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A Molecular Paddlewheel with a Sliding Organometallic Latch: Syntheses, X-Ray Crystal Structures and Dynamic Behaviour of $[Cr(CO)_3\{\eta^6\text{-}2\text{-}(9\text{-triptycyl})indene\}]$, and of $[M(CO)_3\{\eta^5\text{-}2\text{-}(9\text{-triptycyl})indenyl\}]$ (M = Mn, Re)

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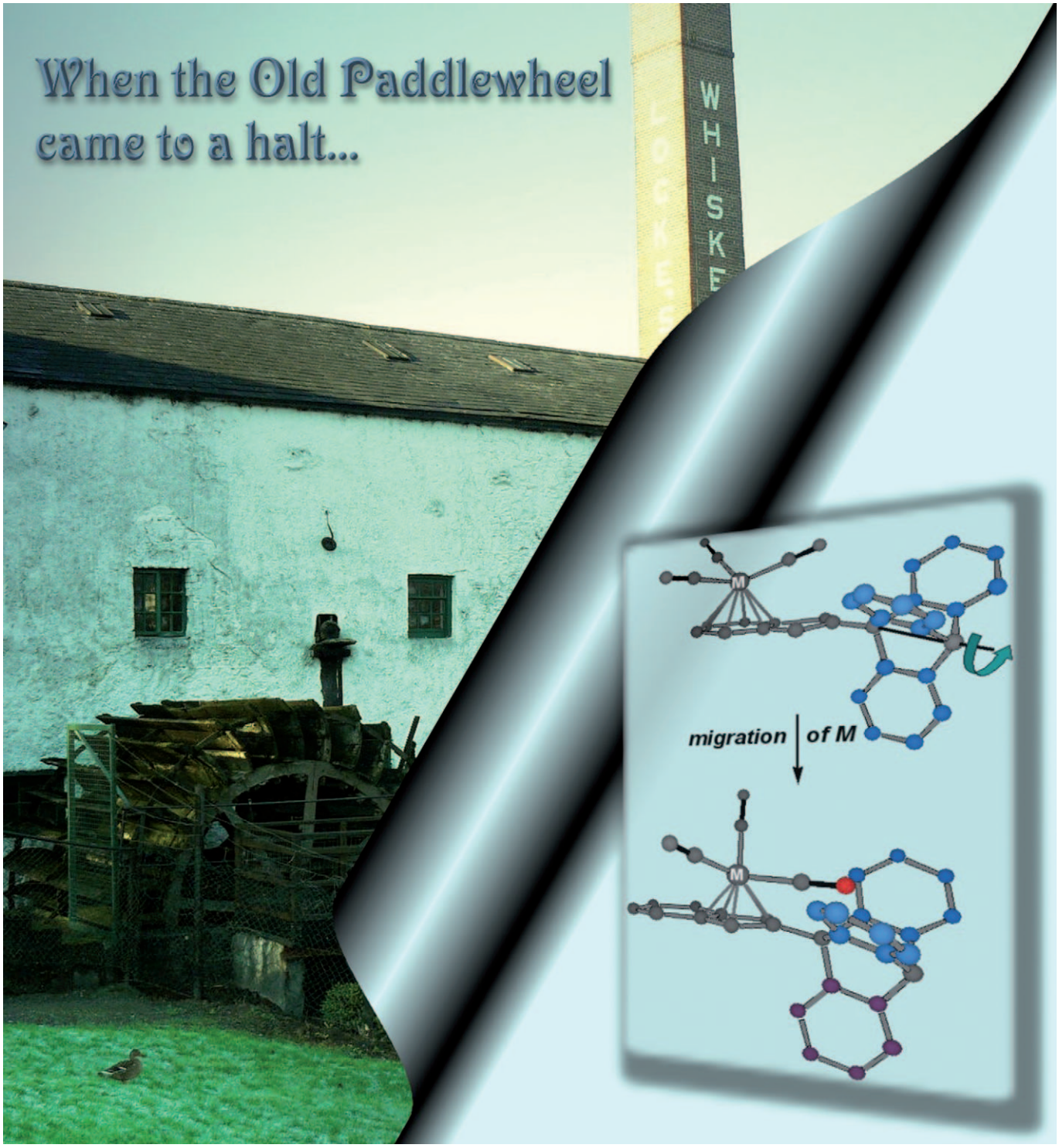

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Abstract: In [η^6-2-(9-triptycyl)-indene]-tricarbonylchromium (**2a**), the indenyl–chromium moiety is linked directly to the axis of the three-bladed triptycene paddlewheel. However, the molecular structure of **2a** reveals that there is no steric interaction between these components, and the paddlewheel is free to rotate. Accordingly, its NMR spectrum indicates the full equivalence of the blades of the triptycene. Deprotonation of the indene induces a haptotropic shift of the organometallic fragment from the six-membered to the five-membered ring of the indene and, in the sodium [η^5-2-(9-triptycyl)-indenyl]tricarbonylchromium salt (**3a**), so formed, rotation of the three-bladed molecular paddlewheel is now blocked by the bulky tripod. NMR data for **3a**, and also for the isostructural η^5-$Mn(CO)_3$ and η^5-$Re(CO)_3$ complexes, **3b** and **3c**, respectively, reveal a 2:1 splitting of the blades of the triptycyl moiety, thus breaking its original three-fold symmetry. The X-ray crystal structures of the chromium complex, **2a**, and of the manganese and rhenium complexes, **3b** and **3c**, provide pictures of the system in both its "ON" and "OFF" states, whereby the $M(CO)_3$ tripod has moved about 2 Å towards the triptycene, thus blocking its rotation. Comparison of the rotational barriers in 2-(9-triptycyl)indene (**1**) and its complexes **2** and **3**, suggests that rotation of the paddlewheel can be slowed by a factor of approximately 10^8.

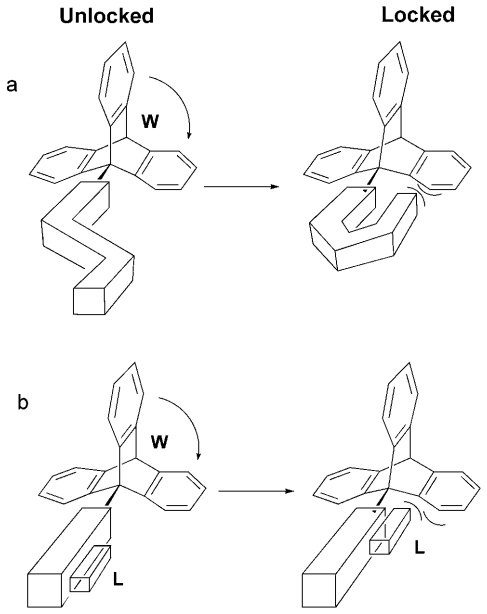
Keywords: haptotropic shifts · molecular devices · NMR spectroscopy · structure elucidation

Introduction

Molecular machines that can mimic the behaviour of macroscale objects, such as shuttles,[1] switches,[2] gears,[3] brakes,[4] turnstiles,[5] ratchets,[6] rotors,[7] motors[8] or even a nanocar,[9] continue to attract enormous attention, because of the possibility of using such devices to manipulate objects on a nanometer scale or store information at extraordinarily high densities.[10] The motions of the constituent molecular components may be driven in many ways, for example, photo- or electrochemically, or induced by proton or ion transfer. However, very few artificial molecular devices so far are able to control either the rate or direction of internal molecular rotation.[4,7d,8c,f]

Recent years have witnessed a number of spectacularly elegant syntheses of molecular machines.[4e,8,11] In particular, several of these have incorporated the three-bladed triptycene paddlewheel as an integral component of a molecular gear or brake.[3a,4a,6a,12] Importantly, these molecules are not merely *iconic* (resembling the macroscale object in appearance) but are *analogic* in that they also exhibit the appropriate mechanical behaviour.[3c] Typically, ditriptycyl ether behaves as a tightly intermeshed bevel gear that only exhibits slippage at elevated temperatures.[3a]

In such molecular "brakes" or "ratchets" one must have the means of blocking and allowing thermal rotational motion at will, and one potentially viable approach could involve a freely rotating molecular paddlewheel (**W**), the rotation of which can be arrested by the sliding motion of a complementary molecular fragment. Such molecular locking mechanisms typically include a covalently bonded bulky moiety, the internal conformation of which can be adjusted either by applying a complexation reagent,[4a] or by a photochemically promoted *trans*-to-*cis* isomerisation;[4f] this latter possibility is depicted schematically in Scheme 1a



Scheme 1. a) A *trans*-to-*cis* isomerisation induces steric hindrance to paddlewheel rotation. b) Lateral movement of fragment **L** blocks rotation of **W**.

An alternative approach could involve a *translational* sliding movement of a molecular latch such that its movable component (**L**) obstructs the rotation of the wheel (**W**) as shown in Scheme 1b. The mobile moiety **L** should be firmly attached to the body of the latch in a *lateral position* and yet be able to slide, ideally reversibly, under appropriate conditions; to the best of our knowledge, this approach has not

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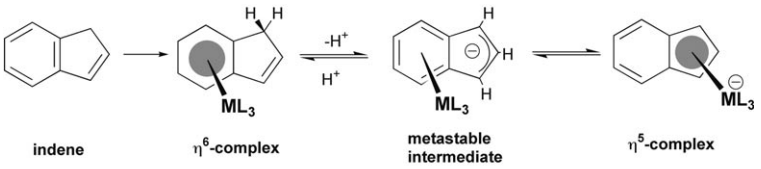
yet been realised. Although one might consider an interlocked rotaxane-type molecular shuttle[1,2] as a potential candidate for this function, the internal conformational flexibility and dynamic distribution of co-conformations of known rotaxane-based Brownian shuttles would probably seriously diminish their ability to control the rotational motion of an attached paddlewheel. Instead, we propose to take advantage of the known ability of organometallic fragments to migrate in a controlled manner over a polycyclic framework. We here describe how the "wheel–latch" concept utilises the sliding movement of a metal–carbonyl tripod, so as to block rotation of a triptycene molecular paddlewheel. This combines for the first time the directed suprafacial migration of an organometallic shuttle with the rotational motion of a molecular paddlewheel in a compact molecular design.

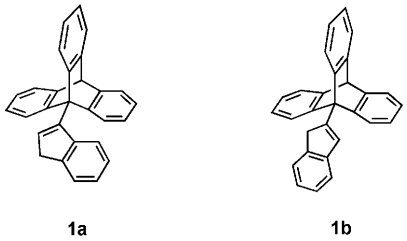
Results and Discussion

Our understanding of the phenomenon of haptotropic shifts, whereby the migration of organometallic fragments over the surfaces of polycyclic frameworks can be controlled electronically, is now very well developed.[13] Thus, our ability to move organometallic fragments ML_n, such as $Fe(C_5H_5)$,[13e] $Rh(C_2H_4)_2$,[13f] or metal–carbonyl moieties, $Mn(CO)_3$ or $Cr(CO)_3$,[13g] across the surfaces of fused polyaromatic hydrocarbon molecules has become a well-established protocol.[13b] These migrations, termed haptotropic shifts, are typically driven by the relative affinity of the ML_n fragment to the available docking sites provided by the aromatic rings of hydrocarbons. As shown in Scheme 2, an ML_3 moiety can be attached to the six-membered aromatic ring of indene (as an η^6-complex); however, upon deprotonation with a strong base, the ML_3 moiety undergoes a sliding movement driven by its ability to delocalise the negative charge on the five-membered ring of the indenide anion. This movement is approximately 2 Å, and can be reversed upon acidification.[13f]



Scheme 2. Haptotropic shifts in an indene system.

We therefore sought a simple way to take advantage of this phenomenon, whereby the haptotropic shift of an organometallic fragment across (and back) an indenyl framework could block (or release) rotation of the adjacent paddlewheel; the system could thus operate as a molecular latch or brake. Several years ago, we prepared and characterised 3-(9-triptycyl)-indene (**1a**); however, variable-temperature NMR data revealed that rotation of the 9-triptycyl fragment in **1a** has to overcome a barrier of 12 kcal mol^{-1}, because of steric clashes between an *ortho*-hydrogen atom in the six-membered ring of the indenyl and the proximal *ortho*-hydrogen atoms in the triptycyl unit. Moreover, presumably because of steric crowding, it was not possible to place a metal–carbonyl tripod on the indenyl fragment; the only isolable products were those in which $Cr(CO)_3$ units were complexed to blades of the paddlewheel.[14] In contrast, the triptycene paddlewheel in the very recently described 2-(9-triptycyl)-indene, **1b**, undergoes essentially free rotation at ambient temperature.[15] We therefore prepared chromium, manganese and rhenium tricarbonyl derivatives of **1b** in which the $M(CO)_3$ unit was attached to the indenyl moiety in either an η^6- or η^5-fashion, with the aim of investigating its possible haptotropic interconversion so as to engage or release the molecular brake (Scheme 3).



1a **1b**

When treated with $[Cr(CO)_6]$, the hydrocarbon **1** furnished $[Cr(CO)_3\{\eta^6$-2-(9-triptycyl)indene$\}$ (**2a**), which was chromatographically separated from other products in which chromium was attached to one of the blades of the paddlewheel. The structure of the η^6-complex **2a** was determined by X-ray crystallography (Figure 1a), from which it was evident that the tripodal $Cr(CO)_3$ fragment is sufficiently distant from the triptycyl paddlewheel as to pose no steric hindrance to its continued free rotation, even though the triptycyl moiety is bent through 18° towards the $Cr(CO)_3$ tripod. The simplicity of the ^{1}H and ^{13}C NMR spectra of **2a**, showing the time-averaged equivalence of the three blades of the paddlewheel (Scheme 3), clearly indicated that triptycyl rotation continued unhindered.

The manganese– and rhenium–carbonyl fragments, $Mn(CO)_3$ and $Re(CO)_3$, respectively, have also been attached to the hydrocarbon **1**, leading to the η^5-complexes **3b** and **3c**, respectively, in which the tripodal $M(CO)_3$ moieties coordinate only to the five-membered ring of the indenyl unit. X-ray crystallographic studies revealed that in each case one of the carbonyl ligands obtrudes directly between two of the blades of the triptycyl fragment (Figure 1b), thus blocking rotation of the paddlewheel. This blockage is illustrated even more clearly in the space-filling representations

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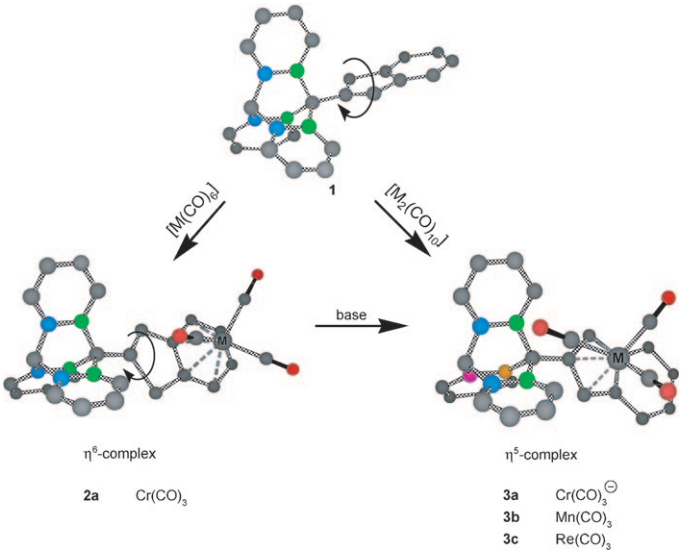

Scheme 3. In the hydrocarbon **1**, and also in the η^6-metal–carbonyl derivative **2a**, free rotation of the paddlewheel allows its three aromatic rings rapidly to interchange their relative orientations, such that all three atoms labelled ● become equivalent (as are atoms ●). In contrast, in the η^5-metal–carbonyl complexes **3a**–**3c**, rotation of the wheel is stopped, on the NMR timescale, so that the two ● atoms are no longer equivalent to atom ●, and the two ● atoms are no longer equivalent to atom ●.

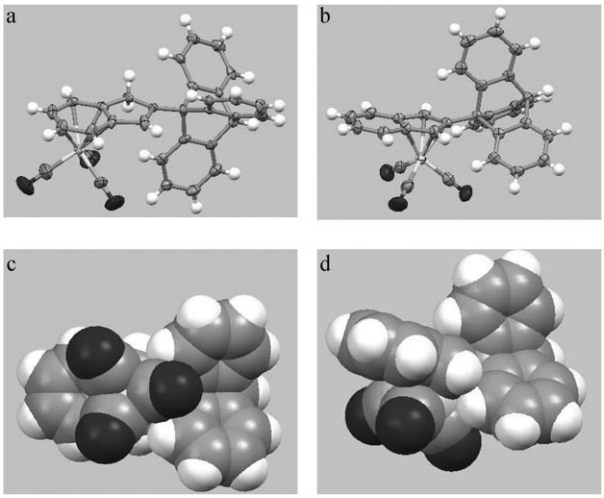

Figure 1. X-ray crystal structures of a) η^6-$Cr(CO)_3$ complex **2a** and b) η^5-$Mn(CO)_3$ complex **3b**. c) Space-filling representation (view from below) of the manganese complex **3b**. d) Space-filling representation of **3b** (side view).

(Figure 1c and d) of the X-ray crystal structure of **3b**. It is noticeable that the presence of the bulky $Mn(CO)_3$ tripod in the η^5-complex **3b** causes a perturbation of the molecular framework, such that the indenyl fragment bends through 18° away from the nominal threefold axis of the triptycene wheel.

The structure of the analogous η^5-$Re(CO)_3$ complex **3c**, shown in Figure 2, closely parallels that of **3b**. Of course, the metal-to-ring centroid distance is greater in the rhenium case (1.797 Å for Mn; 1.977 Å for Re), but once again the

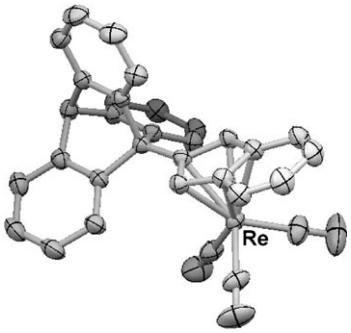

Figure 2. X-ray crystal structure of the η^5-$Re(CO)_3$ complex **3c**.

indenyl fragment is bent through 18° away from the threefold axis of the triptycene wheel.

This situation of arrested internal rotation about the single bond linking the indenyl and triptycyl units is very clearly reflected in the ^1H and ^{13}C NMR spectra of **3b** and **3c** in which the resonances attributable to the paddlewheel blades are now each split in a 2:1 ratio, as shown in Figure 3. A variable-temperature ^{13}C NMR study on the rhenium complex **3c** revealed the gradual onset of line-broadening above 70 °C, and computer simulation of the spectra yielded a substantial rotational barrier of 19.5 ± 0.5 kcal mol^{-1}. A very recent shuttle-based molecular brake exhibited a 100-fold decrease in the shuttling rate.[4e] In the present case, rearrangement from an η^6- to an η^5-structure increases the barrier to paddlewheel rotation by ≈ 12 kcal mol^{-1}, corresponding to an approximately 10^8-fold relative rate decrease. Such a rate decrease is comparable to that observed in the cleverly designed, very recently reported, pentiptycene-based system that uses a *trans–cis* isomerisation process as the braking mechanism.[4f]

Having established that the η^5-complexes **3b** and **3c** bring about the cessation of paddlewheel rotation, the indenyl fragment in the η^6-$Cr(CO)_3$ complex **2a** was then deprotonated with sodium *tert*-butoxide to generate the corresponding anion. As indicated in Scheme 3, this deprotonation allows the $Cr(CO)_3$ group to migrate onto the adjacent five-membered ring, thus yielding the negatively charged η^5-complex **3a**. Gratifyingly, the resulting ^1H and ^{13}C NMR spectra of **3a** exhibited a 2:1 splitting of the triptycene blade resonances, paralleling the behaviour of **3b** and **3c**, and once again revealing that, on the NMR timescale, paddlewheel rotation had been arrested.

We note that, as the metal migrates from the six-membered ring in **2a** to the five-membered ring in **3a**, it actually moves a substantial distance (≈ 2 Å) closer to the paddlewheel. However, it is now well-established that the migrating organometallic fragment does not follow the least-motion trajectory directly across the common bond between the six-membered benzene ring and five-membered cyclopentadienyl ring, but rather undertakes a circuitous route via the molecular periphery, such that the metal temporarily has only a 16-electron configuration.[13] Hence, reprotonation of η^5-**3a** to reverse the function of the brake by regen-

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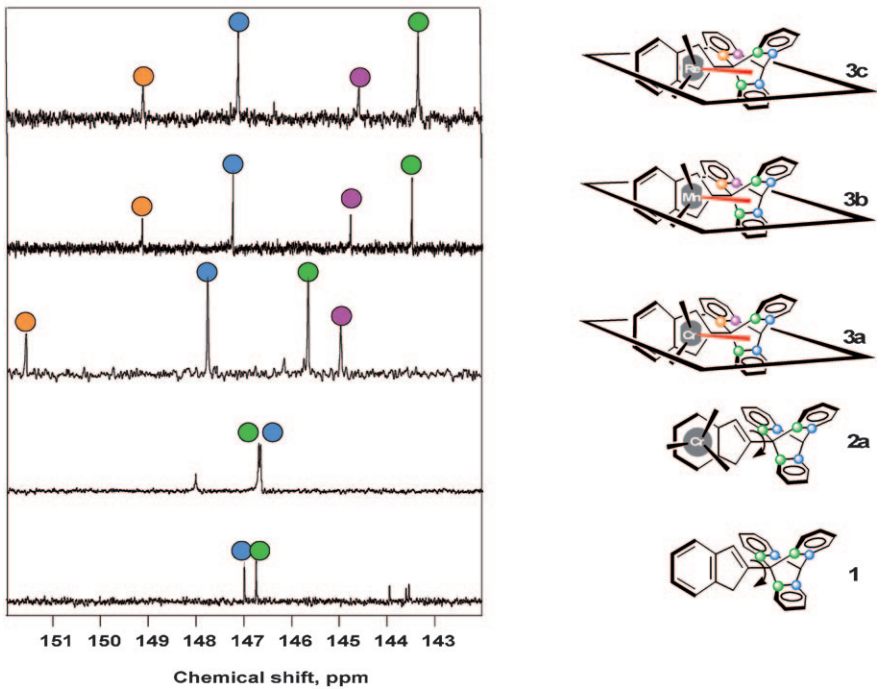

Figure 3. Sections of the 125 MHz ^{13}C NMR spectra of hydrocarbon **1**, η^6-Cr complex **2a**, η^5-Cr complex **3a**, η^5-Mn complex **3b** and η^5-Re complex **3c**. Free rotation of the triptycene paddlewheel in **1** and **2a** allows the ring junction carbon atoms C(14), C(20), C(26) labelled in green, and C(19), C(25), C(31) labelled in blue, to maintain their time-averaged threefold degeneracy; thus, each set gives rise to a single peak. In the η^5-complexes **3a–c** these carbon environments are no longer threefold degenerate, and their resonances are split into distinctive 2:1 patterns in accord with the presence of only a single molecular mirror plane, as shown.

erating η^6-**2a** (c.f. Scheme 2) also brings about some decomplexation of the metal fragment.[16] Similarly, protonation of the η^5-Re(CO)$_3$ complex **3c** leads to decomposition, presumably because of competitive protonation at the metal centre.

We emphasise that this report merely provides proof of principle for this novel approach towards the development of organometallic-based molecular machines. Since the initial work by Stoddart and others on rotaxane-based systems,[1] that area has burgeoned almost exponentially; to the best of our knowledge, the present work is the first to use an organometallic moiety as the mobile component of molecular machinery, and its potential will undoubtedly be realised in the coming years. In this particular instance, we have chosen to provide an organometallic analogue of Kelly's molecular brake,[4a] but it is evident that one can readily envisage improvements and modifications to the basic concept of using a haptotropic shift to control the rotational freedom of a molecular fragment. Thus, one could strengthen the attachment of the metal moiety to the polycyclic surface, over which it migrates, by incorporating a tether. Further planned modifications involve a redox process, such as those described by Amatore and Ceccon,[17] rather than a deprotonation/reprotonation sequence, to change the electron density distribution across the indenyl moiety. Moreover, one can foresee other developments: the use of a chiral triptycene, the inclusion of a quenchable luminescent probe to indicate the proximity of the metal, the attachment of a thiol or other linker to a surface and the incorporation of additional freely-rotating fragments (as in bis-indenyl triptycenes) to open up the possibility of a haptotropically controlled organometallic molecular gearbox.

To conclude, we here describe the structure and dynamics of a short-stroke molecular mechanical shuttle, or latch, whereby, for the first time, both the "ON" and "OFF" positions have been fully characterised by both X-ray crystallography and NMR spectroscopy, and so demonstrate the potential viability of this novel organometallic approach towards the construction of functional analogic molecular machinery.

Experimental Section

General: All reactions and chromatographic separations were carried out under an atmosphere of dry nitrogen. Column chromatography separations were run on a Buchi Sepacor machine with UV absorbance detector using silica gel particle size 40–63 mm. NMR spectra were acquired on Varian 500 or 600 MHz spectrometers. Assignments were based on standard ^{1}H–^{1}H and ^{1}H–^{13}C two-dimensional techniques, and NOE measurements. Mass spectra were recorded on a Micromass LCT instrument. Elemental analyses were carried out by the Microanalytical Laboratory at University College Dublin. 2-(9-Triptycyl)-indene (**1**) was prepared by benzyne addition to 2-(9-anthracenyl)-indene according to the previously described procedure.[14]

Preparation of [Cr(CO)$_3${η^6-2-(9-triptycyl)indene}] (2a): Compound **1** (37 mg, 0.10 mmol) was heated with [Cr(CO)$_6$] (22 mg, 0.10 mmol) in dioxane (2 mL) at 130 °C in a sealed tube for four days, and the products were separated on silica to give **2a** (11 mg, 0.022 mmol, 22 %) as a yellow solid; X-ray diffraction quality crystals of **2a** were obtained from ethyl acetate. ^{1}H NMR (500 MHz, [D$_6$]DMSO, 30 °C, numbering in accord with Figure 4): δ = 7.52 (m, 6H; H15, H18, H21, H24, H27, H30), 7.25 (s, 1H; H11), 7.05 (d, J = 6.4 Hz, 3H; H16, H22, H28), 7.02 (d, J = 6.4 Hz, 3H; H17, H23, H29), 6.44 (s, 2H; H6, H9), 5.80 (s, 2H; H7, H8), 5.67 (s, 1H; H32), 4.76 (d, J = 23 Hz, 1H; H4), 4.11 ppm (d, J = 23 Hz, 1H; H4); ^{13}C NMR (125 MHz, [D$_6$]DMSO, 30 °C, numbering in accord with Figure 4): δ = 235.4 (C1, C2, C3), 148.0 (C12), 146.7 (C14, C20, C26), 146.5 C19, C25, C31), 125.8 (C16, C22, C28), 125.3 (C17, C23, C29), 124.3 (C18, C24, C30), 123.8 (C15, C21, C27), 116.0 (C10), 114.9 (C5), 93.8 (C7, C8), 92.9 (C9), 91.4 (C6), 58.2 (C13), 53.6 (C32), 43.2 ppm (C4); HRMS (ES): m/z calcd for $C_{32}H_{19}CrO_3$ [$M-$H]$^+$: 503.0739; found: 503.0716; elemental analysis calcd (%) for $C_{32}H_{20}CrO_3{\cdot}0.5\,C_4H_8O_2$ (548.6): C 74.44, H 4.41; found: C 74.26, H 4.36.

Preparation of [Mn(CO)$_3${η^5-2-(9-triptycyl)indenyl}] (3b): Compound **1** (37 mg, 0.10 mmol) was treated with butyllithium (0.2 mmol) in diethyl ether (1 mL) at ambient temperature after which [Mn(CO)$_5$Br] (28 mg, 0.10 mmol) in THF (0.5 mL) was added at −20 °C and the resulting mixture was heated at 60 °C in a sealed tube for one day. The products were separated on silica to give **3b** (10 mg, 0.02 mmol, 20 %) as a pale brown solid; X-ray diffraction quality crystals of **3b** were obtained from cyclo-

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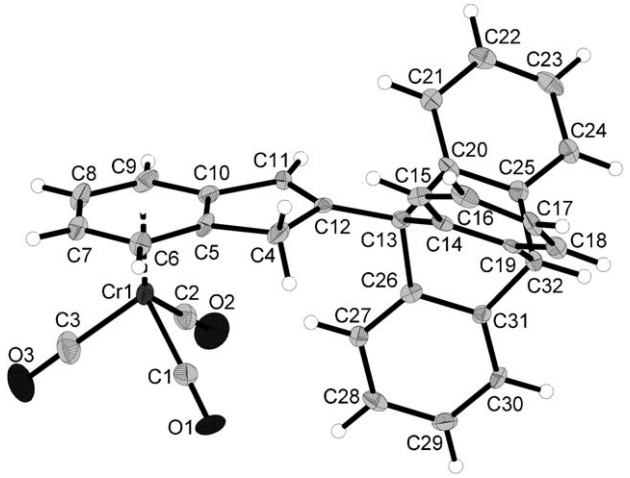

Figure 4. Structure of the η^6-bonded chromium complex **2a** showing the atom numbering; **3a**, **3b** and **3c** follow the same numbering sequence.

hexane. ^{1}H NMR (500 MHz, $CDCl_3$, 30 °C, numbering in accord with Figure 4): $\delta = 8.12$ (d, $J = 7.6$ Hz, 2H; H15, H27), 7.71 (d, $J = 6.6$ Hz, 2H; H6, H9), 7.44 (d, $J = 7.4$ Hz, 2H; H18, H30), 7.43 ($J = 7.4$ Hz, 1H; H24), 7.33 (d, $J = 7.4$ Hz, 2H; H7, H8), 7.16 (t, $J = 7.0$ Hz, 2H; H16, H28), 7.07 (t, $J = 7.0$ Hz, 2H; H17, H29), 7.02 (t, $J = 7.4$ Hz, 1H; H23), 6.80 (t, $J = 7.4$ Hz, 1H; H22), 6.20 (d, $J = 7.4$ Hz, 1H; H21), 5.74 (s, 2H; H4, H11), 5.42 ppm (s, 1H; H32); ^{13}C NMR (125 MHz, $CDCl_3$, 30 °C, numbering in accord with Figure 4): $\delta = 224.4$ (C1, C2, C3), 149.1 (C20), 147.0 (C19, C31), 144.5 (C25), 143.3 (C14, C26), 127.2 (C7, C8), 125.8 (C6, C9), 125.8 (C23), 125.4 (C17, C29), 124.9 (C22), 124.7 (C16, C28), 124.0 (C15, C18, C27, C30), 123.6 (C21), 122.9 (C24), 107.5 (C12), 103.7 (C5, C10), 74.4 (C4, C11), 54.8 (C32), 54.5 ppm (C13); HRMS (ES): m/z calcd for $C_{32}H_{18}MnO_3$ $[M-H]^-$: 505.0636; found: 505.0610.

Preparation of $[Re(CO)_3\{\eta^5$-2-(9-triptycyl)indenyl$\}]$ (3c): Compound **1** (37 mg, 0.10 mmol) was heated with $[Re_2(CO)_{10}]$ (130 mg, 0.2 mmol) in 1,3-dichlorobenzene (0.6 mL) at 150 °C in a sealed tube for one day. The products were separated on silica to give **3c** (19 mg, 0.03 mmol, 30 %) as a white solid; X-ray diffraction quality crystals of **3c** were obtained from cyclohexane. ^{1}H NMR (600 MHz, $CDCl_3$, 30 °C, numbering in accord with Figure 4): $\delta = 7.95$ (d, $J = 7.5$ Hz, 2H; H15, H27), 7.70 (dd, $J = 6.6$, 3 Hz, 2H; H5, H8), 7.41 (d, $J = 7.1$ Hz, 2H; H18, H30), 7.41 ($J = 7.1$ Hz, 1H; H24), 7.26 (m, 2H; H6, H7), 7.11 (t, $J = 7.5$ Hz, 2H; H16, H28), 7.05 (t, $J = 7.5$ Hz, 2H; H17, H29), 7.03 (t, $J = 7.5$ Hz, 1H; H23), 6.80 (t, $J = 7.5$ Hz, 1H; H22), 6.16 (d, $J = 7.5$ Hz, 1H; H21), 6.25 (s, 2H; H4, H11), 5.38 ppm (s, 1H; H32); ^{13}C NMR (150 MHz, $CDCl_3$, 30 °C, numbering in accord with Figure 4): $\delta = 192.8$ (C1, C2, C3), 148.9 (C20), 147.0 (C19, C31), 144.6 (C25), 143.3 (C14, C26), 127.2 (C7, C8), 126.1 (C23), 123.9 (C6, C9), 125.5 (C17, C29), 125.1 (C22), 124.9 (C16, C28), 124.0 (C15,C27), 124.1 (C18, C30), 124.1 (C21), 123.1 (C24), 110.9 (C12), 108.9 (C5, C10), 74.5 (C4, C11), 54.8 (C32), 54.7 ppm (C13); elemental analysis (%) calcd for $C_{32}H_{19}ReO_3$ (637.71): C 60.27, H 3.00; found: C 60.28, H 3.03.

Preparation of sodium $[Cr(CO)_3\{\eta^5$-2-(9-triptycyl)indenyl$\}]$ (3a): Chromium complex **2a** (5.0 mg, 10 μmol) was dissolved in $[D_6]$DMSO (0.8 mL) in an NMR tube, and sodium *tert*-butoxide (3 mg, 30 μmol) was added. The reaction mixture was kept in the dark for two days, after which time full conversion of **2a** into the anionic complex **3a** was observed: ^{1}H NMR (500 MHz, $[D_6]$DMSO, 30 °C, numbering as for **3b** in accord with Figure 4): $\delta = 8.54$ (d, 7.6 Hz, 2H; H15, H27), 7.52 (d, 6.6 Hz, 2H; H6, H9), 7.40 (d, $J = 7.4$ Hz, 2H; H18, H30), 7.40 ($J = 7.4$ Hz, 1H; H24), 6.83 (d, $J = 7.4$ Hz, 2H; H7, H8), 7.08 (t, $J = 7.0$ Hz, 2H; H16, H28), 6.98 (t, $J = 7.0$ Hz, 2H; H17, H29), 6.94 (t, $J = 7.4$ Hz, 1H; H23), 6.73 (t, $J = 7.4$ Hz, 1H; H22), 6.03 (d, $J = 7.4$ Hz, 1H; H21), 5.25 (s, 2H; H4, H11), 5.55 ppm (s, 1H; H32); ^{13}C NMR (125 MHz, $CDCl_3$, 30 °C, numbering in accord with Figure 4): $\delta = 244.2$ (C1, C2, C3), 151.6 (C20), 147.8 (C19, C31), 145.7 (C14, C26), 145.0 (C25), 120.9 (C7, C8), 125.8 (C6, C9), 125.5 (C23), 124.8 (C17, C29), 124.8 (C22), 124.5 (C16, C28), 126.2 (C15, C27) 123.6 (C18, C30), 124.6 (C21), 128.8 (C24), 106.3 (C12), 106.2 (C5, C10), 75.6 (C4, C11), 53.8 (C32), 55.7 ppm (C13). The reaction mixture was subsequently treated with trifluoroacetic acid (60 μmol) to regenerate **2a**; after two days neither **2a** nor **3a** was detectable, and only the hydrocarbon **1** was observed.

X-ray crystallography measurements for 2a, 3b and 3c: Crystal data were collected using a Bruker SMART APEX CCD area detector diffractometer, and are listed in Table 1. A full sphere of the reciprocal

Table 1. X-ray collection and refinement parameters for **2a**, **3b** and **3c**.

	2a	**3b**	**3c**
formula	$C_{66}H_{46}O_7Cl_2Cr_2$[a]	$C_{70}H_{50}O_6Mn_2$	$C_{70}H_{50}O_6Re_2$
molecular formula	$(C_{32}H_{20}O_3Cr)_2{\cdot}CH_2Cl_2{\cdot}CH_3OH$	$(C_{32}H_{19}O_3Mn)_2{\cdot}C_6H_{12}$	$(C_{32}H_{19}O_3Re)_2{\cdot}C_6H_{12}$
M_r	1128.33	1096.98	1359.50
T [K]	100(2)	100(2)	293(2)
λ [Å]	0.71073	0.71073	0.71073
crystal system	monoclinic	triclinic	triclinic
space group	Cc (#9)	$P\bar{1}$ (#2)	$P\bar{1}$ (#2)
a [Å]	14.0659(17)	10.1758(17)	10.2398(8)
b [Å]	13.8323(17)	11.3942(18)	11.6491(9)
c [Å]	28.022(3)	12.654(2)	12.8553(10)
α [°]	90	108.669(3)	107.227(1)
β [°]	100.271(2)	104.867(3)	104.133(1)
γ [°]	90	100.343(4)	102.769(1)
V [Å^3]	5364.6(11)	1287.5(4)	1347.20(18)
Z	4	1	1
ρ_{calcd} [Mg m^{-3}]	1.394	1.415	1.676
μ [mm^{-1}]	0.562	0.549	4.545
$F(000)$	2320	568	668
crystal size [mm^3]	$1.00\times0.80\times0.03$	$0.30\times0.30\times0.01$	$0.40\times0.15\times0.15$
θ range [°]	2.08–26	1.80–24.75	1.76–28.29
index ranges	$-17\le h\le17$	$-11\le h\le11$	$-13\le h\le13$
	$-17\le k\le17$	$-13\le k\le13$	$-15\le k\le15$
	$-34\le l\le34$	$-14\le l\le14$	$-17\le l\le17$
reflns collected	22217	9938	27552
independent reflns	10459	4374	6681
	[R(int) = 0.0324]	[R(int) = 0.0383]	[R(int) = 0.0223]
data/restraints/parameters	10459/2/650	4374/0/352	6681/0/352
GOF on F^2	1.044	1.058	1.083
final R indices [$I>2\sigma(I)$]	$R1 = 0.0553$	$R1 = 0.0480$	$R1 = 0.0229$
	$wR2 = 0.1334$	$wR2 = 0.1091$	$wR2 = 0.0571$
R indices (all data)	$R1 = 0.0588$	$R1 = 0.0640$	$R1 = 0.0246$
	$wR2 = 0.1356$	$wR2 = 0.1154$	$wR2 = 0.0579$
absolute structure parameter	0.121(19)		
largest difference peak/hole [e Å^{-3}]	0.459/−0.691	0.520/−0.393	1.142/−0.603

[a] The methanol and dichloromethane molecules could not be located in the unit cell. PLATON SQUEEZE was used to compensate for the spread electron density.

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space was scanned by phi-omega scans. Pseudo-empirical absorption correction based on redundant reflections was performed by the program SADABS.[18] The structures were solved by direct methods using SHELXS-97[19] and refined by full-matrix least-squares methods on F^2 for all data using SHELXL-97.[20] All hydrogen atoms except those of solvent molecules were located in the difference Fourier map and were allowed to refine freely with isotropic thermal displacement factors. Hydrogen atoms of the solvents were added at calculated positions and refined using a riding model. Their isotropic displacement parameters were fixed to 1.2 times the equivalent isotropic displacement parameters of the parent carbon atom. Anisotropic temperature factors were used for all non-hydrogen atoms. CCDC 680866 (**2a**), 680865 (**3b**) and 680864 (**3c**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

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