Controlled haptotropic rearrangements – towards a stereospecific molecular switch based on chiral arene chromium complexes†‡

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A stereospecific molecular switch has been designed based on a reversible thermo- or photo-induced haptotropic shift of a Cr(CO)₃ fragment along a naphthohydroquinone skeleton.

The development of molecular switches is a major goal for nano-scale applications in supramolecular architectures.[2] Molecular photochromics predominate the research in this field.[3] Both organic and metal ion based switches[4] have been reported, but examples for thermo-optical switches based on organometallics are very limited; the few systems reported so far involve binuclear cyclopentadienyl complexes of ruthenium, molybdenum or tungsten.[5] A single study deals with a switchable mononuclear molybdenum complex.[6] We now report on a novel system based on a reversible migration of a tricarbonyl chromium moiety along a fused aromatic system (Scheme 1). It represents a rare example of a mononuclear organometallic species which is suited to be incorporated into a molecular switch. The coordination of the metal fragment to different rings of the aromatic ligand defines the distinct states of the system. A migration of the metal fragment from one arene ring to another is known as a haptotropic rearrangement, which has been studied in more detail for naphthalene derivatives, but may occur in more extended arene ligand systems as well.[7]

Studies employing enantiopure complexes highlight that the metal shift proceeds by an intramolecular mechanism if suitable reaction conditions are applied.[8] Both isomeric forms of the complex pair discussed in this work (**1** and **2**) are chiral, which – in principle – allows the construction of an organometallic molecular switch carrying chiral information.

Up to this point, haptotropic metal migrations were exclusively initiated by thermal induction. These rearrangements proceed irreversibly, if the regioisomeric complexes differ significantly in their thermodynamic stabilities. This is true for the pair of complexes **1** and **2**: Warming a solution of complex **1** above 50 °C generates its thermodynamically more stable regioisomer **2**. The reverse course of the reaction has been observed only for complex systems with comparable thermodynamic stabilities of the two isomeric forms. In these cases a
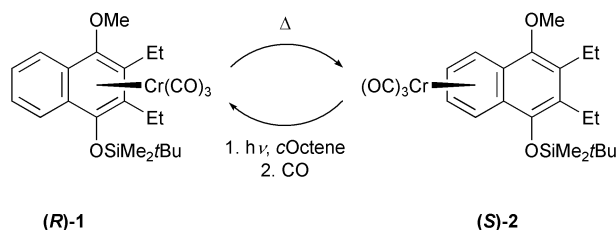
dynamic equilibrium has been detected, while the reaction was always induced thermally.[7]

Racemic tricarbonyl chromium complex **1** was synthesised *via* metal-assisted [3+2+1]-benzannulation of pentacarbonyl-[methoxy(phenyl)carbene]chromium and 3-hexyne followed by protection of the phenolic functionality with *tert*-butyldimethylsilyl chloride.[9] By this method complex **1** is obtained regioselectively as the kinetic product of the reaction.

The kinetics of the haptotropic isomerisation of benzannulation product **1** to its regioisomer **2** have been analysed in hexafluorobenzene at 333 K by NMR spectroscopy; the quantitatively proceeding reaction is of first order with a rate constant of $k = (6.5 \pm 0.7)$ s^{-1} and a free activation enthalpy of $\Delta G^{\ddagger} = (108.5 \pm 0.3)$ kJ mol^{-1}.

In order to apply different methods of induction, complexes **1** and **2** were exposed to visible light and ultraviolet radiation, respectively. Decomposition of the complexes without any evidence for a haptotropic metal shift was observed with visible light. Since UV irradiation is known to cause decarbonylation, complex **2** was reacted under CO atmosphere in order to stabilise potential dicarbonyl intermediates. Again, instead of a haptotropic rearrangement only decomposition of the complex was observed.

We then applied a strategy based on an *in situ*-stabilisation of the dicarbonyl intermediate by a suitable ligand, which should be subsequently exchanged again for CO in the dark – regenerating a tricarbonyl chromium complex. UV irradiation of complexes **1** or **2** in the presence of an excess of cyclooctene afforded a brown-black dicarbonyl cyclooctene complex, which was identified by the characteristic CO stretching frequencies in the IR spectrum.[10] Interestingly, the IR spectra were identical, regardless of which regioisomer was exposed to irradiation, indicating the formation of the same complex intermediate in both cases for which structures **3** and **4** have to be discussed (Fig. 1). The thermolability of the dicarbonyl cyclooctene complex hampered its isolation and further characterisation. After complete removal of one equivalent CO the irradiation was stopped, and the solution was flushed with a slight stream of CO in the dark. The colour of the solution slowly brightened until an orange colour typical for tricarbonyl chromium complexes remained. By this method only the thermodynamically less favoured isomer **1** was obtained (59%) along with some de-metalated hydroquinone as a by-product (35%). This result suggests that the photo-substitution has produced cyclooctene complex intermediate **3**.
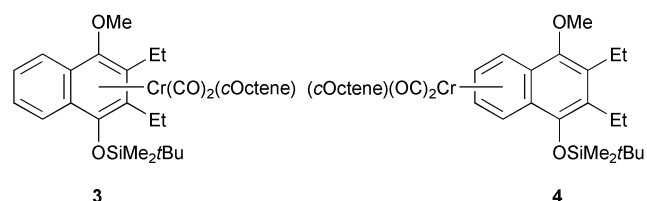
(*R*)-**1**   (*S*)-**2**

Scheme 1 Tricarbonyl naphthalene chromium complexes as an organometallic molecular switch.

3   **4**

Fig. 1 Possible intermediates of the photolysis of **1** and **2** in the presence of cyclooctene.

Complexes **1** and **2** were characterised by IR and NMR spectra as well as by high resolution mass spectroscopy and crystal structure analysis (Fig. 2).[11] Crystals for the X-ray analysis of compound **1** originate from the photo-reaction of complex **2**. Suitable single crystals were obtained by slow evaporation of the solvent from a diethyl ether–heptane solution. While both enantiomers are present in the crystal of complex **1**, complex **2** crystallised in enantiopure form (absolute configuration: *S*) from the solution of the racemic mixture. Whereas the molecular structure of complex **1** reveals a nearly eclipsed conformation of the chromium tricarbonyl moiety with respect to carbon atoms C1, C3 and C4a, its isomer (*S*)-**2** adopts a staggered conformation. This might reflect the influence of the silyl protecting group, which is located on the same face of the arene as the chromium moiety in (*S*)-**2**, while it points in the opposite direction in the crystal structure of **1**.

As evident from the experimental results the cyclooctene complex intermediate plays a crucial role in the mechanism of the haptotropic metal migration. The assumption that irradiation of complexes **1** and **2** generates complex intermediate **4** lacks an explanation for the formation of tricarbonyl complex **1** upon exposure to CO. On the other hand, the shift of the metal fragment is unlikely to proceed at the stage of the coordinatively unsaturated dicarbonyl species, since no evidence for a metal migration is found during photolysis in the absence of cyclooctene. Therefore, it is reasonable to assume that formation of complex intermediate **4** is instantaneously followed by a photochemical conversion into its regioisomer **3**. A haptotropic metal shift accompanying the cyclooctene association to the coordinatively unsaturated dicarbonyl species would be in accordance with the experimental results as well.

The intramolecular mechanism of the thermal rearrangement of complex **1** to its regioisomer **2** is evident from the kinetic data. In order to evaluate whether the reverse reaction is an intramolecular process as well, the enantiomers of complex **2** have been separated by preparative high performance liquid chromatography on a chiral stationary phase (Daicel Chiralcel OD, hexane/2-propanol 99 : 1, 20 °C). The absolute configuration has been established by X-ray analysis, assigning the (*R*)-configuration to the (−)-enantiomer. The (+)-enantiomer (*S*)-**2** was subjected to the photo-induced haptotropic rearrangement; the product of the reaction was analysed by HPLC and was compared to the racemic mixture of **1**. Only a single enantiomer was produced indicating an intramolecular course of the photo-induced isomerisation. These results are incompatible with an alternative two-step decomplexation/recomplexation pathway and corroborate an intramolecular haptotropic metal migration along the same face of the fused arene ligand.

The pair of complexes **1** and **2** represents the first example of a stereospecific molecular switch based on an organometallic complex. It allows the gain of unprecedented control over haptotropic metal migrations of tricarbonyl chromium moieties along extended aromatic systems which is also relevant for the stereocontrolled addition of nucleophiles to coordinated fused arenes and the selective modification of polycyclic arenes.

Notes and references

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10 In order to avoid thermal reactions, a temperature of −50 °C was applied during photolysis with a medium pressure mercury lamp (125 W).

11 Structural data for **1**: $C_{24}H_{32}CrO_5Si$, M_r = 480.60, monoclinic, space group $P2_1/c$, (No. 14), a = 11.4329(3), b = 12.4050(3), c = 18.1159(5) Å, β = 106.186(1)°, V = 2467.45(11) Å^3, Z = 4, ρ_{calc} = 1.294 g cm^{-3}, 0.30 × 0.15 × 0.10 mm, $2\theta_{max}$ = 50°, of 12750 reflexes 4322 were independent (R_{int} = 0.0346), 280 parameters, w$R2$ = 0.0974 (for all data), $R1$ = 0.0377 (for I, > 2σ(I)), S = 1.06. Structural data for (*S*)-**2**: $C_{24}H_{32}CrO_5Si$, M_r = 480.60, hexagonal, space group $P6_1$ (No. 169), a = b = 10.4461(1), c = 39.4227(4) Å, V = 3725.50(6) Å^3, Z = 6, ρ_{calc} = 1.285 g cm^{-3}, 0.30 × 0.12 × 0.07 mm, $2\theta_{max}$ = 50°, of 23954 reflexes 4366 were independent (R_{int} = 0.0471), 280 parameters, 1 restraint, w$R2$ = 0.0541 (for all data), $R1$ = 0.0247 (for I > 2σ(I)), S = 0.99, the absolute configuration has been determined: x = −0.01(1). Structural data for (*R*)-**2**: $C_{24}H_{32}CrO_5Si$, M_r = 480.60, hexagonal, space group $P6_5$ (No. 169), a = b = 10.4375(1), c = 39.4397(4) Å, V = 3720.98(6) Å^3, Z = 6, ρ_{calc} = 1.287 g cm^{-3}, 0.40 × 0.20 × 0.10 mm, $2\theta_{max}$ = 55°, of 32874 reflexes 5624 were independent (R_{int} = 0.0442), 280 parameters, 1 restraint, w$R2$ = 0.0545 (for all data), $R1$ = 0.0376 (for I > 2σ(I)), S = 0.984, the absolute configuration has been determined: x = −0.015(11). CCDC 205869 **1**, CCDC 205870 (*S*)-**2**, CCDC 205871 (*R*)-**2**. See http://www.rsc.org/suppdata/cc/b3/b307487k/ for crystallographic data in .cif or other electronic format.
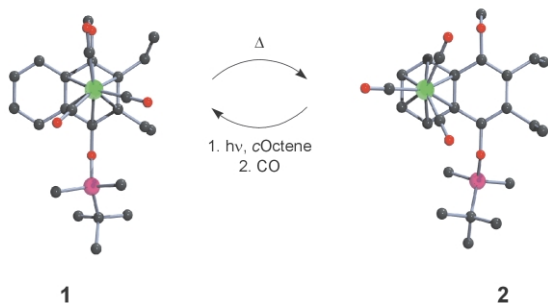
Fig. 2 Crystal structures of the product of thermal rearrangement **2** and the photochemically reconverted complex **1**.