^4J_{A'N} = 1.2$ Hz, $^4J_{AA'} = {}^4J_{MM'} = 1.0$ Hz and $^5J_{AM'} = {}^5J_{A'M} = 0.6$ Hz obtained from computer simulation. The proton spectrum shows also an AA′MM′X pattern for the phenylcyanamide protons (A = H_{PHOS2},

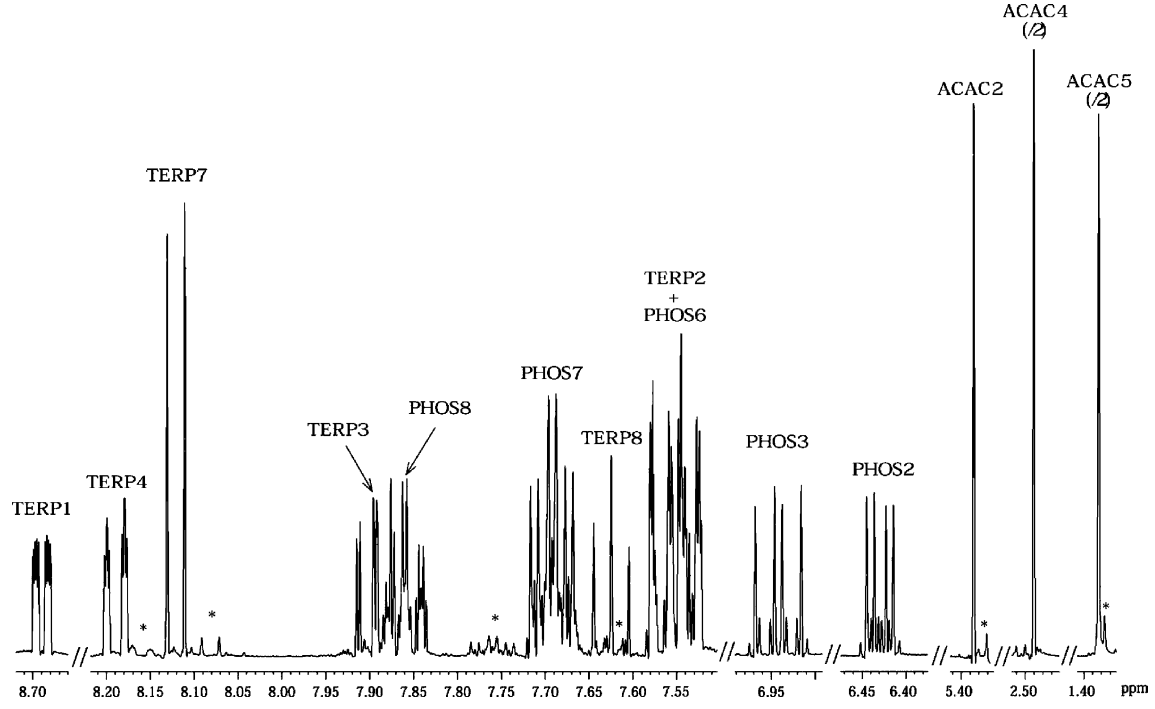


Fig. 1. 1H NMR spectra of [Ru(tpy)(acac)(PPh_4cyd)][PF_6] complex in CD_2Cl_2 at 293 K (* are mainly due to traces of unreacted materials such as [Ru(tpy)(acac)Cl]).

Table 1
UV–Vis and electrochemical data

Complex	UV–Vis data[a] λ/nm ($\varepsilon/10^3$ M^{-1} cm^{-1})					Redox potentials[a,b] $E_{1/2}$/mV (ΔE, mV)
1	279	320	402	563	629	251
	(26.6)	(20.3)	(7.8)	(5.3)	(3.6)	(83)
2	277	301	390	568	634	244
	(51)	(38)	(10.2)	(5.5)	(5.1)	(88)
3	277	316	382	560	624	381
	(62.9)	(57.1)	(37.7)	(9.4)	(7.7)	(68)

[a] In CH_2Cl_2.
[b] Versus SCE, 0.1 V/s.

M = H_{PHOS3}, X = P) with $^3J_{AM} = {}^3J_{A'M'} = 8.4$ Hz, $^4J_{AA'} = {}^4J_{MM'} = 2.2$ Hz and $^5J_{AM'} = {}^5J_{A'M} = 0.0$ Hz.

In the $^{13}C\{^1H\}$ NMR spectrum (supplementary materials), the phenyl carbons are observed in the usual aromatic region except for the strongly shielded C_{PHOS1} signal (δ 97.0) and the strongly deshielded C_{PHOS4} signal (δ 162.8). These chemical shifts can be tentatively explained by π electron density transfer within the delocalized π system. The cyanamide carbon signal appears as a broad singlet (δ 123.4, half-height linewidth 8 Hz) [11].

The terpyridine unit is symmetrical with one set of signals for the central pyridine and one set of signals for the two equivalent terminal pyridines.

The acetylacetone unit is unsymmetrical with two C=O resonances C_{ACAC1}, C_{ACAC3} (δ_C 187.2, 187.1), two methyl resonances C_{ACAC4} and C_{ACAC5} (δ_H/δ_C 1.38/27.2 and 2.48/28.5) and one methine resonance C_{ACAC2} (δ_H/δ_C 5.38/99.3) in the ^1H and ^{13}C spectra. The deshielded H_{ACAC4} resonance can be explained by a localization of these protons in the deshielding cone of the pyridine rings and possibly also of the phenylcyanamide ring. This hypothesis was confirmed by the observation of weak NOE correlations of H_{ACAC4} with the terpyridine H_{TERP1} protons and with the phenylcyanamide H_{PHOS2} in 1D NOE experiments (supplementary material). The same 1D NOE experiment applied to H_{ACAC5} shows only a NOE correlation with the methine H_{ACAC2}.

3.3. Redox and spectroscopic properties

Cyclic voltammetry (CV) data for the complexes are given in Table 1. The $E_{1/2}$ potentials were determined from the average of the anodic and cathodic peak potentials. All the waves are reversible with peak to peak separation of about 70–80 mV. Compounds **1** and **2** have almost the same $E_{1/2}$ potentials (251 vs 244 mV) because of the anionic character of the ligand (Cl or Ipcyd) which stabilizes the Ru(III) state. However, for compound **3**, the wave is shifted to more positive potentials (381 mV), ca. 150 mV more than **1** and **2**. This would agree with the increasing acceptor character of the ligand due to the cationic charge on the phosphonium substituent compared to the unsubstituted ones. In addition, for compound **2**, one can notice an irreversible process with an anodic peak around 1000 mV and a cathodic peak at 650 mV, These two waves are very probably due to irreversible oxidation of Iodophenylcyanamide ligands as demonstrated by our previous studies on [Ru(tpy)(bpy)Ipcyd] [1]. These irreversible waves are also present for compound **3** but with the anodic peak shifted to higher potentials (1400 mV) even though the cathodic peak stays at the same potential (650 mV).

UV–Vis data are shown in Table 1. Absorption bands look like the same in shape but differ in intensity. Three regions can be distinguished. In the UV region, the two intense bands (around 280 and 320 nm) are attributable to terpyridine ligand ($\pi \rightarrow \pi^*$). In the visible region, the two lower energy absorption bands (between 560 and 634 nm) are more MLCT in character, i.e., $d\pi(Ru(II)) \rightarrow \pi^*(tpy)$ [1]. The band which lies between 382 and 402 nm in the three complexes is more controversial. Its intensity in complex **3** and presence in complex **1** suggest that it could be an intra-ligand charge transfer which is enhanced in complex **3** because of the strongly polarized N^-–Ph–P^+ entity.

In conclusion, this work presents the successful coupling of a phosphine onto a new iodo-functionalized Ru(II) complex leading to a stable cationic ruthenium complex containing a zwitterionic form of a phosphoniophenylcyanamide ligand which represents an advancement in chemical knowledge. Progress are made to use this iodo-functionalized Ru(II) complex, [Ru(tpy)(acac)Ipcyd)] as starting material for building long dinuclear complex which can be seen as molecular wires useful for molecular electronics.

Supplementary materials

Table with NMR spectral data for [Ru(tpy)(acac)(PPh_4cyd)][PF_6] complex in CD_2Cl_2; Figure A: ^{13}C NMR spectrum of [Ru(tpy)(acac)(PPh_4cyd)][PF_6] complex in CD_2Cl_2 at 293 K; Figure B: 1D DPFGSE-NOE

with selection of H_{PHOS2} proton in CD_2Cl_2 at 293 K (mixing time 600 ms); Figure C: idem with H_{ACAC4}; Figure D: idem with H_{ACAC5}; Figure E: idem with H_{TERP1}.

Acknowledgements

We thank the European Union for an ERASMUS scholarship (L.D., M.H. and D.R.) and the ''Service d'analyse'' of LCC (Laboratoire de Chimie de Coordination) and the 'Service commun de spectrométrie de masse' of UPS (Université Paul Sabatier).

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