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# Electron Transfer through Norbornadiene and Quadricyclane Moieties as a Model for Molecular Switching

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The bis(pentaammineruthenium(II)) complex of dicyanonorbornadiene has been prepared and characterized. Its photochemical conversion into a dicyanoquadricyclane complex by irradiation in methanol has been followed by UV−visible spectroscopy, IR spectroscopy, $^1$H NMR spectroscopy, and cyclic voltammetry. The dicyanonorbornadiene complex exhibits an intervalence transition in the 1000−1600 nm range when oxidized to the ruthenium(II)−ruthenium(III) state. This allows the determination of the effective coupling $V_{ab}$ through the dicyanonorbornadiene ligand, which is found as 0.023 eV. No such band is observed in the case of the dicyanoquadricyclane complex. These results show the possibility to modulate an intramolecular electron transfer process by using a photoisomerizable bridging ligand.

## Introduction

The synthesis of molecular switches is one of the major challenges in molecular electronics. A number of molecular switches have been already claimed in the literature.[1] However in none of the mentioned compounds there has been a true characterization of the fundamental property of a switch, i.e. the ability to allow or block the complete transfer of electron(s) between two parts of a structure. In the present work we describe the properties of binuclear complexes in which the metal atoms are linked by a two-state ligand containing the norbornadiene/quadricyclane moieties, using the photoisomerization scheme described in Figure 1. The intramolecular electron transfer between the two metallic sites is detected and characterized by the intervalence method, and the effect of photoisomerization of the norbornadiene moiety into quadricyclane is studied. To our knowledge, this is the first study associating photoisomerization of a bridging ligand and intramolecular intervalence electron transfer through the active part.[2]

## Experimental Section

**Dicyanonorbornadiene (dcnor)**. It was prepared according to the method of Taniguchi *et al.*[3]

Anal. Calcd for $C_9H_6N_2$: C, 76.04; H, 4.25; N, 19.70. Found: C, 75.98; H, 4.28; N, 19.98.

IR (KBr, cm$^{-1}$): 2214 (nitrile).

$^1$H NMR ($CDCl_3$ or $CD_3OD$, 250 MHz): $\delta$ 2.29 (dt, 1H, $J$ = 7.0, 1.5 Hz), 2.36 (dt, 1H, $J$ = 7.0, 1.5 Hz), 3.99 (ddd, 2H, $J$ = 1.5, 1.5 Hz), 6.88 (dd, 2H, $J$ = 1.5, 1.5 Hz). The proton nomenclature, assignments and couplings are shown on Figure 1 and Table 1.

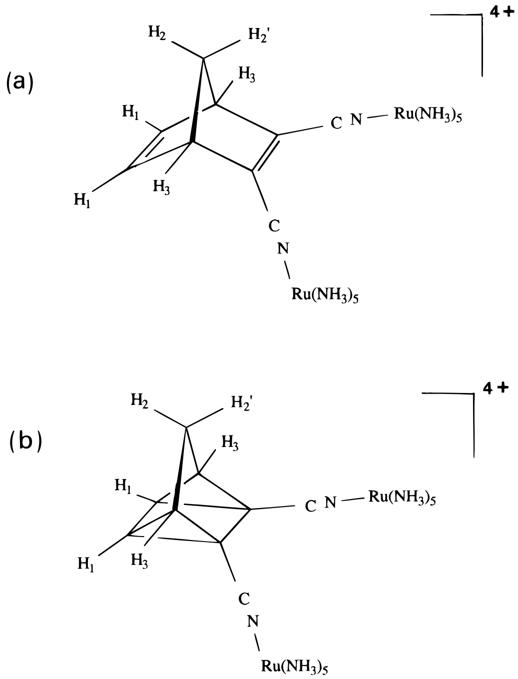

**Figure 1.** Schematic structures of (a) dcnor and (b) dcqc complexes with proton nomenclature for NMR.

**Dicyanoquadricyclane (dcqc)**. Using a modification of Edman's method,[4] 500 mg of dicyanonorbornadiene were dissolved in 500 mL of deaerated methanol and irradiated for 4 h with a Hanovia 679A mercury lamp in a photochemical reactor. Then the solvent was evaporated and the white residue was purified by chromatography on $SiO_2$ with $CH_2Cl_2$ as eluant ($R_f$ = 0.52).

IR (KBr, cm$^{-1}$): 2229 (nitrile).

$^1$H NMR ($CDCl_3$, 250 MHz): $\delta$ 2.30 (dt, 1H, $J$ = 12.5, 1.4 Hz), 2.40 (dt, 1H, $J$ = 12.5, 1.4 Hz), 2.51 (ddd, 2H, $J$ = 4.8,1.4,1.4 Hz), 2.69 (d, 2H, $J$ = 4.8 Hz). The proton nomenclature, assignments and couplings are shown in Figure 1 and Table 1. It is difficult to compare with the earlier poorly resolved 60 MHz NMR spectrum given by Edman,[4] but in the present case, the pattern of chemical shifts and couplings leaves no ambiguity for the identity of the product.

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(2) A recent report by Bonfantini and Officer (Bonfantini, E. E.; Officer D. L. *J. Chem. Soc., Chem. Commun.* **1994**, 1445) describes norbornadienes conjugatively linked to tetraphenylporphyrin and anthracene. These compounds have been synthesized with the same purpose as in the present work, but their electron transfer properties are not yet described.

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**Table 1.** $^1H$ NMR Chemical Shifts ($\delta$, ppm) and Coupling Constants (Hz) in $CD_3OD$, Where the Assignment of $H_2$ and $H_{2'}$ May Eventually Be Reverted with Respect to Figure 1

| compounds | $H_1$ | $H_2$ and $H_{2'}$ | | $H_3$ | $J_{13}$ | $J_{22'}$ | $J_{23}$ and $J_{2'3}$ | |
|---|---|---|---|---|---|---|---|---|
| dcnor | 6.88 | 2.29 | 2.36 | 3.99 | 1.5 | 7.0 | 1.5 | 1.5 |
| dcqc | 2.69 | 2.30 | 2.51 | 2.40 | 4.8 | 12.5 | 1.4 | 1.4 |
| $[Ru{-}dcnor{-}Ru]^{4+}$ | 6.72 | 2.48[a] | | 4.02 | 6 | | | |
| $[Ru{-}dcqc{-}Ru]^{4+}$ | 2.87 | 2.38 | 2.57 | 2.59 | 4 | 12 | | |

[a] Unresolved peaks due to accidental degeneracy, $H_2$ and $H_{2'}$ chemical shifts being closer in dcnor compounds than in dcqc ones.

**$[(NH_3)_5Ru{-}dcnor{-}Ru(NH_3)_5]\ (PF_6)_4$.** A 254 mg (0.49 mmol) sample of $[(NH_3)_5Ru(H_2O)](PF_6)_2{\cdot}H_2O$ prepared according to[5] was dissolved in 5 mL of deaerated acetone in a Schlenk tube. In another Schlenk tube, 34 mg (0.24 mmol) of dcnor was dissolved in 10 mL of deaerated acetone. The ligand solution was transferred by pressure gradient in the ruthenium precursor solution under argon, and the mixture was stirred for 5 h in the dark. Then it was transferred in 400 mL of sodium-dried diethyl ether. The red precipitate was collected, washed with diethyl ether, and dried under vacuum. (Yield: 192 mg, 73%.)

Anal. Calcd for $C_9H_{36}N_{12}Ru_2P_4F_{24}$: C, 9.88; H, 3.32; N, 15.35. Found: C, 9.88; H, 3.25; N, 15.30.

Mass spectrum with FAB in glycerol matrix: peak at 515.5 for $[(NH_3)_5Ru{-}dcnor{-}Ru(NH_3)_5]^{4+}$.

IR (KBr, $cm^{-1}$): 2152 (coordinated nitrile).

$^1H$ NMR ($CD_3OD$, 250 MHz): $\delta$ 2.48 (m, 2H), 4.02 (m, 2H), 6.72 (s, 2H).

**Spectroscopic Studies.** UV−vis−near-IR spectra were recorded with a Shimadzu UV-3101 PC spectrophotometer. UV−vis spectra were also recorded with a Kontron Uvikon 860 spectrophotometer. FTIR spectra were acquired with a Model IFS88 Bruker spectrophotometer. NMR spectra were recorded with a Bruker WM-250 instrument. FAB mass spectra were obtained with a Kratos MS-50 spectrometer using a *m*-nitrobenzyl alcohol matrix.

**Electrochemistry.** Cyclic voltammetry measurements were performed on Ar-purged $CH_3OH$ and dimethyl sulfoxide (DMSO) solutions in the presence of 0.1 M tetrabutylammonium tetrafluoroborate by using a three-electrode cell (Pt or glassy carbon as working electrodes, SCE as reference electrode) and an Electromat 2000 system from ISMP Technologie or an Amel 552 potentiostat coupled to an Amel 568 programmable function generator. Controlled-potential electrolyses were performed using a platinum grid as working electrode.

**Photochemistry.** Photochemical experiments were performed with a medium-pressure Hanovia 679 A mercury lamp surrounded by a Pyrex cooling jacket, with a low pressure mercury lamp, and with an Applied Physics irradiation system equipped with a 250- or 150-W xenon lamp and a high radiance monochromator. Irradiations were performed on argon-degassed $(1-2) \times 10^{-4}$ M solutions. The intensity of the monochromatic exciting light was measured by chemical actinometry with potassium ferrioxalate in the UV region[6] and, in the visible, with a calibrated Si photodiode from UDT Technologies.

In-situ irradiations were performed in NMR tubes using concentrated degassed solutions (*ca.* $5 \times 10^{-3}$ M) in $CD_3OD$. After the initial NMR spectrum was recorded, the tube was irradiated until the color had faded almost completely, and a new NMR spectrum was recorded.

**Intervalence Band Measurements.** A $1.18 \times 10^{-3}$ M solution of $[(NH_3)_5Ru{-}dcnor{-}Ru(NH_3)_5]^{4+}$ in $CD_3OD$ was prepared, and 2 mL were placed in a low height 1 cm spectrophotometric cell. The oxidation was performed by adding 50 $\mu$L aliquots of a $9.8 \times 10^{-3}$ M solution of $NBu_4^+Br_3^-$ in $CD_3OD$ with a micropipet. The optical density increased and then decreased, and the spectrum showing the maximum absorption was selected for treatment.

## Results and Discussion

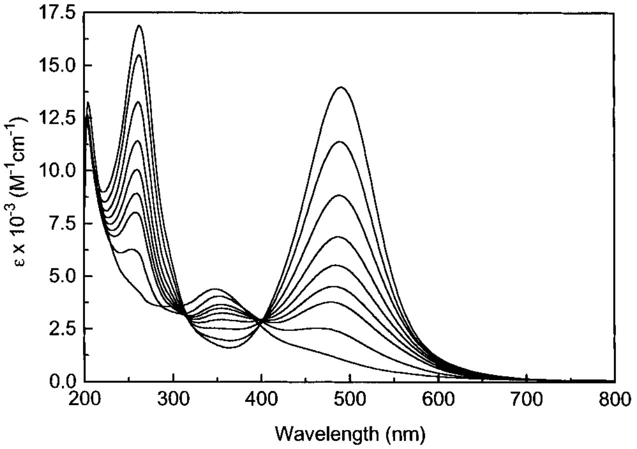

**Figure 2.** UV−vis spectra of $[(NH_3)_5Ru{-}dcnor{-}Ru(NH_3)_5]^{4+}$ upon irradiation at 532 nm in methanol.

**Ruthenium Complex of Dicyanonorbornadiene.** The bis(pentaammineruthenium) complex of dicyanonorbornadiene, $[(NH_3)_5Ru{-}dcnor{-}Ru(NH_3)_5]^{4+}$ has been prepared using the $[(NH_3)_5Ru(H_2O)]^{2+}$ precursor as for similar compounds.[5,7−9] Microanalysis, mass spectroscopy with FAB, infrared spectroscopy, and finally $^1H$ NMR spectroscopy confirm the identity of the product. Proton chemical shifts and couplings are in particular very similar to those of the free ligand. Curiously the main $^1H$ NMR difference occurs for $H_1$ protons (see Figure 1), for which $\delta$ moves from 6.88 to 6.72 upon complexation. This is attributed to the interaction between the two ethylenic bonds which transfers the perturbation induced by complexation as far as $H_1$ (Note that the existence of an interaction between the two ethylenic bonds is demonstrated by photoelectron spectroscopy of dicyanonorbornadiene.[10])

Particular attention was paid to the possibility that ruthenium fixation might have involved the outer double bond. This eventuality appears excluded by the $^1H$ NMR data (fixation on the double bond would have shifted the $H_1$ signal upfield by 3 ppm[11]) and by infrared spectroscopy (the nitrile frequency is modified and no free nitrile is observed; taking into account the stoichiometry, this leaves no possibility for an extra ruthenium).

Additional properties are consistent with the proposed formulation. Thus the UV−vis spectrum shows two bands, one at 260 nm (ligand $\pi\pi^*$) and one at 490 nm in MeOH or 535 nm in dmso (see Figure 2). This last one presents a marked solvatochromic effect as observed for $d\pi-\pi^*$ metal-to-ligand charge transfer (MLCT) transitions in $[(L)Ru^{II}(NH_3)_5]^{2+}$ complexes (L = pyridine, 4,4′-bipyridine).[7] The red shift observed for this band from methanol to DMSO can be rationalized in terms of an increased electron pair donation from the solvent molecules to the metal moieties.[7] Furthermore, its position is consistent with electrochemical data. Thus a reversible oxidation is observed at + 0.52 V vs SCE in methanol, which is ascribed to the ruthenium II/III couple. The coordinated dcnor ligand gives an irreversible cathodic wave at −1.24 V. The energy difference between metal oxidation and ligand reduction is consistent with the assignment of the 490 or 535 nm band to a MLCT transition.[7]

Coming back to the oxidation wave, no wave splitting is detected, as usual for binuclear complexes exhibiting similar metal−metal distances with weak electronic coupling.[12] Finally, cyclic voltammetry excludes also a ruthenium fixation on the double bond, because in such cases, the oxidation would occurs near 1 V.[11]

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**Attempts To Prepare Directly the Dicyanoquadricyclane Complex.** Reaction of dicyanoquadricyclane with the precursor complex $[(NH_3)_5Ru(H_2O)]^{2+}$ was performed in acetone under the same conditions as for dicyanonorbornadiene. The obtained product exhibited UV–visible and IR spectra *identical to the ones of the dicyanonorbornadiene complex*. It is clear that a back-isomerization occurs under these conditions, probably by catalysis of the quadricyclane-to-norbornadiene reaction induced by free $[(NH_3)_5Ru(H_2O)]^{2+}$. A number of similar cases involving electron rich metal complexes are described in the literature.[13] The preparation of the dicyanoquadricyclane complex is however possible by photoisomerization of the dicyanonorbornadiene complex as described below.

**Photoisomerization of the Dicyanonorbornadiene Complex.** The photochemical behaviour of the $[(NH_3)_5Ru{-}dcnor{-}Ru(NH_3)_5]^{4+}$ complex was studied in methanol and DMSO. In methanol solutions, the spectral variations upon irradiation of the complex in the MLCT or $\pi-\pi^*$ regions were qualitatively similar, showing a decrease of the intensity of the intraligand $\pi-\pi^*$ band at 260 nm and of the MLCT band at 495 nm, while a new band appeared at 350 nm (Figure 2). Isosbestic points at 317 and 400 nm were observed up to 80% conversion of the initial spectrum. For DMSO solutions, less clean spectral changes were observed, with loss of isosbestic points after a 30% conversion of $[(NH_3)_5Ru{-}dcnor{-}Ru(NH_3)_5]^{4+}$.

Informations on the relevant photochemical process were obtained from NMR of the photolyzed solutions. The NMR spectrum of a $5 \times 10^{-3}$ M solution of the complex in $CD_3OD$ showed, after photolysis, the disappearance of characteristic signals of the dicyanonorbornadiene moiety, and the apparition of new peaks characteristic of dicyanoquadricyclane (Table 1). Peak position and coupling were different with respect to those of the free ligand indicating complexation of dicyanoquadricyclane to the metal moiety. These results are consistent with a photoisomerization of the dicyanonorbornadiene complex into a dicyanoquadricyclane complex. A confirmation is given by cyclic voltammetry and IR spectroscopy. Thus after visible irradiation of $10^{-3}$ M $CH_3OH$ solutions of $[(NH_3)_5Ru{-}dcnor{-}Ru(NH_3)_5]^{4+}$, the initial Ru(II)/Ru(III) wave at +0.53 V vs SCE is replaced by a wave with anodic peak potential at +0.40 V (scan rate = 100 mV/s). This *cathodic* shift for the Ru(II)/(III) wave is assigned to a decreased back-bonding interaction between the metal unit and the coordinated dicyanoquadricyclane ligand.[14] Similar shifts have been observed for nitrile complexes of Os(II), $[Os(NH_3)_5(NCR)]^{2+}$, where changes at R modify the $\pi^*$ acceptor ability of the nitrile ligand, thus changing the extent of metal-ligand electronic delocalization ($E_{1/2}[Os(NH_3)_5(NCR)]^{2+/3+}$) = −0.17 V vs NHE for R = $-CH{=}CH_2$ and −0.29 V vs NHE for R = $-CH_3$).[15]

The decreased back-bonding interaction from $[(NH_3)_5Ru{-}dcnor{-}Ru(NH_3)_5]^{4+}$ to $[(NH_3)_5Ru{-}dcqc{-}Ru(NH_3)_5]^{4+}$is clearly demonstrated by the nitrile stretching frequencies of the two complexes. The former shows a strong $\nu$(CN) at 2152 $cm^{-1}$ while the latter shows a *ca* 10 times less intense $\nu$(CN) band at 2234 $cm^{-1}$, consistent with a smaller change in dipole moment experienced by the nitrile stretch of dicyanoquadricyclane[16,17] and a reduced metal–nitrile back-bonding.[15,18]

Photoelectrochemical experiments on DMSO solutions of $[(NH_3)_5Ru{-}dcnor{-}Ru(NH_3)_5]^{4+}$ reveal that the initial wave at +0.34 V vs SCE is replaced by a more *anodic* reversible wave at +0.51 V vs SCE, which is identical with the one observed for $[(NH_3)_5Ru(DMSO)]^{2+}$ in this medium.[19] Since the spectral changes upon irradiation show a more complex evolution than in methanol, with rapid loss of isosbestic points, we conclude that irradiation in DMSO is accompanied by decomplexation, which is favored by the high thermodynamic affinity of the ruthenium pentaammine moiety for the S-bonded DMSO ligand.[20]

The efficiency of photoisomerization of $[(NH_3)_5Ru{-}dcnor{-}Ru(NH_3)_5]^{4+}$ was studied in methanol and found to be wavelength dependent. Photoisomerization quantum yields ($\Phi_i$) of $(2.2 \pm 0.2) \times 10^{-2}$ were determined by exciting at 260 and 290 nm, while $\Phi_i$ values of $(8.3 \pm 0.6) \times 10^{-4}$ were determined upon irradiation in the MLCT region at 450, 480, 500, and 550 nm.

Photoisomerization of norbornadiene to quadricyclane derivatives have attracted much attention in the past years for the considerable amount of chemical potential energy that can be stored with these systems.[21] It has been shown that the isomerization can be effectively induced by direct[22,23] and photosensitized excitation by organic[21,24] or inorganic photosensitizers.[25] While organic compounds effectively sensitize the isomerization through a triplet–triplet energy transfer mechanism, inorganic photosensitizers, such as Cu(I) compounds, may lead to the formation of a metal–olefin complex that allows the transformation of norbornadiene to quadricyclane by direct population of a metal-to-olefin charge-transfer excited state.[25]

The lower photoisomerization quantum yields observed for $[(NH_3)_5Ru{-}dcnor{-}Ru(NH_3)_5]^{4+}$ in the MLCT region could be explained on the basis of an activated surface crossing from a lower lying $^3$MLCT state to the upper lying $^3\pi-\pi^*$ excited state, as in the case of endothermic sensitization of norbornadiene ($^3\pi-\pi^*$ energy *ca.* 70 kcal/mol) by organic photosensitizers with $^3\pi-\pi^*$ energies in the range 70–50 kcal/mol.[21,25] For the Ru–dcnor–Ru complex, however, the reactivity observed upon irradiation in the visible region does not seem to be due to thermal upconversion from the MLCT to the $\pi-\pi^*$ state given the constancy of $\Phi_i$ in the 450–550 nm spectral range. This suggests a direct involvement of the MLCT state in the photoisomerization process of the coordinated dcnor ligand, due to the weakening of the double bond by excitation in the charge transfer $d\pi(Ru)-\pi^*(dcnor)$ state. The lower reactivity exhibited by the Ru–dcnor–Ru complex with respect to the norbornadiene/Cu(I) $\pi$ complex ($\Phi_i$ = 0.2–0.3)[25] could be due to an

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(14) Cyclic voltammetry of $[Ru(NH_3)_5(CH_3OH)]^{2+}$ (obtained by dissolution of $[(NH_3)_5Ru\ (H_2O)]\ (PF_6)_2$. $H_2O$ in methanol) showed an anodic wave at −0.3 V vs SCE. Thus the +0.40 V observed in the photolysis experiment cannot be assigned to a decomplexed metal fragment.

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(18) It is known that nitrile stretching frequency is affected by kinematic coupling as well as by electronic effects arising from $\pi$-back-bonding or a $\sigma$ bond between a metal atom and the nitrogen end of the nitrile group.[15] The negative frequency shift observed between the free and complexed dcnor ($\Delta\nu = -62$ $cm^{-1}$) indicates that the dominant effect is due to back-bonding. For dcqc $\Delta\nu$ is +5 $cm^{-1}$ indicating that the kinematic coupling effect introduced by metalation prevails on the back-bonding interaction.

(19) The cyclic voltammetry of $[(NH_3)_5Ru(DMSO)]^{2+}$ (obtained by dissolution of $[(NH_3)_5Ru\ (H_2O)]\ (PF_6)_2$. $H_2O$ in DMSO) has been performed. Under these conditions, a reversible anodic wave is obtained at +0.5 V vs SCE. This shows that the substitution of the water molecule by DMSO is fast and is consistent with the report by Taube et al.[20] that the complexation by DMSO shifts strongly the redox potential of the ruthenium(II)/(III) couple toward positive values.

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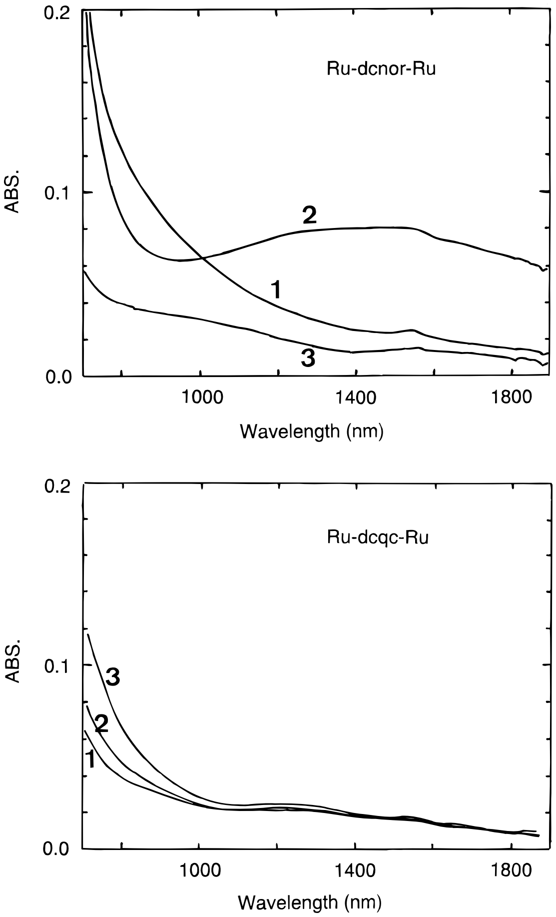

**Figure 3.** Near-IR absorption in 1 cm cells during oxidation of (top) $[(NH_3)_5Ru{-}dcnor{-}Ru(NH_3)_5]^{4+}$ ($1.2 \times 10^{-3}$ M) and (bottom) $[(NH_3)_5\text{-}Ru{-}dcqc{-}Ru(NH_3)_5]^{4+}$ ($8.9 \times 10^{-4}$ M) in $CD_3OD$: (1) starting solution; (2) half-oxidized solution (spectra uncorrected from comproportionation); (3) fully oxidized solution.

extensive electronic delocalization in the $\pi^*$ orbitals of the dicyanonorbornadiene ligand.

**Intervalence Transitions.** In order to test the ability of the dicyanonorbornadiene/dicyanoquadricyclane system to work as a molecular switch, it was necessary to study intramolecular electron transfer in the two states.

**(a) Electron Transfer through Dicyanonorbornadiene.** The ruthenium complex of dicyanonorbornadiene could be oxidized by tetrabutylammonium tribromide in $CD_3OD$, this solvent presenting a good spectral transparency up to 1900 nm. The complex concentration was $1.2 \times 10^{-3}$ M and the tribromide was $9.8 \times 10^{-3}$ M. The oxidized solution could be reduced back by Zn amalgam, showing the reversibility of the process. During oxidation, UV−visible spectra showed the progressive decay of the metal-to-ligand charge transfer band, which disappeared completely for 1 mol (2 equiv) of $Br_3^-$ per mole of complex. In the near infrared, the intervalence band was observed as a broad band centered at 1400 nm, which increased and then decreased during the process of oxidation (Figure 3).

The analysis of the intervalence band provides some insight on the degree of metal-metal coupling. Ideally, it would have been useful to determine the comproportionation constant corresponding to the equilibrium Ru(II)−Ru(II) + Ru(III)−Ru(III) $\rightleftarrows$ 2Ru(II)−Ru(III), in order to obtain the true corrected spectrum of the mixed valence complex. This was not possible in the present case, due to the difficulties of performing complete and accurate spectrophotometric titrations in small volumes of $CD_3OD$. However, we can use for qualitative purposes the value $K_c = 32$ determined by Taube *et al.* in the case of $[(NH_3)_5\text{-}Ru\text{-}1,2\text{-}dcbz\text{-}Ru(NH_3)_5]^{4+}$ (1,2-dcbz = orthodicyanobenzene),[8] which presents an anologous molecular and electronic structure. With this value, the true extinction coefficient at 1400 nm is 86 $M^{-1}$ $cm^{-1}$. The intervalence band can be fitted according to a procedure already described assuming that $\epsilon/\nu = f(\nu)$ is a Gaussian function,[26] which gives a band position of $\nu_{max} = 5950$ $cm^{-1}$, a full width at half-maximum $\Delta\nu_{1/2} = 6900$ $cm^{-1}$, and a maximum extinction coefficient of 71 $M^{-1}$ $cm^{-1}$. Introducing these values in the Hush equation[27] valid for weakly coupled (class II) mixed valence complexes gives the metal−metal coupling through the bridging ligand $V_{ab} = 185$ $cm^{-1}$ (0.023 eV). This value is close to the one observed for the bispentaammineruthenium complex of 1,2-dicyanobenzene (0.029 eV).[8] Changing the comproportionation constant from $K_c = 20$ to $K_c = 50$ changes the $V_{ab}$ coupling by only 0.001 eV.

**(b) Electron Transfer through Dicyanoquadricyclane.** A $8.9 \times 10^{-4}$ M solution of the dicyanonorbornadiene complex in $CD_3OD$ was irradiated with the medium-pressure mercury lamp in a glass vessel with stirring, while monitoring the UV−vis spectrum. When the conversion to the dicyanoquadricyclane complex was complete, after 1 h, a titration with tetrabutylammonium tribromide was performed. The consumption of $Br_3^-$ was spectrophotometrically observed, with an end point for 1 mol (2 equiv) of $Br_3^-$ as previously. In the near infrared (1000−1900 nm), some residual absorption was already present at the beginning of the titration of the photolyzed sample, *but it did not change at all upon oxidation* and thus cannot be assigned to an intervalence transition (see Figure 3). Thus the dicyanoquadricyclane complex does not present any detectable intervalence transition, at least under our experimental conditions. Assuming the same comproportionation constant as above, an upper limit of the intervalence band extinction coefficient can be estimated as 5 $M^{-1}$ $cm^{-1}$. Finally, in another version of the experiment, the original dicyanonorbornadiene complex was first half-oxidized so that the intervalence transition had its maximum intensity, and then irradiation was performed. A marked decrease of the intervalence band was observed, suggesting that the mixed valence species can also be photoisomerized.

Thus in a qualitative way, it can be said that *the conversion of the coordinated dicyanonorbornadiene moiety into a quadricyclane moiety has switched OFF the electronic interaction between the metal centers, at least from a spectroscopic point of view.*[28] For the thermal electron transfer, which is not amenable to a direct measurement, we can only say that its rate must have been severely reduced.

## Conclusion

The present study has shown that it is possible to detect the intervalence electron transfer through dicyanonorbornadiene. The conversion to the dicyanoquadricyclane complex is possible by photochemistry. Finally, the dicyanoquadricyclane complex does not exhibit any detectable intervalence transition. We consider these results constitute an important step towards the realization of a true molecular switch because photoisomerization *and* intramolecular electron transfer have been studied on the same system.

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(28) One could argue that the absence of intervalence absorption could be due to a vanishingly small comproportionation constant. This appears unlikely because even in the worst case of very weakly coupled metal centers, there is no reason for the comproportionation constant to fall below the statistical limit ($K_c = 4$). Under such conditions, there is enough mixed valence species at half-oxidation (50% of the total dimer concentration) to detect an intervalence band if its extinction coefficient is sufficient.