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Photoinduced synthesis and electrochemical properties of new ruthenium(mono)bipyridine dialkylcyanamide and propiononitrile complexes

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Abstract

Photochemical exchange of carbonyls was used to produce new ruthenium dialkylcyanamide and nitrile compounds [$RuCl_2$(bpy)(CO)($NCNMe_2$)] (**2**), [$RuCl_2$(bpy)(CO)($NCNEt_2$)] (**3**), and [$RuCl_2$(bpy)(CO)(NCEt)] (**4**) from *trans*(Cl)-[$RuCl_2$(bpy)$(CO)_2$] (**1**). The reaction energetics, steric effects and electronic effects induced by the dialkylcyanamide and nitrile ligands were studied using computational DFT methods and cyclic voltammetry. In all cases the photochemical exchange reaction favors rearrangement of the ligands and formation of the *trans*(Cl,L)-[$RuCl_2$(bpy)(CO)L] (L = $NCNMe_2$, $NCNEt_2$ or NCEt) isomer as the main products. The oxidation potential of the complexes decreases with the increase of the HOMO energy and of net electron-donor character of the ligands, the dialkylcyanamides (whose electrochemical Lever E_L ligand parameter has been estimated) behaving as stronger net electron donors than propiononitrile or CO. The electronic effect of the dialkylcyanamide and nitrile ligands is also reflected into the HOMO–LUMO energy difference, which is slightly reduced compared to the original dicarbonyl compound **1**. The computational results show that the geometry of the isomer plays also an important role in the determination of orbital energies.

Keywords: Ruthenium; Bipyridine; Carbonyl; Photolysis

1. Introduction

Ruthenium(II) polypyridines, such as bipyridines and phenanthrolines, have attracted a lot of interest because of their catalytic, photochemical and photophysical properties. Sensitizer and luminescent properties of such complexes and the possibility to use them as photo-redox catalysts or sensitizers for reduction or oxidation of water have been among the original reasons for the interest [1]. Use of ruthenium(II) polypyridines as dyes in sensitized photovoltaic cells has also been a subject of intense study over the past decade [2]. Furthermore, mixed ligand complexes with polypyridines and carbonyls have been investigated as potential catalysts in several processes including CO_2 reduction and catalysts for water gas shift reaction [3].

It is well known that the chemical and electrochemical properties of ruthenium polypyridine complexes can be effectively modified by manipulating the ligand sphere of the metal. This can be done either by adding peripheral substituents on polypyridine rings or by varying the metal coordinated ligands [2d,4]. For example, thiocyanate ligands have been used to enhance the absorption properties of ruthenium(II) bipyridine complexes. One of the most commonly used dye in dye-sensitized photovoltaic cells, [$Ru(NCS)_2$(dcbpy)$_2$] (dcbpy = 4,4′-dicarboxylic acid-2,2′-bipyridine), takes advantage of this effect. The thiocyanate

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derivative has proved to be superior compared to the halide containing $[RuCl_2(dcbpy)_2]$ [2c,2d]. Especially, ligands with strong electron-donating character, such as dialkylcyanamides, can be expected to have high impact on the electrochemical properties of the complexes. Although it has been well established that dialkylcyanamides form complexes with several metals, including Re, Mo, Cr, Fe and Pt [5], ruthenium complexes are rare. The ruthenium phosphine derivative *trans*-$[(dppe)_2Ru(\eta\text{-}H_2)(NCNMe_2)]$ {where dppe is diphenylphosphinoethane} is one of the few reported ruthenium dialkylcyanamides [6].

Photolytic reactions of bipyridine containing ruthenium, osmium and rhenium carbonyls have been used to obtain several solvent coordinated complexes [7,8]. Photoirradiation of *trans*(X)-$[RuX_2(bpy)(CO)_2]$ (X = Cl, Br, I) in the presence of suitable coordinating solvents, such as CH_3CN, CH_3OH, or CH_3CH_2OH has been shown to lead to replacement of a carbonyl by the solvent molecule [7a,7b,7c,8]. It has been suggested that the excitation of *trans*(Cl)-$[RuCl_2(bpy)(CO)_2]$ is followed by fast removal of CO resulting in the formation of a 5-coordinated intermediate and finally attachment of the acetonitrile ligand [7c]. In extended reactions the second carbonyl as well as the chlorides can be replaced [7b]. Without suitable strongly coordinating solvent or ligand, the irradiation can still result in the loss of a carbonyl but in such case it is typically followed by the formation of dimeric $[RuCl_2(bpy)(CO)]_2$ [9].

In the current paper we have used the photosubstitution technique for the synthesis of new dialkylcyanamide ($NCNR_2$) and propiononitrile (NCEt) complexes of ruthenium. The electrochemical behavior of the photoproducts has been studied by cyclic voltammetry and the contribution of the nitrile and dialkylcyanamides to the frontier molecular orbitals is discussed. We also studied the computational reaction energies of the photochemical formation of dialkylcyanamide and propiononitrile containing ruthenium(II) bipyridine complexes and the electronic effects induced by this type of nitrogen ligands by computational DFT methods. We have earlier studied the electronic effects induced by peripheral bipyridine substituents on ruthenium bipyridine complexes [4t]. The effects were monitored by following the changes in the HOMO–LUMO energy gap, spectroscopic properties and electrochemical behavior. The same approach has now been applied to novel ruthenium dialkylcyanamides.

2. Results and discussion

It has been found, that in acetonitrile solutions the photochemical replacement of the first carbonyl in *trans*(Cl)-$[RuCl_2(bpy)(CO)_2]$ (**1**) is combined with a rearrangement of the ligands [7b]. Similar rearrangement has also been observed in ethanol solution [8b]. In the current work, we studied further the rearrangement by using $NCNMe_2$, $NCNEt_2$, and NCEt as the coordinating ligand. The dialkylcyanamide reactions are summarized in Fig. 1.

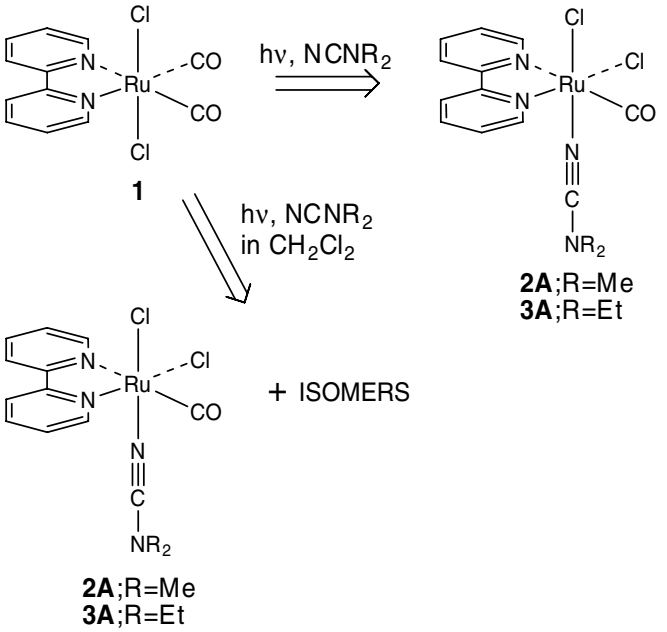

Fig. 1. Photolysis of *trans*(Cl)-$[RuCl_2(bpy)(CO)_2]$ (**1**).

When *trans*(Cl)-$[RuCl_2(bpy)(CO)_2]$ (**1**) was irradiated with UV light in dialkylcyanamide solution without any additional solvent the two initial CO bands (2066, 2003 cm^{-1} in CH_2Cl_2) in the IR spectrum gradually disappeared within an hour and a new single band appeared at ca. 1965 cm^{-1} (in CH_2Cl_2), clearly indicating the replacement of one of the carbonyl ligands.

Reaction in both dimethylcyanamide (R = Me) and diethylcyanamide (R = Et) produced selectively the *trans*(Cl,$NCNR_2$)-isomer of $[RuCl_2(bpy)(CO)(NCNR_2)]$ (**2A** and **3A** in Fig. 2). Since the starting compound was pure *trans*(Cl)-$[RuCl_2(bpy)(CO)_2]$ isomer (OC-6-13-$[RuCl_2(bpy)(CO)_2]$), the formation of the *trans*(Cl,$NCNR_2$) (isomer **A**, Fig. 3) product requires reorganization of the ligands. Similar reorganization from a *trans* chloride starting compound to the *cis* chloride product has been observed during the photoinduced replacement of CO with MeCN [7b]. The reorganization is most likely related to the pentacoordinated intermediate $[RuCl_2(bpy)(CO)]$ [7c], which can allow such geometry change. However, if an additional solvent is used it can also affect on the geometry of the final product. When a mixture of dialkylcyanamide/CH_2Cl_2 (vol. ratio 1:15) a ca. 1:1 mixture of two isomers was obtained. The isomer mixtures were characterized by ^1H NMR and by $^{13}C\{^1H\}$ NMR. The first components were again identified as isomers **2A** and **3A**, while the second components were either the *trans*(Cl) isomer (isomer **2B** and **3B**, Fig. 3) or the *trans*(Cl,CO) complex with a chloride ligand trans to CO (isomer **2C** and **3C**, Fig. 3). Both components showed patterns of eight aromatic proton signals and ten aromatic $^{13}C\{^1H\}$ signals in the NMR spectra. Such patterns indicate that the two rings of the bipyridine ligand are unequal and the product must have different ligands *trans* to aromatic nitrogens. Clear

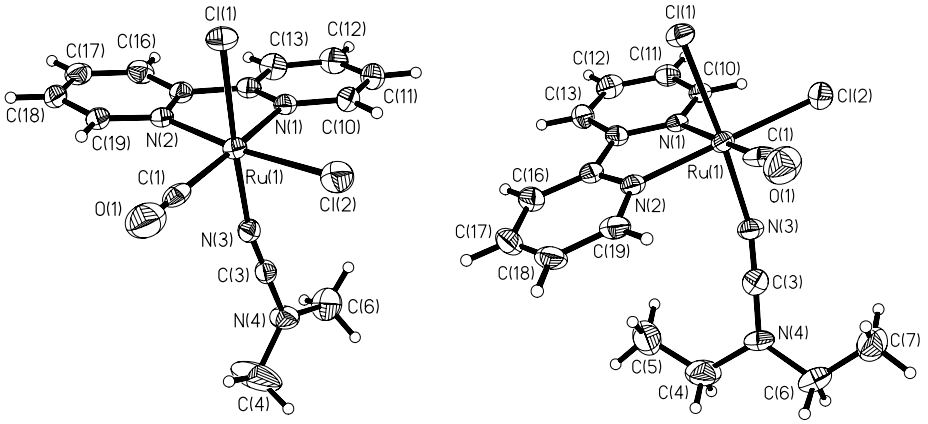

Fig. 2. Thermal ellipsoid view of *trans*(Cl,$NCNMe_2$)-[$RuCl_2$(bpy)(CO)($NCNMe_2$)] (**2A**) and *trans*(Cl,$NCNEt_2$)-[$RuCl_2$(bpy)(CO)($NCNEt_2$)] (**3A**).

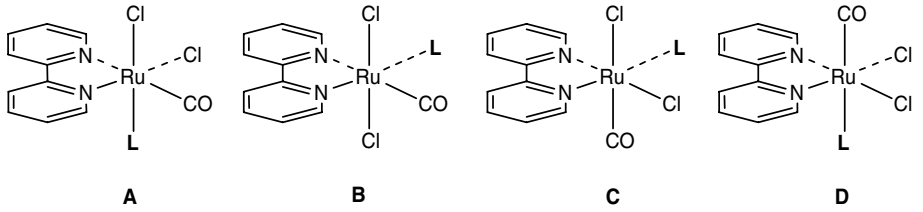

Fig. 3. Possible isomers of [$RuCl_2$(bpy)(CO)(L)] (L = $NCNMe_2$, $NCNEt_2$, NCEt and NCMe for **2**–**5**, respectively). A = OC-6-32-[$RuCl_2$(bpy)(CO)(L)], B = OC-6-14-[$RuCl_2$(bpy)(CO)(L)], C = OC-6-42-[$RuCl_2$(bpy)(CO)(L)], and D = OC-6-22-[$RuCl_2$(bpy)(CO)(L)].

splitting refers to the isomer **B**, with carbonyl and dialkylcyanamide or propiononitrile trans to bipyridine nitrogens [7b,10].

The fourth possible isomer (**2D** and **3D**, Fig. 3) should have chlorides *trans* to both bipyridine nitrogens, which would lead to a more symmetrical environment for bipyridine and the appearance of only half of the aromatic proton or carbon signals found for the other isomers [7b,10]. Formation of the **D** isomer was not observed in any experiment. In all cases the elemental analysis and NMR indicated the presence of only the monosubstituted [$RuCl_2$(bpy)(CO)($NCNR_2$)] products and no formation of [$RuCl_2$(bpy)($NCNR_2$)$_2$] was observed in any reactions run in pure dialkylcyanamides. However, use of dialkylcyanamide/CH_2Cl_2 did lead to the formation of minor amounts of side products including bi- and tri-dialkylcyanamide substituted complexes as well as the dimeric [$RuCl_2$(bpy)-(CO)]$_2$.

Photoirradiation of *trans*(Cl)-[$RuCl_2$(bpy)(CO)$_2$] (**1**) in propiononitrile followed the same basic pattern as the reaction in dialkylcyanamides and in acetonitrile reported earlier [7b]. Again the reaction was continued until the original pair of ν(CO) bands in the IR spectrum was replaced by a single band at 1962 cm^{-1}. The product contained a mixture of two isomers with ca. 75% of the dominant component *trans*(Cl,NCEt)-[$RuCl_2$(bpy)(CO)(NCEt)] (isomer **4A**, Fig. 3). Also in this reaction, the solvent had an impact on the product distribution. When a mixture of propiononitrile/CH_2Cl_2 (vol. ratio 1:2) solvent was used, a ca. 1:1 mixture of two isomers was obtained. The NMR patterns suggest that the product contained a similar mixture of isomers found in the dialkylcyanamide/CH_2Cl_2 reaction. Thus, the product distribution in the propiononitrile reactions resembles clearly the outcome of the dialkylcyanamide/CH_2Cl_2 reactions and the previously reported acetonitrile reactions [7b] where the **A** geometry (Fig. 3) is the dominating isomeric form (*trans*(Cl,NCMe)-[$RuCl_2$(bpy)(CO)(NCMe)] (**5A**)). As in the case of dialkyl cyanamides the second isomer in propiononitrile is thus most probably **4B** (Fig. 3). All the results indicate that the rearrangement of the ligands during the photosubstitution of CO is favored. Similarly, the **D** isomer is the most unfavorable one in all cases.

2.1. Electrochemistry

The electrochemical behavior of the new dialkylcyanamide and propiononitrile complexes, as well as of the parent dicarbonyl compound **1**, was investigated by cyclic voltammetry (CV) in 0.2 mol dm^{-3} [NBu_4][BF_4]/CH_2Cl_2. All compounds exhibit, apart from irreversible reductions (in the range from −1.1 to −1.9 V vs. SCE), which were not further investigated, one single-electron reversible oxidation (with $E^{ox}_{1/2}$ in the range from 1.0 to 1.9 V vs. SCE) assigned to $Ru^{II} \rightarrow Ru^{III}$ (Table 1).

Table 1
Cyclic voltammetric data for the ruthenium complexes[a]

Complex	$E^{ox}_{1/2}$ (V)
trans(Cl)-[$RuCl_2(bpy)(CO)_2$] (**1**)	1.89
trans(Cl,$NCNMe_2$)-[$RuCl_2(bpy)(CO)(NCNMe_2)$] (**2A**)	1.05
trans(Cl,$NCNEt_2$)-[$RuCl_2(bpy)(CO)(NCNEt_2)$] (**3A**)	1.03
trans(Cl,NCEt)-[$RuCl_2(bpy)(CO)(NCEt)$] (**4A**)	1.20

[a] Values in V ± 0.02 vs. SCE, measured by CV at 200 mV s^{-1} scan rate, at a carbon-disc electrode, in 0.2 mol dm^{-3} $[NBu_4][BF_4]/CH_2Cl_2$ in the presence of ferrocene as the internal standard; in case of complex **1**, the dimethylcyanamide complex **2A** was used as the internal standard.

The dicarbonyl complex **1** exhibits, as expected, the highest half-wave oxidation potential ($E^{ox}_{1/2}$ = 1.89 V vs. SCE), being followed by the monocarbonyl-propiononitrile derivative **4A** ($E^{ox}_{1/2}$ = 1.20 V vs. SCE) and these values are in accord with those (1.75 and 1.12 V, respectively, upon conversion to the SCE scale) estimated by using the Lever electrochemical parameterization method [11] based on the linear relationship (Eq. (1)) in which E is the redox potential of a complex (in V vs. NHE), E_L is the ligand parameter for each ligand, and S_M and I_M depend of the specific metal redox couple, the spin state and stereochemistry [for the current case, S_M = 0.97, I_M = 0.04; E_L = 0.99 (L = CO), 0.33 (L = NCEt), −0.24 (L = Cl), 0.259 (L = bpy)] [11]

$$E = S_M \sum E_L + I_M. \quad (1)$$

The dialkylcyanamide complexes display lower oxidation potentials (1.05 and 1.03 V vs. SCE, for the dimethyl and the diethylcyanamide compounds, respectively), in agreement with the expected [5g] stronger net electron-donor character of the dialkylcyanamide ligands compared with carbonyl or even with propiononitrile (a more effective net electron donor than CO). In fact, from the experimental oxidation potentials of complexes **2** and **3**, and by application of Eq. (1) we estimate the values of 0.27 and 0.25 V vs. NHE for E_L of the $NCNMe_2$ and $NCNEt_2$ ligands, respectively. These values are lower than those of CO and NCEt (E_L = 0.99 and 0.33 V vs. NHE, respectively) [11]. The dialkylcyanamide ligands exhibit a net electron-donor ability which is identical to that of pyridine (E_L = 0.25 V vs. NHE) [11], considerably stronger than those of organonitriles and much stronger than those of effective π-electron acceptors such as CO or N_2 (E_L = 0.68 V vs. NHE) [11].

2.2. Computational results

The energetics of the photosubstitution of CO and the geometries of the suggested photoproducts were studied by computational DFT methods. The results are summarized in Fig. 4.

The gas phase calculations predict that energetically the isomers **C** or **D** should be the most favorable ones among the complexes **2**–**5**. However, the energy differences between the isomers are relatively small, especially when compared to the high energy of 180 kJ/mol required for the removal of a carbonyl ligand from complex **1**. The maximum difference of 25 kJ/mol in favor of **D** can be found between **2A** and **2D**. Experimentally the **A** isomers are clearly the dominating ones. In fact, only **A** isomers of dialkylcyanamide and acetonitrile [7b] complexes have been isolated and characterized crystallographically. There is spectroscopic evidence of the formation of **B** and **C** isomers as discussed above, but isomer **D** is either not formed at all or it is obtained only as a minor product.

It was shown experimentally that the solvent has an impact on the product distribution. In a solvent the release

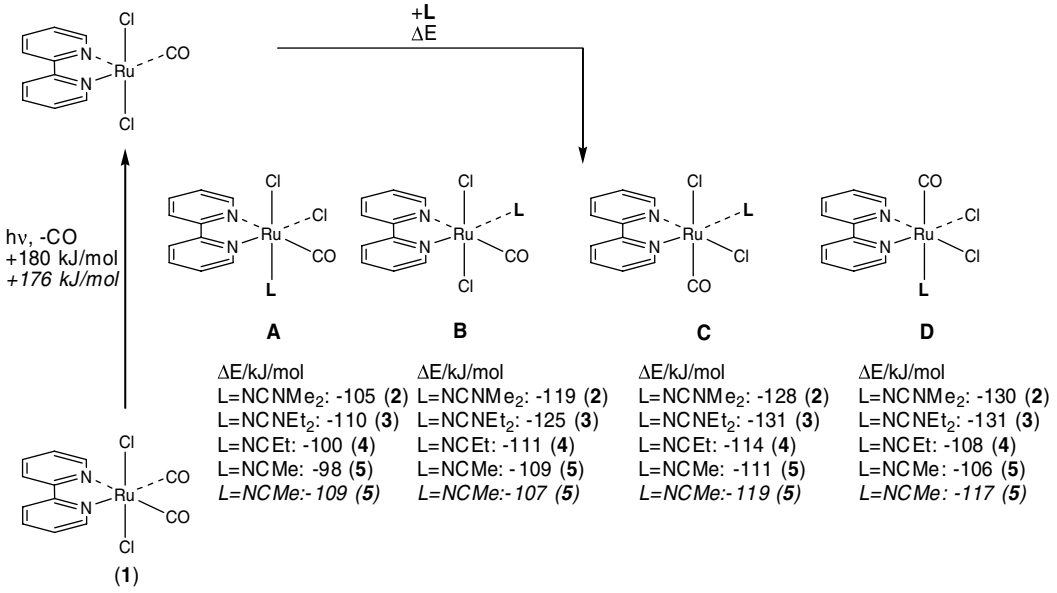

Fig. 4. Energetics of the photoreactions. The reaction energies for the addition of nitrile or dialkylcyanamide to the pentacoordinated intermediate have been calculated for all isomers **A**–**D** in gas phase. The values in italics have been obtained by using PCM solvent model.

of the carbonyl and attachment of the nitrile/dialkylcyanamide are probably more or less simultaneous processes and a pure pentacoordinated intermediate may not be formed at all. In order to estimate the effect of the solvent on the ligand exchange we reoptimized the structures of the acetonitrile compounds (**5A**–**5D**) by using the PCM solvent model (Fig. 4) [12,13]. The energy difference between the isomers was further reduced. According to the model used, the overall solvent effect on the energies was relatively small. The energy difference between the highest (**5B**) and the lowest energy isomers (**5C**) was only 12 kJ/mol. Compared to the gas phase calculations the main difference was that the isomer **A** was no longer the most unfavorable one. This also shows that the reaction energies in gas phase must be interpreted with caution. When no solvent model is used the weak intramolecular interactions between alkyl hydrogens and chloride ligands are overestimated, especially in the case of more flexible dialkylcyanamides. This overemphasis of the weak interactions affects the apparent energies favoring certain isomers. It is probable that even the PCM solvent model is not accurate enough to describe the energetics of the exchange reactions. However, both gas phase and solvent phase calculations show that energetically the isomers are very similar. Thus, the total reaction energy does not explain the experimental observation that **A** is the favored isomer. Comparison of the Ru–N(nitrile or dialkylcyanamide) bond lengths (Table 2) suggests that both the trans weakening effect caused by the carbonyl ligand and steric effects caused by bulkier dialkylcyanamides may play a role in determination of the final isomer. In all cases the optimized structures show clear elongation of the Ru–N bond in isomers **D**, where the nitrile or dialkylcyanamide ligand is opposite to CO. In the case of nitriles, Ru–N distances are practically constant among isomers **A**–**C**. However, when dialkyl cyanamides are placed in the equatorial plane with bipyridine (isomers **B** and **C**) the Ru–N bonds are already elongated compared to the **A** isomer. This refers to steric stress caused by bulkier dialkylcyanamide ligands. Similar effect is not observed with nitriles, so the steric effects are less pronounced with these compounds. To explain the isomer distribution thoroughly the properties and geometries of the transition states and excited states should also be analyzed in details.

Table 2
Calculated (gas phase optimizations) Ru–N(nitrile/dialkylcyanamide) distances (Å) in $[RuCl_2(bpy)(CO)(L)]$

	2	3	4	5
A	2.044	2.045	2.027	2.026
B	2.049	2.047	2.037	2.037
C	2.165	2.139	2.042	2.041
D	2.265	2.248	2.164	2.164

L = $NCNMe_2$, $NCNEt_2$, NCEt, and NCMe in **2**–**5**, respectively. Experimental Ru–N bond lengths are 2.043(3), 2.041(3), and 2.023(5) [7b] Å, respectively, for **2A**, **3A**, and **5A**.

The replacement of a carbonyl by dialkylcyanamide or nitrile affects the electronic properties such as the HOMO–LUMO gap and the CO stretching frequencies of the complexes. The results are summarized in Table 3.

Both nitrile and dialkylcyanamide ligands have similar affect on the LUMO energies in all four geometries **A**–**D**; the LUMO energies of the nitriles are slightly lower than the corresponding energies in dialkylcyanamide compounds. In the case of the HOMO orbitals, the effect of

Table 3
Calculated ν(CO) frequencies and HOMO–LUMO energies (gas phase optimizations) for compounds **1**–**5**

Compound	ν(CO)		Correlated ν(CO)[a]	Experimental ν(CO)[b]	HOMO (a.u.)	LUMO (a.u.)	ΔE (eV)
1	2107	2159			−0.21142	−0.10170	2.99
2A	2093		1965	1965	−0.18377	−0.08604	2.66
2B	2086		1958		−0.18194	−0.08216	2.72
2C	2081		1954		−0.19806	−0.08727	3.01
2D	2096		1968		−0.18780	−0.09116	2.63
3A	2092		1964	1965	−0.18382	−0.08611	2.66
3B	2086		1958		−0.18320	−0.08258	2.74
3C	2081		1953		−0.19732	−0.08711	3.00
3D	2097		1969		−0.18789	−0.09157	2.62
4A	2100		1971	1973	−0.18760	−0.08961	2.67
4B	2092		1964		−0.18683	−0.08648	2.73
4C	2086		1958		−0.19560	−0.09028	2.87
4D	2108		1979		−0.18354	−0.09406	2.43
5A	2101		1972	1969[c]	−0.18812	−0.09020	2.66
5B	2092		1964		−0.18761	−0.08709	2.74
5C	2086		1958		−0.19571	−0.09070	2.86
5D	2108		1979		−0.18374	−0.09457	2.43

[a] Corrected ν(CO) values have been matched with the experimental (measured in CH_2Cl_2) ones by multiplying the calculated frequencies by a factor of 0.9387.
[b] All experimental values of **1**–**4** have been measured in CH_2Cl_2.
[c] Ref. [7b] (in CH_3CN).

the ligands depends on the geometry. In **A** and **B** geometries also HOMO energies of the nitriles are lower than in the case of dialkylcyanamides but in **C** and **D** geometries the HOMOs of the nitriles are higher. This shows that the geometry has an important role in orbital energies even if the direct contribution of the nitrile and dialkylcyanamide ligands on the frontier orbitals is very small. HOMO orbitals mainly consist of ruthenium d-orbitals and p-orbitals of the chloride ligand. The lowest unoccupied orbital is almost solely formed by the π^*-orbitals of the bipyridine (Fig. 5), which is typical for this type of compounds.

The energy of the HOMO can be related to the oxidation potential ($E^{ox}_{1/2}$) and, although for the limited number of data points available (complexes **1**, **2A**–**4A**), an inverse linear relationship appears to be followed between those parameters: an increase of the HOMO energy (destabilization of the HOMO resulting from an increase of the net electron-donor character of the ligands in the order CO < NCEt < alkylcyanamides) corresponds to a lowering of $E^{ox}_{1/2}$. Similar behavior of other carbonyl, isocyanide or nitrile complexes have been reported in the literature, e.g., for some manganese [14] and rhenium [15] complexes.

The nitrile and dialkylcyanamide ligand does have a slight effect on the ν(CO) frequencies (see Table 3). In general, the nitrile compounds have higher stretching frequencies than the dialkylcyanamide ones, in accord with the stronger net electron-donor ability of the latter ligands which promotes the metal π-electron release to π^*(CO) (π-back bonding component of the metal–CO bond). However, the geometry of the molecule seems to have even stronger impact on the stretching frequencies than the type of the ligand. For all the ligands, the order of the frequencies is **D** > **A** > **B** > **C**, i.e., the highest frequencies are obtained when the nitrile or dialkylcyanamide is in the *trans* position to CO.

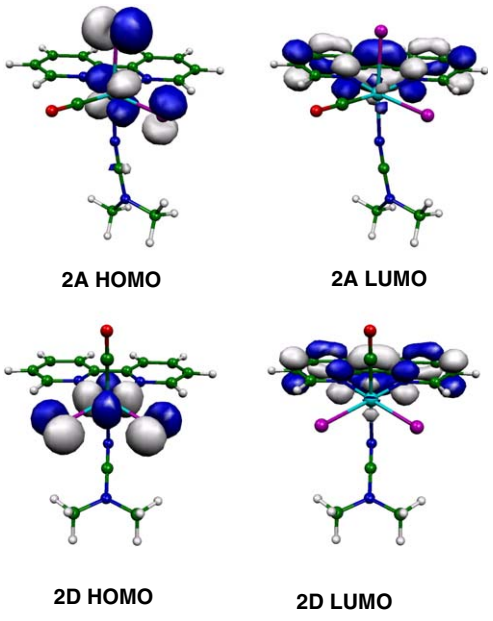

Fig. 5. HOMO and LUMO orbitals of the **A** and **D** isomers of [Ru(bpy)(CO)Cl_2(NCNMe_2)].

3. Conclusions

Photochemical carbonyl exchange is an effective method to produce nitrile and dialkylcyanamide complexes of the type [RuCl_2(bpy)(CO)(L)] (L = NCNMe_2, NCNEt_2, NCEt, or NCMe) from *trans*(Cl)-[RuCl_2(bpy)$(CO)_2$]. The process favors *trans*(Cl,L)-[RuCl_2(bpy)(CO)(L)] and involves rearrangement of the ligands. Both trans weakening effect by the remaining CO ligand in the metal coordination sphere and the steric stress caused by the bulkier dialkylcyanamides have an impact on the final geometry of the product. The isomer distribution can also be affected by the solvent used.

Electronically the dialkylcyanamide ligands are stronger net electron donors than propiononitrile or CO. Although neither the nitrile nor dialkylcyanamide have strong direct contribution to the frontier orbitals, the electronic effects induced by these ligands are reflected into the HOMO–LUMO energy difference. When compared with the original dicarbonyl compound, the energy difference is slightly decreased.

4. Experimental

4.1. Materials and instrumentation

Solvents were obtained from commercial sources and used as received. Dichloromethane for electrochemical study was dried and distilled before use. The complex *trans*(Cl)-[RuCl_2(bpy)$(CO)_2$] was prepared according to the published method [10]. C, H and N elemental analyses were carried out by use of a EA1110 CHNS-O (Carlo Erba) instrument. Infrared spectra (4000–400 cm^{-1}) were recorded on a Nicolet magna 750 FTIR spectrometer in KBr pellets and in dichloromethane solution. UV–Vis spectra were recorded on Perkin–Elmer Instruments Lambda 900 UV/Vis/NIR spectrometer. ^{1}H and $^{13}C\{^1H\}$ spectra were measured on a Bruker 250 spectrometer at ambient temperature.

The electrochemical experiments were performed on an EG&G PARC 273 potentiostat/galvanostat connected to a PC computer through a GPIB interface (National Instruments PC-2A) or on an EG&G PAR 173 potentiostat/galvanostat and an EG&G PARC 175 Universal programmer. Cyclic voltammetry (CV) experiments were undertaken in a two-compartment three-electrode cell, at a carbon-disc working electrode probed by a Luggin capillary connected to a silver-wire pseudo-reference electrode. The electrochemical experiments were performed in a N_2 atmosphere at room temperature. The potentials were measured by CV in 0.2 mol dm^{-3} [NBu_4][BF_4]/CH_2Cl_2 in the presence of ferrocene as the internal standard (unless stated otherwise), and the values are quoted relative to the saturated calomel electrode (SCE) by using the $[Fe(\eta^5\text{-}C_5H_5)_2]^{0/+}$

redox couple (E^0s = 0.525 V vs. SCE, in CH_2Cl_2). They can be converted relatively to the NHE by adding 0.245 V. The use, as the reference electrode, of the SCE or other electrode in aqueous medium, was avoided due to the sensitivity of the systems to water.

4.2. Syntheses

4.2.1. Syntheses of [$RuCl_2$(bpy)(CO)($NCNR_2$)] (L = Me (**2**) or Et (**3**)) and [$RuCl_2$(bpy)(CO)(NCEt)] (**4**) in CH_2Cl_2

trans(Cl)-[$RuCl_2$(bpy)$(CO)_2$] (**1**) (25 mg, 0.065 mmol) was dissolved in CH_2Cl_2 (15 mL). The amount of 1 mL of $NCNR_2$ (R = Me, Et) ($NCEt_2$ 12 mmol, $NCMe_2$ 16 mmol) or 7 mL of EtCN (165 mmol) was added to the solution and the reaction mixture was illuminated with a UV lamp (450 W Xe discharge lamp, Oriel model 8540). The progress of the photolysis was monitored by IR and TLC. After 1 h the disappearance of the two strong CO bands of the starting complex was observed. Simultaneously, a new peak appeared at 1965 cm^{-1} in $NCNMe_2$ or $NCNEt_2$ and at 1962 cm^{-1} in EtCN. Two alternative procedures were used to isolate the final products:

Procedure I for ***2–4***. The reaction mixture was evaporated under vacuum and the new complex was purified by column chromatography on SiO_2 (silica gel Merck 60; eluent acetone:CH_2Cl_2 = 1:1), the solvent was removed by evaporation and the crystalline residue formed was dried in air at room temperature. Yields of **2–4** were 62–67%.

Procedure II for ***2*** *and* ***3***. The reaction mixture was evaporated under vacuum until 2–3 mL and Et_2O (15 mL) was added to obtain an orange-brown precipitate. The precipitate was then filtered and dried in air. The yields of **2** and **3** were 75%.

4.2.2. Syntheses of [$RuCl_2$(bpy)(CO)($NCNR_2$)] (R = Me, Et, isomers ***2A*** *and* ***3A***) and [$RuCl_2$(bpy)(CO)(NCEt)] (isomer mixture of ***4A*** *and* ***4B***) without additional solvent

trans(Cl, $NCNR_2$)-[$RuCl_2$(bpy)(CO)($NCNR_2$)] (isomer **A**) could be synthesized selectively by irradiating *trans*(Cl)-[$RuCl_2$(bpy)$(CO)_2$] (0.065 mmol) in 2 mL of pure dialkylcyanamide solution ($NCEt_2$ 24 mmol, $NCMe_2$ 32 mmol). The UV irradiation of *trans*(Cl)-[$RuCl_2$(bpy)$(CO)_2$] (0.065 mmol) in 5 mL of propiononitrile (118 mmol) gave, in turn, an isomer mixture of [$RuCl_2$(bpy)(CO)(NCEt)] with 75% of the form **4A** and 25% of the form **4B**. The isolation of the products was carried out following the procedures I or II above and the yields were comparable with the yields in CH_2Cl_2.

4.2.3. Characterization of the products

The characterization of the isomers is based on single-crystal X-ray diffraction and NMR data. Both isomers gave separate aromatic signals in NMR for the two rings of the bipyridine ligand. Such signal pattern is indicative for a complex with different ligands *trans* to bipyridine nitrogens. The isomers **2A** and **3A** could be obtained selectively, which allowed assignment of the NMR data for these isomers. The second observed isomeric form could, in principle, be either **B** or **C**. However, the relatively clear separation of the aromatic NMR signals into two patterns indicates carbonyl and dialkylcyanamide (or propiononitrile) at the *trans* position to bipyridine nitrogens (isomers **B**). If the *trans* nitrogen positions are occupied by chloride and dialkylcyanamide (or propiononitrile), as in the case of isomer **C**, splitting of the aromatic signals is expected to be less pronounced [7b]. In the case of **4A** and **4B**, the $^{13}C\{^1H\}$ NMR spectrum could not be unambiguously assigned for the isomers.

In IR both isomeric forms **A** and **B** of compounds **2–4** gave similar ν(CO) signals. Furthermore, in CH_2Cl_2 both dialkylcyanamide products **2** and **3** were slowly decomposed to give insoluble dimeric [$RuCl_2$(bpy)(CO)]$_2$ (IR in KBr: 1948 vs ν(CO)).

*[$RuCl_2$(bpy)(CO)($NCNMe_2$)] (isomers **2A** and **2B**).* Anal. Calc. for $C_{14}H_{14}N_4Cl_2ORu$: C, 39.45; H, 3.31; N, 13.14. Found: C, 39.76; H, 3.63; N, 12.75%. TLC on Merck 60 F_{254} SiO_2 plates: R_f = 0.33 (eluent CH_2Cl_2:acetone = 1:1). IR spectrum of isomers **2A** and **2B** in CH_2Cl_2, selected bands, cm^{-1}: 1965 vs ν(CO). IR spectrum in KBr, selected bands, cm^{-1}: 2266 s ν(C≡N), 1955 vs ν(CO). UV–Vis of **2A** and **2B** in CH_2Cl_2: λ_{max}, 485 nm.

*Isomer **2A***. ^1H NMR in CD_2Cl_2, δ: 10.02 (d, 1*H*, H_6), 9.12 (d, 1*H*, $H_{6'}$), 8.24 (d, 1*H*, H_3), 8.12 (m, 2*H*, $H_{3'}$ and H_4), 7.77 (two t, 2*H*, $H_{4'}$ and H_5), 7.33 (t, 1*H*, $H_{5'}$), 2.65 (s, 6*H*, CH_3). $^{13}C\{^1H\}$ NMR in CD_2Cl_2, δ: 203.70 (CO), 157.98 (C_2), 156.94 (C_6), 155.58 ($C_{2'}$), 151.00 ($C_{6'}$), 139.30 (C_4), 137.20 ($C_{4'}$), 126.72 (C_3), 126.52 ($C_{3'}$), 123.49 (C_5), 122.55 ($C_{5'}$), 121.92 (NCN), 40.80 (*C*H_3);

*Isomer **2B***. 9.29 (d, 1*H*, H_6), 9.19 (d, 1*H*, $H_{6'}$), 8.25 (d, 1*H*, H_3), 8.17 (m, 2*H*, $H_{3'}$ and H_4), 7.77 (two t, 2*H*, $H_{4'}$ and H_5), 7.34 (t, 1*H*, $H_{5'}$), 3.04 (s, 6*H*, CH_3). $^{13}C\{^1H\}$ NMR in CD_2Cl_2, δ: 203.96 (CO), 157.69 (C_2), 157.04 (C_6), 155.47 ($C_{2'}$), 150.20 ($C_{6'}$), 139.18 (C_4), 137.05 ($C_{4'}$), 126.76 (C_3), 126.49 ($C_{3'}$), 123.34 (C_5), 122.82 ($C_{5'}$), 41.24 (*C*H_3), N*C*N was not detected.

*[$RuCl_2$(bpy)(CO)($NCNEt_2$)] (isomers **3A** and **3B**).* Anal. Calc. for $C_{16}H_{18}N_4Cl_2ORu$: C, 42.30; H, 3.99; N, 12.33. Found: C, 42.73; H, 4.27; N, 12.47%. TLC on Merck 60 F_{254} SiO_2 plates: R_f = 0.53 (eluent CH_2Cl_2:acetone = 1:1). IR spectrum of **3A** and **3B** in CH_2Cl_2, selected bands, cm^{-1}: 1965 vs ν(CO). IR spectrum of **3A** and **3B** in KBr, selected bands, cm^{-1}: 2280 s ν(C≡N), 1952 vs ν(CO). UV–Vis of **3A** and **3B** in CH_2Cl_2: λ_{max}, 488 nm.

*Isomer **3A***. ^1H NMR in CD_2Cl_2, δ: 10.00 (d, 1*H*, H_6), 9.12 (d, 1*H*, H_6), 8.25 (d, 1*H*, H_3), 8.15 (d, 1*H*, $H_{3'}$), 8.03 (t, 1*H*, H_4), 7.74 (t, 1*H*, $H_{4'}$), 7.70 (t, 1*H*, H_5), 7.30 (two m, 4*H*, $H_{5'}$), 2.28 (q, 7.4 Hz, 4*H*, CH_2CH_3), 0.88 (two t, 7.4 Hz, 6*H*, CH_2CH_3). $^{13}C\{^1H\}$ NMR in CD_2Cl_2, δ: 203.77 (CO), 157.90 (C_2), 156.83 (C_6), 155.54 ($C_{2'}$),

150.88 ($C_{6'}$), 139.39 (C_4), 137.28 ($C_{4'}$), 126.63 (C_3), 126.50 ($C_{3'}$), 123.67 (C_5), 122.71 ($C_{5'}$), 119.94 (NCN), 46.34 (CH_2CH_3), 12.73 (CH_2CH_3).

*Isomer **3B***. 9.28 (d, 1*H*, H_6), 9.14 (d, 1*H*, $H_{6'}$), 8.25 (d, 1*H*, H_3), 8.13 (m, 2*H*, $H_{3'}$ and H_4), 7.72 (m, 2*H*, $H_{4'}$ and H_5), 7.30 (t, 1*H*, $H_{5'}$), 3.23 (q, 7.4 Hz, 4*H*, CH_2CH_3), 1.34 (t, 7.4 Hz, 6*H*, CH_2CH_3). $^{13}C\{^1H\}$ NMR in CD_2Cl_2, δ: 203.78 (CO), 157.61 (C_2), 156.58 (C_6), 155.40 ($C_{2'}$), 149.97 ($C_{6'}$), 139.18 (C_4), 137.04 ($C_{4'}$), 126.60 (C_3), 126.38 ($C_{3'}$), 123.48 (C_5), 122.96 ($C_{5'}$), 119.89 (NCN), 46.88 (CH_2CH_3), 13.43 (CH_2CH_3).

*[RuCl$_2$(bpy)(CO)(NCEt)] (isomers **4A** and **4B**)*. Anal. Calc. for $C_{14}H_{13}N_3Cl_2ORu$: C, 40.89; H, 3.19; N, 10.22. Found: C, 40.70; H, 3.22; N, 9.92%. TLC on Merck 60 F_{254} SiO_2 plates: $R_f = 0.31$ (eluent CH_2Cl_2:acetone = 1:1). IR spectrum of **4A** and **4B** in CH_2Cl_2, selected bands, cm^{-1}: 1973 vs ν(CO). IR spectrum of **4A** and **4B** in KBr, selected bands, cm^{-1}: N≡C was not observed, 1962 vs ν(CO). UV–Vis of **4A** and **4B** in CH_2Cl_2: λ_{max}, 464 nm.

^1H NMR in CD_2Cl_2, δ: (**4A**): 10.03 (d, 1*H*, H_6), 9.15 (d, 1*H*, $H_{6'}$), 8.27 (t, 1*H*, H_4), 8.15 (two d, 2*H*, H_3 and $H_{3'}$), 7.86(t, 1*H*, $H_{4'}$), 7.76 (t, 1*H*, H_5), 7.37 (t, 1*H*, $H_{5'}$), 2.44 (q, 7.4 Hz, 2*H*), 1.05 (t, 7.4 Hz, 3*H*) (CH_3CH_2); (**4B**): 9.25 (d, 1*H*, H_6), 9.17 (d, 1*H*, $H_{6'}$), 8.29 (t, 1*H*, H_4), 8.13 (two d, 2*H*, H_3 and $H_{3'}$), 7.86 (t, 1*H*, $H_{4'}$), 7.69 (t, 1*H*, H_5), 7.37 (t, 1*H*, $H_{5'}$), 2.93 (q, 7.4 Hz, 2*H*), 1.46 (t, 7.4 Hz, 3*H*) (CH_3CH_2). $^{13}C\{^1H\}$ NMR in CD_2Cl_2, δ: (**4A** and **4B**): 202.06 and 201.59 (CO), 156.13, 155.68, 150.37 and 149.29 (C_6 and $C_{6'}$), 138.58, 138.51, 136.63 and 136.58 (C_4 and $C_{4'}$), 126.07 and 125.92 (C_3 and $C_{3'}$), 122.59, 122.56, 122.14 and 121.68 (C_5 and $C_{5'}$), 13.06 and 12.57 (CH_2), 10.02 and 9.73 (CH_3), CN was not detected.

4.3. X-ray crystallography

The crystals were immersed in perfluoropolyether, mounted in a cryo-loops and measured at 150 K temperature. The X-ray diffraction data were collected with a Nonius KappaCCD diffractometer using Mo Kα radiation ($\lambda = 0.71073$ Å). The Denzo-Scalepack [16] program package was used for cell refinements and data reductions. Both structures were solved by direct methods using the SHELXS-97 program with the WinGX graphical user interface [17,18]. An empirical absorption correction based on equivalent reflections was applied to all data (XPREP in SHELXTL v. 6.12) [19]. The maximum/minimum transmission factors were 0.16123/0.12509 and 0.33879/0.29185, respectively, for **2A** and **3A**. Structural refinements were carried out with SHELXL-97 [20]. All hydrogens were placed in idealized positions and constrained to ride on their parent atom. The crystallographic data are summarized in Table 4 and the selected bond lengths and angles in Table 5.

4.4. Computational work

The full geometry optimization of the structures was conducted by using the non-local hybrid density functional method B3PW91, as implemented in the GAUSSIAN 98 program [21]. The basis set was the standard 6-31G* for all elements except Ru, for which the Huzinaga's basis 433321/4331/421 was used [22]. The Huzinaga's basis set was augmented by a polarization function of p-type with an exponent of 0.086 [22]. The Hessian matrix was calculated analytically for all structures in order to verify the location of global minima (none of the structures have imaginary frequencies).

Table 4
Crystallographic data for **2A** and **3A**

	2A	**3A**
Empirical formula	$C_{14}H_{14}Cl_2N_4ORu$	$C_{16}H_{18}Cl_2N_4ORu$
F_w	426.26	454.31
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$
a (Å)	10.3237(2)	8.8920(2)
b (Å)	12.7216(2)	16.9174(4)
c (Å)	12.2844(3)	12.4909(7)
β (°)	96.5954(8)	107.097(3)
V (Å^3)	1602.68(6)	1795.96(12)
Z	4	4
ρ_{calc} (Mg/m^3)	1.767	1.680
μ(Mo Kα) (mm^{-1})	1.317	1.181
R_1[a] ($I \geqslant 2\sigma$)	0.0301	0.0363
wR_2[b] ($I \geqslant 2\sigma$)	0.0670	0.0737

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$.
[b] $wR_2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$.

Table 5
Selected bond lengths (Å) and angles (°) for **2A** and **3A**

	2A	**3A**
Ru(1)–Cl(1)	2.3931(8)	2.4003(10)
Ru(1)–Cl(2)	2.3989(10)	2.3939(11)
Ru(1)–C(1)	1.954(4)	1.882(5)
C(1)–O(1)	0.980(4)	1.084(5)
Ru(1)–N(1)	2.127(2)	2.128(3)
Ru(1)–N(2)	2.063(2)	2.067(3)
Ru(1)–N(3)	2.043(3)	2.041(3)
N(3)–C(3)	1.150(4)	1.148(5)
C(3)–N(4)	1.308(4)	1.317(5)
Cl(1)–Ru(1)–Cl(2)	92.69(3)	91.73(4)
C(1)–Ru(1)–N(3)	92.78(11)	91.81(15)
N(1)–Ru(1)–N(2)	77.88(10)	78.15(12)
Ru(1)–N(3)–C(3)	170.0(2)	162.7(3)
N(3)–C(3)–N(4)	178.3(3)	174.4(4)

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 288875 and 288876 for compounds **2A** and **3A**, respectively. Copies of this information can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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