[$Me_2C(\eta^5\text{-}C_5H_4)_2Ru_2(CO)_4$]—An Organometallic Thermo-Optical Switch[**]

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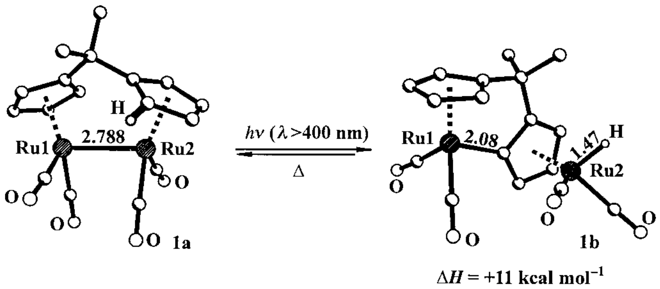
Potential applications of molecular devices and molecular machines have generated an extended area of research within the realm of supramolecular chemistry.[1, 2] Most of these systems are either based on organic units or incorporate inorganic coordination chemistry fragments.[1, 2] Besides a report by Vollhardt and co-workers, to the best of our knowledge, there are no further publications in which organometallic complexes/transformations have been applied.[3] In the latter system, reversible C–C, M–M, and M–C bond-cleavage steps were observed leading to a photochemical process, which can be thermally reversed. Recently, we have entered this area and have described a diruthenium system, in which a photochemical, albeit thermally irreversible rearrangement by Si–C bond cleavage was observed.[4] Herein, we report on the CMe_2 bridged dicyclopentadienyl diruthenium complex [$Me_2C(\eta^5\text{-}C_5H_4)_2Ru_2(CO)_4$] (**1a**) which is a fully reversible *organometallic thermo-optical* switch, that is, a photochromic system (Figure 1). When toluene or benzene solutions of complex **1a** are irradiated with a Hg medium-pressure lamp using a UV cutoff filter with $\lambda > 400$ nm, the *quantitative* and *very efficient* rearrangement to complex **1b** shown in Figure 1 was observed.[5] Both complexes **1a** and **1b** were fully characterized by one- and two-dimensional NMR spectroscopic methods and their structures unambiguously confirmed by single-crystal X-ray diffraction.[6]



yellow-orange ($\lambda_{max} = 430$ nm) **colorless** ($\lambda_{max} = 290$ nm)

Figure 1. X-ray crystal structures of complexes **1a**, **b** (selected bond lengths [Å] are shown) and their photochemical and thermal interconversion.

Based on known and estimated C–H, Ru–H, Ru–C, and Ru–Ru bond dissociation enthalpies[3, 8–11] and the aforementioned results by Vollhardt and co-workers,[3] we were suspicious that the photochemical transformation led to the thermodynamically unfavorable product **1b**. Indeed, in a quite slow reaction, clean and quantitative conversion into the starting material **1a** was observed within 1 day when complex **1b** was heated to 140 °C in a [D_8]toluene solution (Figure 1). Interestingly, the thermal reaction also took place when neat (solid) **1b** was heated to 160 °C (see below). This result clearly indicated a higher free enthalpy of the rearranged photochemical product **1b** and established a sizable barrier for the reverse thermal reaction which enabled the isolation of **1b**.

Before we address the kinetic and thermodynamic aspects of the forward and backward transformations, it should be noted that the low-yield synthesis of compound **1a** was first reported by Bitterwolf et al.[12] This group also studied the photochemistry of **1a** and isolated and crystallographically characterized the chloro substituted analogue of **1b**.[12] As a result of the absence of a UV cutoff filter, however, these reactions were not found to be clean and secondary photochemical processes involving **1b**, initiated by UV light exposure, were observed. The use of a UV cutoff filter in the photolysis experiments is therefore crucial for a complete and quantitative photochemical conversion. It allowed us to preclude photochemical pathways for the reverse reaction, which is readily apparent in that the rearranged product **1b** is colorless ($\lambda_{max} = 290$ nm) and displays no absorption band above 400 nm.

Insights into the thermodynamics of the Ru system **1a**,**b** stem from density functional theory (DFT) calculations[13] for which the Becke–Perdew 86 (BP-86)[14] and also the B3LYP[15] functionals were used. The fully geometrically optimized structures for **1a**, **b** were characterized as stationary points and displayed only slight deviations from the X-ray crystal structures with either the B3LYP or the BP-86 optimized geometries. The calculated energy differences for **1a** and **1b** are 11.3 kcal mol^{-1} for the B3LYP functional and 10.5 kcal mol^{-1} with the BP-86 functional. In both cases and in full agreement with experiment, the photochemically rearranged product **1b** was calculated to be energetically less favorable than **1a**.

The theoretical results were later confirmed experimentally by differential scanning calorimetry (DSC) measurements for compound **1b**. The transformation **1b** → **1a** was found to be irreversible and the ^1H NMR spectrum of the product obtained in these experiments displayed the signals corresponding to the pure complex **1a**. In excellent agreement with the DFT calculations, we obtained an *exothermic* enthalpy change of -11.2 kcal mol^{-1} for this process. Noteworthy is that the thermal conversion is preceded by an endothermic melting process (m.p. 125 °C, $\Delta H_{melt} = 15.8$ cal g^{-1}, 7.7 kcal mol^{-1}) of **1b**, which explains the aforementioned transformation of **1b** in the solid state.

In an attempt to gain insights into the mechanism(s) of the process presented in Figure 1, further information was sought. The transformation **1a** → **1b** is a dramatic rearrangement and includes C–H bond cleavage of the cyclopentadienyl C–H group *ortho* to the bridgehead carbon atom and rupture of the M–M bond, which is not maintained in the rearranged product **1b**. At first glance two primary, equally likely photochemical transients can be envisaged,[18] these are

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[**] This work was supported by funds of the University of Zürich. I am indebted to Prof. Heinz Berke for his generous support.

1433-7851/01/4010-1917 $ 17.50+.50/0

a) the homolytic metal–metal bond cleavage product, that is, the 17 electron ruthenium-centered diradical, $[Me_2C\{(C_5H_4)Ru^{\bullet}(CO)_2\}_2]$, for which there are ample precedents through the M–M bond homolysis in the unbridged complexes $[\{CpM^{\bullet}(CO)_n\}_2]$, where $M(CO)_n$=$Mo(CO)_3$, $W(CO)_3$ and $Fe(CO)_2$, $Ru(CO)_2$;[19–24] b) irradiation may lead to loss of a CO ligand to yield the unsaturated tricarbonyl intermediate $[Me_2C(C_5H_4)_2Ru_2(CO)_3]$, observed in a matrix-isolation study by the groups of Bitterwolf and Rest.[25] However, the latter study also clearly showed that a wavelength of <400 nm is required to induce CO loss. This is also in accordance with a wavelength selective study of the parent complex, $[\{Cp(CO)_2Ru\}_2]$, for which the $17e^-$ configured radical, $[CpRu^{\bullet}(CO)_2]$, was proposed as the primary photochemical product if visible light was used.[26]

Although we do not have conclusive mechanistic information for the photochemically initiated steps, we favor mechanism (a) in which the C–H bond activation step is preceded by the homolysis of the Ru–Ru bond. This view is supported by a bandpass restricted photolysis experiment of **1a** in the range 320–370 nm, which, along with decomposition products, gave negligible photochemical conversion into **1b**. Some additional experimental evidence was provided through a photolysis experiment of **1a** in toluene under one atmosphere of ^{13}C labeled CO. While the conversion from **1a** into **1b** was found to proceed with an essentially unchanged rate. By ^1H and ^{13}C NMR spectroscopy we could detect incorporation of the ^{13}C labeled CO group into both the starting material **1a** and the product **1b**. The CO ligand exchange in **1a** is in accordance with the well-documented small ligand-substitution barriers in $17e^-$ transients including the unbridged transient $[CpRu^{\bullet}(CO)_2]$.[27] On the other hand, fast incorporation of the isotopically labeled CO ligand in **1a**, may also be assumed by trapping of the alternative transient $[Me_2C(C_5H_4)_2Ru_2(CO)_3]$ with ^{13}CO. Since the rearrangement rate **1a** → **1b** is apparently not retarded in the presence of CO and the thermal CO exchange process has been found to be significantly slower for **1a** and **1b**, this provides some support for the homolytic cleavage product $[Me_2C((C_5H_4)Ru^{\bullet}(CO)_2)_2]$ as the reactive transient. However, this conclusion should be treated with some care since the photochemical intermediate of the exchange process may not lie on the reaction coordinate for the transformation **1a** → **1b**.

In general, photochemically generated metal-centered radicals, $[CpM^{\bullet}(CO)_n]$, are extremely short-lived transients and recombine with nearly diffusion controlled rates.[20–22, 27, 28] Hence, only sufficiently fast atom-abstraction reactions from suitable organic substrates (mostly organic halides) can compete with the radical recombination process.[19, 22, 27] Recently, however, Wayland et al. have shown that persistent metal-centered porphyrin rhodium(II) complexes are capable of *intermolecular* homolytic C–H bond cleavage even in highly inert alkanes, such as methane.[29, 30] Since the C–H bond activation step in **1a** was *intramolecular*, it might therefore compete with the recombination process of the diradical.

To shed further light on the transformation, we have investigated the reverse reaction (**1b** → **1a**) by ^1H NMR spectroscopy kinetic experiments. In the thermolysis study of **1b** in $[D_8]$toluene at 137 °C, we observed a clean first-order dependence for the disappearance of **1b** ($R^2 = 0.997$ up to 4 half lives) with a rather long half life $\tau_{1/2} = 3.5$ h ($k_{obs,410} = 5.5(1) \times 10^{-5}\,s^{-1}$). Further support for an intramolecular process was evidenced through the observation of identical thermolysis rates when the concentration of complex **1b** was doubled in these experiments. Noteworthy is that we observed a rather significant 10-fold rate enhancement of the thermolysis process in the more polar solvent acetonitrile.

Subsequently, the kinetic parameters were established from an Eyring plot of the temperature-dependent rate constants, determined in the extended temperature range 119–164 °C, which displayed an excellent linear correlation ($R^2 = 0.994$). While the derived enthalpy of activation $\Delta H^{\ddagger} = 36(1)\,kcal\,mol^{-1}$ was within our expectations, we were surprised by the *positive* entropy of activation $\Delta S^{\ddagger} = +10\,cal\,K^{-1}\,mol^{-1}$. Together with the enthalpy of activation, which is in the range of typical ruthenium–carbonyl bond-dissociation enthalpies, this hinted at CO ligand dissociation as the rate-determining step. To address this point, we determined the dependence of the rate constants on the CO concentration. The essentially linear plot ($R^2 = 0.990$) for the reciprocal observed rate constant, $1/k_{obs}$, versus [CO] seemed to support this view. However, this was questioned by the kinetic isotope effect, $k_H/k_D = 2$, which we observed in the thermolysis experiment of the 95% deuterium enriched Ru–D compound **1b**$[D_1]$. Since a maximum isotope effect of four can be estimated for the Ru–H moiety based on its stretching frequency ($\tilde{\nu}(Ru{-}H) = 2030\,cm^{-1}$), in the infrared (IR) spectrum, this also suggested a significant breaking of the Ru–H bond in the rate-determining step and therefore provided strong arguments against simple Ru–CO bond dissociation as the rate-determining step. Furthermore, by comparison with dissociative CO substitution mechanisms in organometallic complexes, we anticipated a somewhat higher entropy of activation, that is $\Delta S^{\ddagger} \approx +15{-}20\,cal\,K^{-1}\,mol^{-1}$, if the rate-determining step were purely limited by CO dissociation.[31] Nevertheless, it is certainly difficult to judge a reaction mechanism based on its entropy of activation. At present, we envisage several potential mechanistic alternatives, without further experimental (in particular thermogravimetry/mass spectrometry (TG/MS) and TG/IR measurements for **1b**) and theoretical results, we prefer not to propose a mechanism for the thermal transformation.

The overall photo-thermal equilibrium of **1a**/**1b** is the first example of a thermo-optical organometallic switch (photochromic system), based on reversible C–H bond breaking and making. We observed analogous rearrangement processes for the tricarbonyl molybdenum and tungsten systems $[Me_2C\{(C_5H_4)M(CO)_3\}_2]$, **2a-Mo** and **2a-W**.[32] In contrast to the ruthenium complex **1b**, however, the reversed thermal reactions for **2b-Mo** and **2b-W** were significantly faster, which is emphasized in that the photolysis of the molybdenum **2a-Mo** complex had to be pursued at −60 °C to slow down the thermal reaction of **2b-Mo**, which displays a low free enthalpy of activation, $\Delta G^{\ddagger}_{213} = 16\,kcal\,mol^{-1}$ ($\Delta G^{\ddagger}(\mathbf{2b\text{-}W}) = 27\,kcal\,mol^{-1}$ at 60 °C). Based on these results, it is anticipated that the thermo-optical switch properties for this class of systems can be adjusted by the proper choice of the metal and ligands. Currently, we are studying the mechanistic steps in further detail by methods including time-resolved IR spectroscopy and are also investigating potential applications.

Received: August 4, 2000
Revised: February 14, 2001 [Z15582]

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[5] Complex **1a** (212 mg, 0.437 mmol) was dissolved in toluene (80 mL) and the solution was transferred to a Teflon tap sealed (Pyrex) Schlenk tube. The tube was immersed in a vessel containing a 1M solution of $NaNO_2$ and placed 2 cm from a mercury medium-pressure lamp (125 HPKW, shielded by a Quartz jacket water cooling mantle) also immersed in the $NaNO_2$ solution. The orange toluene solution of **1a** was irradiated for ca. 4 h during which time the solution decolorized (sometimes faintly red solutions were observed in the photolysis). The reaction mixture was evaporated to dryness and the residue recrystallized from ether/pentane at $-36\,^{\circ}C$ from which complex **1b** was obtained as colorless crystals. Isolated yield of complex **1b**: (satisfactory elemental analysis) >95% in several runs. Monitoring of the photolysis of **1a** in sealed NMR tubes showed that the photolysis was essentially quantitative.

[6] Crystal data **1a**: Orange rectangular parallelepiped $0.5 \times 0.5 \times 0.2$ mm, Monoclinic cell, space group $C2/c$ (No. 15), $Z = 8$, $a = 23.825(2)$, $b = 12.566(2)$, $c = 11.485(2)$ Å, $\beta = 111.45(1)^{\circ}$, $V = 3200.3(9)$ Å^3, $\rho_{calcd} = 2.011$ g cm^{-3}. 3108 reflections collected, thereof 3035 independent; 3010 reflections with $I > 0$ used for structure solution and refinement. The refinement converged at final R values $R(I > 2\sigma(I))$ $I > 0$: $R1 = 0.0234$ and $wR2 = 0.0594$ for 264 parameters; residual electron density: 0.36, -0.56 e Å^{-3}. **1b**: Colorless rectangular parallelepiped $0.3 \times 0.3 \times 0.2$ mm; triclinic cell, space group $P\bar{1}$ No. 2, $Z = 2$, $a = 8.431(1)$, $b = 9.659(1)$, $c = 10.061(1)$ Å, $\alpha = 85.86(1)$, $\beta = 85.10(1)$, $\gamma = 85.63(1)^{\circ}$, $V = 812.2(2)$ Å^3, $\rho_{calcd} = 1.981$ g cm^{-3}. 3251 reflections collected, thereof 3049 independent; 3020 reflections with $I > 0$ used for structure solution and refinement. Final R values (264 parameters) with $I > 0$ of $R(I > 2\sigma(I))$: $R1 = 0.0194$ and $wR2 = 0.0451$; residual electron density: 0.34, -0.37 e Å^{-3}. Data collection: Siemens/Nicolet P4, $Mo_{K\alpha}$ radiation (0.71073 Å); ω scan; $4^{\circ} < 2\theta < 52^{\circ}$ at 205 K for **1a** and 170 K for **1b**. Intensities were corrected for Lorentz and polarization effects. Structure solution: Patterson method using the SHELXS-97 program package; refinement against F^2 with SHELXL-93.[7] All non-hydrogen atoms were refined anisotropically; the hydrogen atoms positions were located in the difference Fourier map and refined isotropically. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-147430 (**1a**) and CCDC-147431 (**1b**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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