PAPER www.rsc.org/njc | New Journal of Chemistry

Synthesis of triester-functionalized molecular motors incorporating bis-acetylide *trans*-platinum insulating fragments†‡

Guillaume Vives, Alexandre Carella, Stéphanie Sistach, Jean-Pierre Launay and Gwénaël Rapenne*

Received (in Montpellier, France) 18th April 2006, Accepted 21st June 2006
First published as an Advance Article on the web 18th July 2006
DOI: 10.1039/b605509e

Bis-ferrocene compounds linked either by two triple bonds (1,4-di(ferrocenyl)butadiyne **1**), or by the triple bond–platinum–triple bond sequence (*trans*-bis(ferrocenylethynyl) bis(triethylphosphine)platinum(II), **2**) have been synthesized. The electronic coupling between the ferrocene groups has been estimated from the intensity of the intervalence transition in the electrochemically generated mixed valence complexes. Upon insertion of a platinum fragment a weak attenuation was observed, with the V_{ab} parameter decreasing from 0.036 eV for **1** to 0.025 eV for **2**. A theoretical study has also been performed, using a combination of DFT for geometry optimization and Extended Hückel Theory for the estimation of the electronic coupling. It was found that the electronic coupling decreases from 0.090 eV for **1** to 0.022 eV for a model of **2**. In a second part of this work, we describe the synthesis of two molecular motors incorporating the ligand hydrotris[6-(ethoxycarbonyl)indazol-1-yl]borate which exhibits three pendant ester groups dedicated to be anchored onto an oxide surface. This stator is connected through a ruthenium centre to a pentasubstituted cyclopentadienyl rotor bearing ferrocene terminal electroactive groups, linked either by a phenylethynyl spacer (complex **4**) or a spacer containing bis-acetylide *trans*-platinum insulating fragments (complex **8**).

Introduction

In the field of nanosciences, the design and chemical synthesis of artificial molecular machines[1] is becoming an important challenge. A molecular-level machine can be defined as an assembly of molecular components designed to perform a controlled movement in response to a stimulus. Among these machines, a motor is a machine that converts energy into work *via* a unidirectional and controlled movement. Molecular rotary motors present a very particular challenge, such as the control of the directionality of a repetitive 360° rotary motion. But among the many examples of molecular rotors which have been described,[2] only a few of them present a control of the directionality and can be considered as potential molecular motors. Indeed, in view of recovering the mechanical work produced by the rotation of a motor, their structure must be relatively rigid and the number of degrees of freedom as low as possible.

Recently, we have presented the concept of an electrically fuelled single molecular rotary motor.[3] The motor is based on an organometallic centre built around a ruthenium cyclopentadienyl trisindazolylborate complex with five ferrocenyl units located at the periphery. The general principle is that the trisindazolylborate part would be grafted on a solid surface, and thus should stay still (stator), while the pentasubstituted cyclopentadienyl part would be able to rotate under the influence of a suitably oriented electrical field (rotor). The two parts are rigid, and the molecule has only one significant possible degree of internal rotation (Fig. 1, left).

In such systems, the major difficulty lies in the capacity to control the parameters which favor the desired process over the unwanted ones.[4] In our case the rotation has to compete with the undesired intramolecular electron transfer without rotation (Fig. 1, right). The rotation, a fifth of a turn in the case of a C_5-symmetric rotor, has to be significantly faster than the intramolecular electron transfer between two electroactive units. If not, the electrons will travel through the carbon skeleton without rotation of the whole rotor. Since a conjugated skeleton can clearly not separate electronically the electroactive groups, our goal is to use platinum acetylide fragments to insulate the ferrocene groups by disrupting the electronic communication between them, possibly due to the σ character of the Pt–C bonds which breaks the conjugation of the different submodules. Therefore the charge localization on one single oxidized ferrocenyl unit, which should be the seat of the oxidoreduction cycles in the desired process, should be favoured.

In the first part of this paper we will present our contribution to the debate about the insulating role of *trans*-platinum centres.[5] For that purpose, we used a combination of theoretical calculations and experiments to compare the electronic

---

NanoSciences Group, CEMES-CNRS, 29 rue Jeanne Marvig, F-31055 Toulouse Cedex 4, France. E-mail: rapenne@cemes.fr; Fax: (+33) 562 25 79 99; Tel: (+33) 562 25 78 41

† Electronic supplementary information (ESI) available: molecular modelling coordinates of 1, 1b and 2. Parameters used in the calculations for the atoms C, H, Fe and Pt, energy of the orbitals and V_{ab} of 1, 1b and 2b as a function of the energy of the iron 3d orbitals. See DOI: 10.1039/b605509e

‡ The HTML version of this article has been enhanced with colour images.

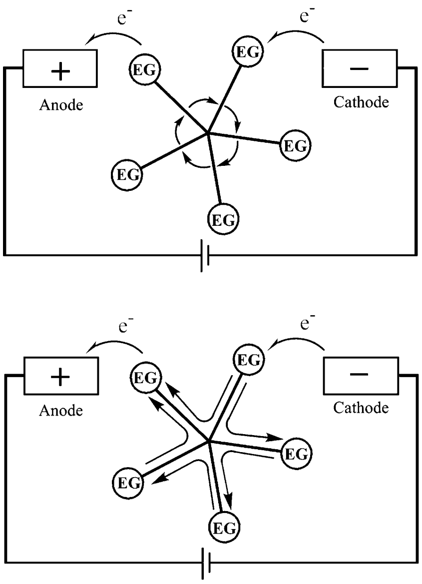


Fig. 1 Desired behaviour (top): electron transport with the rotation of the rotor. Undesired behaviour (bottom) electron transport *via* intramolecular electron transfers without rotation.

communication in two model compounds with two ferrocene electroactive groups bridged by a conjugated organic linker or a platinum fragment. In a second part, we will report the synthesis of two star-shaped molecules which can potentially act as molecular motors since they incorporate ester groups to anchor the molecules onto oxide surfaces. These motors bear ferrocene terminal electroactive groups linked either by a phenylethynyl spacer in complex **4** or a spacer containing bis-acetylide *trans*-platinum insulating fragments in complex **8**.

Results and discussion

Investigation of the insulating role of a *trans*-platinum complex

The question concerning the electronic role of *trans*-platinum centres has still not fully been addressed.[5] On the one hand, the conductivity of a single molecule placed between two gold electrodes has been investigated by Mayor *et al.*[5a] The resistance of the platinum-containing molecule was much higher than with a conjugated organic spacer, which was justified by the pure σ character of the Pt–C(sp) bonds. On the other hand, Marder and co-workers have compared a *trans*-platinum complex with a *p*-phenylene group as spacers between two electroactive organic groups (dianisylphenylamine).[5b] A spectroscopic study of the mixed-valence species and calculations have shown that the electronic coupling between the two redox centres is only slightly decreased with a *trans*-platinum spacer. Diederich also observed an almost complete lack of π-electron conjugation in platinum-tetraethynylethene scaffolding.[5c] In view of confirming the electronic influence of a *trans*-platinum complex incorporated between two ferrocene electroactive units, we have combined two complementary approaches: an experimental approach based on spectroelectrochemistry and a theoretical approach combining geometry optimization by DFT and extended Hückel calculations.

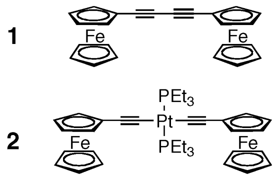


Fig. 2 Complexes used to study experimentally the electronic influence of a *trans*-platinum complex.

For both approaches, simple model compounds incorporating (or not) a platinum linker have been chosen. Although not resembling the target complexes **4** and **8**, the study of such models will give some information about the electronic character of a *trans*-platinum bridge.

Experimental approach

The two symmetrical complexes used in this study (Fig. 2) incorporate ferrocene units as electroactive groups,[6] linked by an alkynyl bridge. One complex contains a *trans*-platinum complex intercalated between two C–C triple bonds. The preparation of platinum acetylide complexes with rigid alkynyl backbones has been described by Stang and Takahashi for their use in the formation of organometallic dendrimers[7] which are thermally robust and stable, even when exposed to air and moisture, and can be obtained in high yields by a well-established synthetic methodology. 1,4-Di(ferrocenyl) butadiyne (**1**) was obtained by the Glaser homocoupling of ethynylferrocene[8] and *trans*-bis(ferrocenylethynyl) bis(triethylphosphine)platinum(II) (**2**) was obtained by reaction of two equivalents of ethynylferrocene with *trans*-dichlorobis(triethylphosphine)platinum(II).[9] A partial oxidation of the complexes yields the mixed valence species, which grants access to the electronic coupling parameter, V_{ab}. This parameter is used as a probe to estimate the electronic communication between the two ferrocene units. Despite the slightly longer Fe–Fe distance in **2**, the comparison of V_{ab} in compounds **1** and **2** can give an estimation of the insulating role of the *trans*-platinum complex.

The redox properties of compounds **1** and **2** have been studied by cyclic voltammetry. The conjugated bisferrocene compound **1** shows two reversible waves sufficiently resolved to measure the potentials (0.58 and 0.68 V/SCE) corresponding to the successive oxidation of both ferrocenes, first yielding the mixed valence complex $[\text{Fc-(CC)}_2\text{-Fc}]^+$ and then the dication $[\text{Fc-(CC)}_2\text{-Fc}]^{2+}$.[10] The potential of the first oxidation wave is very close to the oxidation potential obtained in the same conditions for ethynylferrocene (0.59 V/SCE). Similarly compound **2** shows two waves at 0.32 and 0.40 V corresponding to the mixed valence complex and to the dication, however strongly shifted towards lower potentials. The marked stabilization of the oxidized forms can be explained by the strong σ-donating character of the *trans*-platinum complex electronically enriched by the two triethylphosphine ligands. It must be noted that no oxidation or reduction of the platinum complex has been observed in dichloromethane from −1.8 V to +1.5 V, which shows the redox stability of this centre. The reduction of similar platinum centres is indeed known to occur around −2.4 V.[9]

A spectroelectrochemical study allowed the evaluation of the electronic communication between the two ferrocenes in both complexes. Partial oxidation of the complex at different potentials and examination of the visible–near infrared region of the absorption spectrum grants access to the intervalence band which successively appears and disappears during the process. The intervalence transition can be considered as a special case of charge transfer transition, the donor group being the reduced site and the acceptor group the oxidized site. The mixing of the two electronic states is due to an electronic term, V_{ab}, which is also responsible for the intensity of the intervalence transition. This transition gives a measure of the electronic coupling parameter (V_{ab}) following the Hush formula.[11]

$$V_{ab} = \frac{2.05 \times 10^{-2} (\varepsilon_{max} \bar{\nu}_{max} \Delta\bar{\nu}_{1/2})^{1/2}}{R_{MM}}$$

with ε_{max} the maximum molar extinction coefficient, $\bar{\nu}_{max}$ the position of the transition (cm^{-1}), $\Delta\bar{\nu}_{1/2}$ the bandwidth at half-height (cm^{-1}) and R_{MM} the metal–metal distance (Å).

The spectrum of the mixed valence species obtained by partial oxidation of **1** displays an absorption band at 760 nm (ε = 670 mol^{-1} L cm^{-1}) corresponding to the LMCT transition of the ferrocenium group. The broad band at 1180 nm (ε = 400 mol^{-1} L cm^{-1}) corresponds to the intervalence transition. This is clearly shown by the fact that during electrolysis, the intensity of this band increases before decreasing, whereas the band at 760 nm always increases. The Hush formula allows the evaluation of the electronic coupling parameter. Assuming a *trans* geometry for the two ferrocenes corresponding to a metal–metal distance of 9.58 Å, this gives V_{ab} = 0.036 eV, *i.e.* a moderately coupled class II system.

The visible–near ir spectrum measured during gradual oxidation of complexes **1** and **2** are given in Fig. 3. The monocation of compound **2** displays an absorption band at 1000 nm (ε = 1900 mol^{-1} L cm^{-1}) corresponding to the LMCT transition of the ferrocenium group. The bathochromic shift observed by comparison to compound **1** is due to the platinum complex, which makes the ligand a better donor and thus decreases the energy of the LMCT transition by destabilizing the highest occupied ligand-centred orbital. In this case, the intervalence transition is strongly mixed with the other transition and only appears as a residual absorption in the 1200–1600 nm region, which increases and decreases during the oxidation process. A deconvolution of the two bands enabled the parameters of the intervalence transition to be obtained, in particular V_{ab} = 0.025 eV, a weakly coupled class II mixed valence system, corresponding to an attenuation of the electronic communication by a factor of only 1.5.

Experimentally, the complex incorporating a *trans*-platinum fragment displays a weaker ferrocene–ferrocene coupling *i.e.* an attenuated electronic communication, which goes in the desired direction. However the attenuation factor is moderate and in order to confirm this trend, we have performed theoretical calculations on three model complexes **1**, **1b** and **2b** (Fig. 4).

Theoretical study of the insulating role of the *trans*-platinum complex

The influence of a *trans*-platinum complex on the electronic communication between two metallic centres has been studied by examining the molecular orbitals involved by DFT and by realizing an extended Hückel calculation. We compared **1** and bis(ferrocenylethynyl)bis(trimethylphosphine)platinum(II) **2b** instead of **2**, replacing the triethylphosphines by trimethylphosphines. The comparison between **1** and **2b** will give some information about the effect of the incorporation of the platinum moiety, bearing in mind the different Fe–Fe distance in these two complexes (9.78 Å in **1**, 12.39 Å in **2b**). To free ourselves from the influence of the Fe–Fe distance, we also considered complex **1b** incorporating three triple bonds between the two ferrocenyl groups. Complexes **1b** and **2b** have almost identical Fe–Fe distances (12.22 and 12.39 Å, respectively), which enables us to focus on the pure influence of the platinum complex on V_{ab}.

Contrary to molecular mechanics calculations, where the nature of the interatomic bonds is fixed, DFT calculations yield a geometry which takes into account a possible cumulenic form due to electronic delocalization through the bridge. It is known indeed that pure DFT tends to overestimate the electronic delocalization.[12] On the contrary, Hartree–Fock

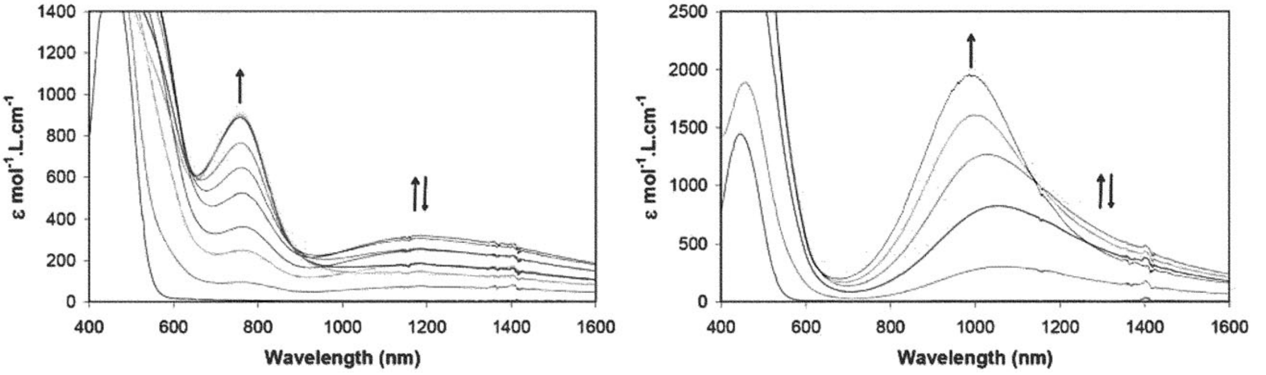


Fig. 3 Visible and near infrared spectra of the partially oxidized complexes obtained during the gradual oxidation of complexes **1** and **2** (CH_2Cl_2, 0.1 M $^{n}Bu_4NBF_4$). The concentration of mixed-valence complexes is maximum for 0.5 electron per ferrocene centre.

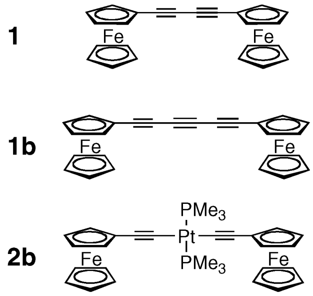


Fig. 4 Complexes used to study theoretically the electronic influence of a *trans*-platinum complex.

calculations tend to underestimate the electronic delocalization[13] and for this reason we have chosen DFT with an hybrid functional (B3PW91) to obtain some more reliable results. The starting structure for DFT optimization has been constructed from the X-ray structure of fragments in order to decrease the CPU time. The structures of two ferrocenyl units separated by two and four carbon–carbon triple bonds have been described[14] and therefore we have taken the average C–C distances to describe a bridge with three C–C triple bonds.

The calculation of vibration frequencies has shown the absence of imaginary frequencies, which confirms that the optimized structure is indeed a minimum of energy. On the optimized structures (Fig. 5) the two Cp cycles covalently linked to the bridge are in the same plane (torsion angle 0.6°), as found in the starting X-ray structures. Besides, the Fe–C distances within the ferrocenes are very similar in the X-ray (2.045 Å) and the calculated (2.041 Å) structures.

Similarly the structure of complex **2b** was optimized by DFT starting from a crystallographic structure published by Mori *et al.*[15] In the optimized structure the Cp cycles are almost coplanar (torsion angle 2°) and the Pt–P distance is relatively close to the crystallographic data (2.329 Å instead of 2.285 Å).

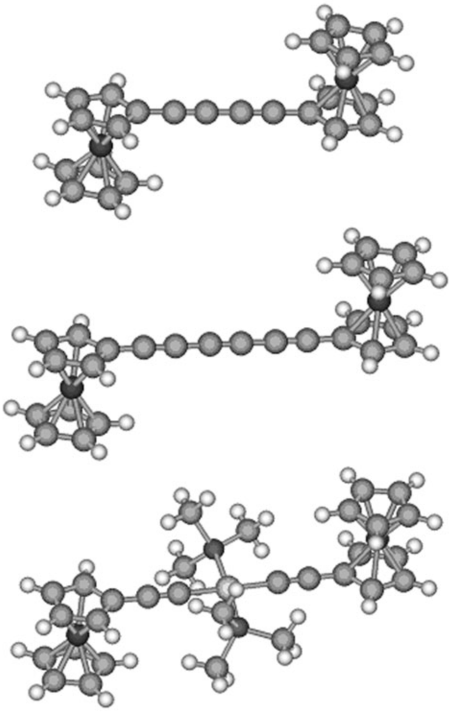


Fig. 5 DFT-optimized structures of complexes **1**, **1b** and **2b**.

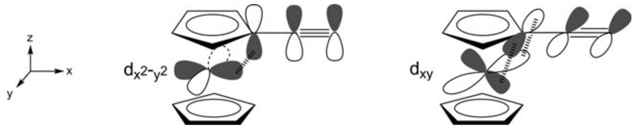


Fig. 6 Overlap between the iron 3d orbitals and the orbitals of the bridge.

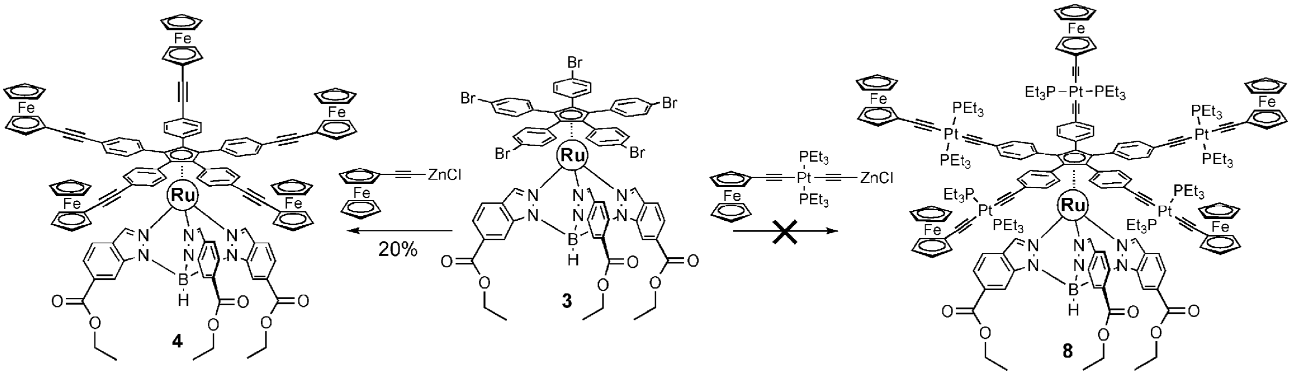
The electronic coupling parameter can be determined from the calculation of molecular orbitals by the dimer splitting method.[16] In the case of complexes bearing a symmetry element, such as here an inversion centre, the system is reduced to two levels: only the two significant metallic molecular orbitals (symmetrical and antisymmetrical) with the largest energy gap are taken into consideration. The energy difference between these two MOs corresponds to 2 V_{ab}.

A significant overlap can take place between the iron 3d orbitals and the orbitals of the bridge. In the ferrocenyl unit, the 3d orbitals of iron split into three groups: (d_{xz}, d_{yz}), d_{z^2}, (d_{xy}, $d_{x^2-y^2}$). Among the filled orbitals, the d_{z^2} orbitals have almost no overlap with the bridge orbitals and therefore do not take part in the electronic communication. However the d_{xy} and $d_{x^2-y^2}$ orbitals strongly overlap (Fig. 6) with the bridge orbitals and are involved in the electronic delocalization through the two orthogonal π systems of the conjugated alkyne bridge.

Since the DFT method tends to underestimate the energy gap between the different orbitals, in particular the HOMO–LUMO gap,[17] we have estimated V_{ab} from Hückel orbitals. An extended Hückel calculation was carried out with the HyperChem Professional 6 program package, using parameters optimized for iron and platinum,[18] and performed on the basis of the DFT-optimized geometry.

V_{ab} was determined from the energy difference between the significant *u*- and *g*-symmetry orbitals on the $3d_{x^2-y^2}$ orbitals of the iron atoms represented on Fig. 6 for **1**, **1b** and **2b**. The contribution of the $3d_{xy}$ orbitals in the electronic communication was neglected because the splitting between the *u*- and *g*-symmetry MOs was significantly smaller than that of the $3d_{x^2-y^2}$ orbitals.

Considering the Hückel parameter for the iron 3d orbital to be −11 eV, the electronic coupling parameter V_{ab} for complex **1** (with two triple bonds between the ferrocenyl groups) is 0.090 eV, which is higher than the value obtained for **1b** (0.077 eV with three triple bonds) and corresponds to a moderately coupled system. As expected this difference illustrates the attenuation of the electronic coupling with an increased distance. The same calculations for complex **2b** gave a V_{ab} value equal to 0.022 eV, *i.e.* it is a weakly coupled system. In the case of **1** and **2b** the highest energy orbital has *g*-symmetry, contrary to **1b**. For a given Fe–Fe distance, the insertion of platinum in a conjugated acetylenic system results in a 3-fold decrease in the electronic coupling, which demonstrates the slight insulating role of the *trans*-platinum complex. This can be interpreted in terms of the pure σ character of the Pt–C



Scheme 1 Palladium-catalysed coupling strategy.

bond, which should insulate the π systems located on either side of the platinum. Platinum thus hinders the electronic delocalization through the molecule and decreases the V_{ab} coupling parameter.

The V_{ab} value depends on the parameters used for the extended Hückel calculation, in particular the energy of the iron 3d orbitals. To validate our calculations, the energy of the 3d orbitals of free iron was varied from −10.5 to −11.5 eV, which greatly influences the absolute V_{ab} value but does not alter the observed trend: the value for the platinum-containing complex is always significantly lower than for the fully-conjugated complex. (see Supplementary Information for details†).

Despite the discrepancy observed between the results obtained from the experimental and theoretical approaches, both converge towards the conclusion that the insertion of a *trans*-platinum complex in the bridging unit increases its insulating character by decreasing the electronic communication within mixed valence complexes.

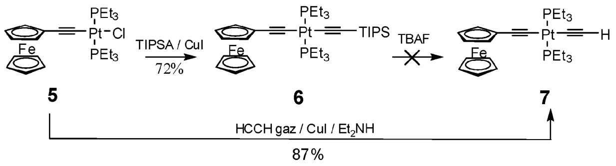
Synthesis of the molecular motor without platinum fragments

Our strategy is based on a quintuple palladium catalysed coupling reaction between the pentabrominated ruthenium complex (**3**) and ethynyl ferrocene. The synthetic scheme is presented in Scheme 1.

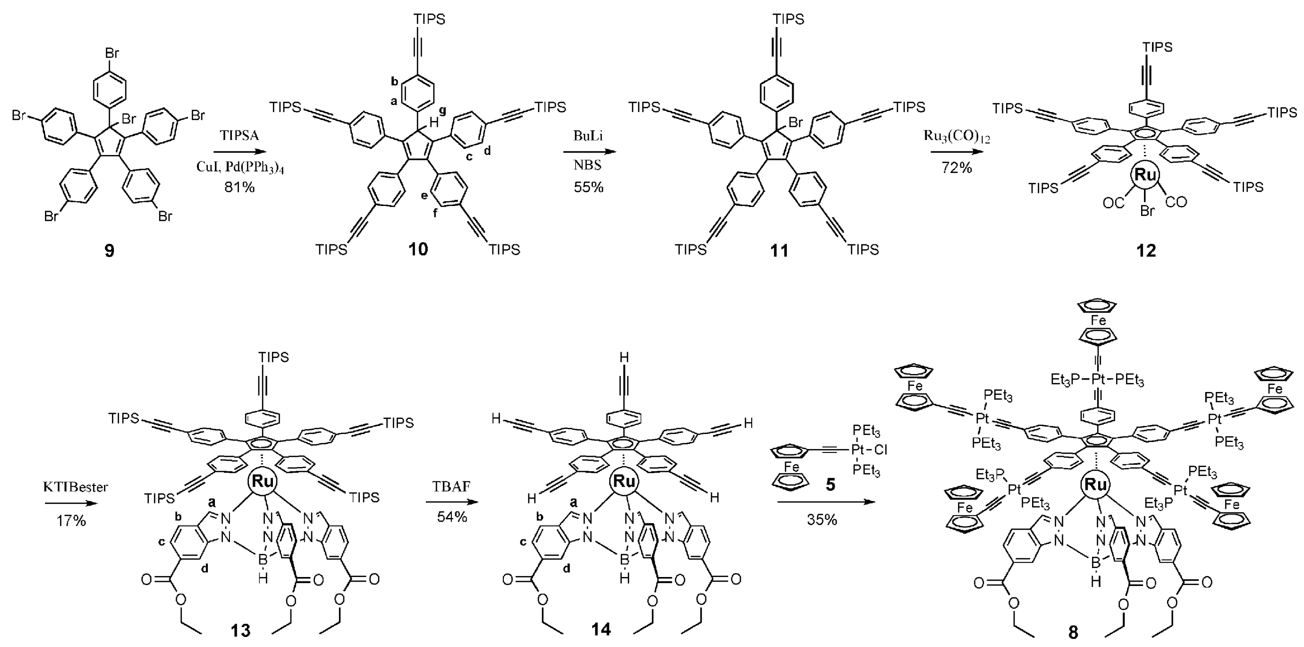
The ruthenium centre **3** was prepared by heating under microwave irradiation in a sealed tube bromo η^5-1,2,3,4,5-penta-(*p*-bromophenyl)cyclopentadienyl dicarbonyl ruthenium(II) with potassium hydrotris[6-(ethoxycarbonyl)indazol-1-yl]borate in a mixture of DMF and acetonitrile. After purification by column chromatography **3** was obtained in a 19% yield. The coupling between an alkyne and an aryl bromide is in general achieved under Sonogashira conditions,[19] *i.e.* using catalytic CuI and Pd(PPh$_3$)$_4$. These conditions were unsuccessful, maybe due to the high electron density of the bromide derivative which is covalently linked to a formal anionic entity (Cp). The electron-rich character of the carbon–bromide bond precludes the oxidative addition on the palladium catalyst. However the synthesis of the motor **4** was achieved by a quintuple Negishi coupling[20] using a solution of [(ferrocenyl)ethynyl]]zinc chloride and Pd(PPh$_3$)$_4$ in refluxing THF · **4** was isolated after purification by column chromatography in 20% yield, which correspond to 72% by coupling reaction. ^{1}H-NMR spectroscopy clearly showed an AA′BB′ pattern for the phenyl groups attached to the central Cp ring, the quadruplet and triplet system of the ethyl groups of the esters and an integration of 45 protons for the ferrocene moieties. The presence of the five ferrocene units was also confirmed by MALDI-TOF spectrometry.

Synthesis of the platinum precursors

trans-Bis(alkynyl)bis(trialkylphosphine)platinum(II) complexes have been chosen to maintain the rigidity and linearity of the assembly and to keep the electroneutrality of the molecule which is essential for its deposition on a surface. Moreover the diameter of the molecule is significantly increased (from 2 to 3 nm) which is interesting for the future near-field microscopy studies. As shown in Schemes 2 and 3, a modular strategy was followed in order to build separately the arms containing the electroactive groups and the ruthenium core, and to couple them in a last step. The synthesis of complex **7**, bearing a free alkyne function for the last coupling step with the ruthenium precursor, was envisaged starting from *trans*-dichlorobis(triethylphosphine)platinum(II), by the successive displacement of the two chloride ligands.[21] The first chloride ligand was substituted by a ferrocenylethynyl fragment, by heating *trans*-Pt(PEt$_3$)$_2$Cl$_2$ with ethynylferrocene in the presence of a base under microwave irradiation (300 W) in a sealed tube for 15 min. Complex **5** was obtained in 86% after chromatography. Its *trans* geometry was confirmed by ^{31}P NMR with the $^1J(^{31}P–^{195}Pt)$ coupling constant. For complex **5** the value of the coupling constant was found to be 2405 Hz, which corresponds to a *trans* geometry, a *cis* coupling constant being much larger (about 3500 Hz).[22] The second alkyne function was introduced as tri(isopropylsilsyl) (TIPS) protected group under Sonogashira conditions in 72% isolated yield. The deprotection of complex **6** was attempted under the classical conditions, using tetrabutylammonium fluoride (TBAF) in THF containing 5% water, at room temperature. Even by heating, using microwaves or KF in combination with a crown ether, no deprotection occurred. This could be



Scheme 2 Synthesis of the platinum-containing electroactive arms.



Scheme 3 Synthesis of the motor with platinum insulating fragments.

explained by the electronic effect of the platinum complex on the acetylenic TIPS group. Complex **7** could nevertheless be obtained in 87% yield by reaction of gaseous acetylene with complex **5**, in the presence of catalytic CuI and diethylamine.

Connection to the ferrocenyl-terminated platinum fragments

Following a modular strategy, the five ferrocene-platinum arms remained to be coupled to the core through a classical palladium-catalyzed coupling reaction between ruthenium complex **3** and the platinum moiety **7**. The Negishi conditions which were successful for the synthesis of the motor **4** failed to prepare the molecular motor incorporating platinum fragments (**8**). This can be due to the instability of the platinum complex in the presence of a strong base such as BuLi. Therefore a second route was followed (Scheme 3), in which the alkyne functions carried by the ruthenium core (**14**) are coupled to a chloroplatinum complex (**5**).

The ruthenium complex **14** was prepared in five steps starting from 1-bromo-1,2,3,4,5-penta(*p*-bromophenyl)cyclopentadiene **9**.[23] The pentayne compound **10** was obtained from **9** in a remarkable 81% isolated yield by a quintuple Sonogashira coupling with mono-TIPS-protected acetylene.[24] Many attempts to coordinate directly **10** with $RuCl_3$[25] or $[Ru(p\text{-cymene})Cl_2]_2$[26] failed, probably due to the sterical hindrance of the phenyl groups on the Cp ligand. The only alternative to introduce ruthenium was Manners methodology which consists in an oxidative addition of the brominated Cp **11** on the ruthenium carbonyl cluster $Ru_3(CO)_{12}$.[27] The bromine atom was introduced on the cyclopentadiene ring using ^{n}BuLi and NBS at low temperature. The ruthenium was subsequently coordinated, yielding complex **12** in a 72% yield after chromatography. The complex **13** incorporating a tripodal ligand with ester anchoring groups[28] derived from the scorpionate family[29] was obtained using microwave irradiation in 17% yield after chromatographic purification. Finally the TIPS protecting groups were removed by overnight reaction with TBAF to yield after chromatography the desired complex **14** in 54% isolated yield.

As mentioned previously, the target molecule **8** could not be obtained when the halide groups were carried on the ruthenium complex **3**. On the contrary, the second approach was successful and the quintuple coupling of chloroplatinum complex **5** with complex **14** gave the desired product in 35% isolated yield, which corresponds to a yield of 81% per coupling. The complex was fully characterised by multinuclear NMR. The AA′BB′ pattern of the protons of the phenyl groups attached to the central Cp ring and an integration of 45 protons for the signals of the ferrocene units were observed in ^{1}H NMR. Both ^{31}P and ^{195}Pt NMR[22,30] are in agreement with the formation of only the *trans* isomer of the platinum diphosphino complex with a coupling constant $^1J_{^{195}\text{Pt–P}}$ of 2393 Hz. The presence of the five platinum units was also confirmed by MALDI-TOF mass spectrometry.

We then investigated the electronic communication between ferrocene units in complexes **4** and **8** by spectroelectrochemistry. We performed a partial oxidation of the ferrocene sites, in search for intervalence transitions but no such transitions were observed, showing that the electronic communication between these sites is not measurable.

Conclusion

A theoretical approach combining geometry optimization by DFT and extended Hückel calculations on bis-ferrocenyl model compounds allowed the electronic communication parameter V_{ab} between ferrocene units to be estimated, showing a four-fold attenuation in the presence of a *trans*-platinum spacer between the two iron centres. The experimental approach based on spectroelectrochemistry led to the same conclusion, although by a factor of only 1.5. Thus the bis acetylide *trans*-platinum spacer has some insulating character, as shown in the decrease in the electronic coupling parameter.

On the basis of these results, we have synthesized two star-shaped molecules incorporating ester anchoring groups on the trisindazolylborate part (stator). One of these ruthenium complexes bears platinum spacers on the rotor, and thus fulfils all the requirements for an electrically driven molecular motor. Work is now underway to anchor these molecules on an oxide surface to prepare their addressing with two metallic electrodes. The demonstration of a controlled rotary movement will then need further experimental developments by physical methods such as scanning probe microscopies or the analysis of the time dependence of the current in a two-electrode configuration.

Experimental

Computational details

Geometries of the ferrocene derivatives were fully optimized at the BP86/6-31G** and B3PW91/6-31G** level or at the BP86/6-31G**/LANL2DZ(Pt) and B3PW91/6-31G**/LANL2DZ(Pt) level for the platinum derivative using Gaussian98.[31] The second generation functional BP86 was chosen because it seemed particularly appropriate for modelling ferrocenyl groups.[32] In the case of the platinum complex, the same BP86 functional was used but the platinum and phosphorus atoms have been modelled by using the effective core potential and the corresponding valence orbitals LanLDZ in order to decrease the number of basis functions. In all cases, the atoms were described by the zeta 6-31G** double base which takes into account the polarization orbitals of all atoms, including hydrogens. Vibrational analysis was performed at the same level in order to check the obtention of a minimum on the potential energy surface.

Syntheses

All commercially available chemicals were of reagent grade and were used without further purification. Ethynylferrocene and *trans*-dichlorobis(triethylphosphine)platinum(II) were purchased from Aldrich. Ruthenium carbonyl and 1,2,3,4,5-pentaphenylcyclopentadiene were purchased from Strem. 1,4-di(ferrocenyl)butadiyne (**1**),[12] 1-bromo-1,2,3,4,5-penta(*p*-bromophenyl)cyclopentadiene (**9**),[23] bromo η^5-1,2,3,4,5-penta-(*p*-bromophenyl)cyclopentadienyldicarbonyl ruthenium (II),[23] and potassium hydrotris[6-(ethoxycarbonyl)indazol-1-yl] borate[27] were prepared according to literature procedures. Toluene was dried over CaH_2, THF over sodium with benzophenone and diethylamine over KOH. All reactions were carried out using standard Schlenk techniques under an argon atmosphere. Flash column chromatography was carried out on silica gel 230–400 mesh from SDS. NMR Spectra were recorded on Bruker AM 250 or Avance 500 spectrometers and full assignments were made using COSY, ROESY, HMBC and HMQC methods. Chemical shifts are defined with respect to TMS = 0 ppm for ^1H and ^{13}C NMR spectra and to H_3PO_4 for ^{31}P NMR spectra and were measured relative to residual solvent peaks. The following abbreviations have been used to describe the signals: s for singlet; d for doublet; t for triplet; q for quadruplet; m: for multiplet. The numbering scheme is given in Schemes 1 and 2 (*vide supra*).

UV–visible–near infra-red spectra were recorded on a Shimadzu UV-3100 spectrometer. FAB and DCI mass spectrometry was performed using a Nermag R10-10. Cyclic voltammetry was performed with an AUTOLAB PGSTAT 100 potentiostat using a Pt disc (1 mm diameter) as working electrode and a Pt counter electrode. The reference electrode used was the saturated calomel electrode (SCE).

***trans*-Bis(ferrocenylethynyl)-bis(triethylphosphine) platinum(II) (2).** CuI (10 mg, 0.05 mmol) was added to a solution of *trans*-dichlorobis(triethylphosphine) platinum(II) (250 mg, 0.5 mmol, 1 eq.) and ethynylferrocene (210 mg, 1 mmol, 2 eq.) in degassed diethylamine (10 mL). The solution was stirred at room temperature during 2 h. Solvents were removed under reduced pressure and the crude material was column chromatographed (SiO_2: cyclohexane–Et_2O, (0–5%)). The product was isolated as an orange solid (300 mg, 70%). MS: (DCI/NH_3) 850 $[M + H]^+$; High Resolution LSI Calculated $[M]^+$: 849.1578 ($C_{36}H_{48}Fe_2P_2Pt$) Found: 849.1582 (100% $[M]^+$); Mp = 193 °C. ^1H NMR: (250 MHz, $CDCl_3$) δ 4.20 (4H, t, J = 1.6 Hz, subst. Cp), 4.13 (10H, s, Cp), 4.04 (4H, t, J = 1.6 Hz, subst. Cp), 2.17 (12H, m, CH_2CH_3), 1.24 (18H, m, CH_2CH_3); ^{13}C NMR: (100 MHz, CD_2Cl_2) δ 104.44; 102.72; 73.13; 70.07; 69.27; 66.93; 16.32; 8.21; ^{31}P NMR (160 MHz, $CDCl_3$) δ: 10.98 (s, $J_{195_{Pt-P}}$ = 2391 Hz).

η^5-1,2,3,4,5-Penta-(4-bromophenyl) cyclopentadienyl hydrotris[6-(ethoxycarbonyl) indazol-1-yl]borate ruthenium(II) (3). Bromo η^5-1,2,3,4,5-penta-(*p*-bromophenyl)cyclopentadienyl dicarbonyl ruthenium(II) (55 mg, 0.05 mmol, 1 eq.) and potassium hydrotris[6-(ethoxycarbonyl)indazol-1-yl]borate (62 mg, 0.1 mmol, 2 eq.) were heated in a sealed tube at 150 °C under microwave irradiation during 10 minutes in a mixture of 2 ml of acetonitrile and 1 ml of DMF. The crude reaction mixture was evaporated under vacuum. The product was adsorbed on silica and purified by column chromatography (SiO_2, dichloromethane) to give a yellow solid (15 mg, 19%). MS: (APCI) 1522 $[M]^+$; ^1H NMR: (250 MHz, CD_2Cl_2) δ 8.76 (s, 3H, H_d), 7.95 (s, 3H, H_a), 7.68 (d, 3H, J = 8.5 Hz, H_c), 7.45 (d, 3H, J = 8.5 Hz, H_b), 7.21 (s broad, 20H, H_{o-m}), 4.47 (q, 6H, J = 7.1 Hz, CH_2), 1.48 (t, 9H, J = 7.1 Hz, CH_3); ^{13}C NMR: (63 MHz, CD_2Cl_2) δ 166.81; 143.22; 140.77; 135.10; 131.82; 130.92; 129.30; 125.35; 122.24; 121.26; 119.86; 113.97; 88.05; 61.38; 14.31.

η^5-1,2,3,4,5-Penta-(4-(ferrocenylethynyl)phenyl) cyclopentadienyl [6-(ethoxycarbonyl) indazol-1-yl]borate ruthenium(II) (4). In a two-necked flask, a solution of η^5-1,2,3,4,5-penta-(4-bromophenyl) cyclopentadienyl hydrotris[6-(ethoxycarbonyl)indazol-1-yl] borate ruthenium(II) (**3**, 40 mg; 0.026 mmol) and $Pd(PPh_3)_4$ (16 mg; 0.5 eq.) in 5 mL of freshly distilled THF was degassed. A solution of (ferrocenylethynyl)zinc chloride 0.2M (0.52 mmol) was then added. The mixture was heated under reflux for 24 h. Additional reactants were added (16 mg $Pd(PPh_3)_4$ and 0.5 mmol of (ferrocenylethynyl)zinc chloride) and heating at reflux was maintained for another 24 h. The crude reaction mixture was evaporated under vacuum. The product was adsorbed on silica and purified by flash column chromatography (SiO_2: cyclohexane–CH_2Cl_2 0–100%, to give an orange solid (11 mg, 20%). MS: (MALDI-TOF) 2166 $[M]^+$; ^1H NMR: (500 MHz, CD_2Cl_2) δ 8.79 (s, 3H, H_d), 8.09 (s, 3H, H_a), 7.70 (d, 3H, J = 8.5 Hz, H_c), 7.49 (d, 3H, J = 8.5 Hz, H_b), 7.36 (d, 10H, J = 8.4 Hz, H_o), 7.19 (d, 10H, J = 8.4 Hz, H_m) 4.47 (q, 6H, J = 7.1 Hz, CH_2), 4.44 (t, 10H, J = 1.8 Hz, subs Cp), 4.22 (t, 10H, J = 1.8 Hz, subs Cp), 4.20 (s, 25H, Cp), 1.48 (t, 9H, J = 7.1 Hz, CH_3); ^{13}C NMR: (126 MHz, CD_2Cl_2) δ 166.84; 143.10; 140.83; 133.46; 132.64; 130.32; 128.95; 125.36; 123.22; 121.01; 119.78; 113.86; 89.58; 88.62; 85.15; 71.38; 69.93; 68.98; 64.85; 61.27; 14.24.

***trans*-Chloro-(ferrocenylethynyl)-bis(triethylphosphine) platinum(II) (5).** *trans*-Dichlorobis(triethylphosphine)platinum(II) (250 mg, 0.5 mmol, 1 eq.) and ethynylferrocene (105 mg, 0.5 mmol, 1 eq.) were dissolved in a mixture of chloroform (4 mL) and diethylamine (1 mL). The mixture was heated in a sealed tube at 113 °C under microwave irradiation over a 15 min period. Solvents were removed under reduced pressure and the crude material was column chromatographed (SiO_2: cyclohexane–Et_2O (0–5%)). The product was isolated as an orange solid (290 mg, 86%). MS: (DCI/NH_3) 677 $[M + H]^+$; High Resolution LSI Calculated $[M]^+$: 675.1213 ($C_{24}H_{39}ClFeP_2Pt$) Found: 675.1215 (100% $[M]^+$); Mp = 94 °C. ^1H NMR: (250 MHz, $CDCl_3$) δ 4.20 (2H, t, J = 1.8 Hz, subst. Cp), 4.12 (5H, s, Cp), 4.05 (2H, t, J = 1.8 Hz, subst. Cp), 2.06 (12H, m, CH_2CH_3), 1.20 (18H, m, CH_2CH_3); ^{13}C NMR: (100 MHz, CD_2Cl_2) δ 96.70; 76.47; 72.72; 70.82; 69.35; 67.07; 14.49; 7.86; ^{31}P NMR: (160 MHz, $CDCl_3$) δ 14.77 (s, $J_{195_{Pt-P}}$ = 2405 Hz).

***trans*-(Triisopropysilyl)ethynyl-(ferrocenylethynyl)-bis(triethylphosphine) platinum(II) (6).** CuI (20 mg, 0.1 mmol, 0.3 eq.) and TIPSA (0.1 mL, 0.44 mmol, 1.3 eq.) were added to a solution of *trans*-chloro-(ferrocenylethynyl)-bis(triethylphosphine)platinum(II) (**5**) (230 mg, 0.34 mmol, 1 eq.) in degassed diethylamine (5 mL). The solution was stirred at room temperature during 40 min. Solvents were removed under reduced pressure and the crude material was column chromatographed (SiO_2: cyclohexane–Et_2O (0–5%)). The product was isolated as an orange solid (200 mg, 72%). MS: (DCI/NH_3) 822 $[M + H]^+$. ^1H NMR: (250 MHz, $CDCl_3$) δ 4.22 (2H, broad s, subst. Cp), 4.13 (5H, s, Cp), 4.05 (2H, broad s, subst. Cp), 2.15 (12H, m, CH_2CH_3), 1.19 (18H, m, CH_2CH_3), 1.04 (21H, m, TIPS); ^{31}P NMR: (160 MHz, $CDCl_3$) δ 11.30 (s, $J_{195_{Pt-P}}$ = 2409 Hz).

***trans*-Ethynyl(ferrocenylethynyl)-bis(triethylphosphine) platinum(II) (7).** CuI (10 mg, 0.05 mmol) was added to a solution of *trans*-chloro-(ferrocenylethynyl)-bis(triethylphosphine)platinum(II) (**5**) (290 mg, 0.43 mmol) in degassed diethylamine (5 mL). Acetylene was bubbled in the solution with stirring at room temperature for 20 min. Solvents were removed under reduced pressure and the crude material was column chromatographed (SiO_2: cyclohexane–Et_2O (0–5%)). The product was isolated as an orange solid (250 mg, 87%). MS: (FAB^+, MNBA) 665 $[M]^+$; High Resolution LSI Calculated $[M]^+$: 665.1603 ($C_{26}H_{40}FeP_2Pt$) Found: 665.1604 (100% $[M]^+$); Mp = 71 °C. ^1H NMR: (250 MHz, $CDCl_3$) δ 4.19 (2H, t, J = 2.0 Hz, subst. Cp), 4.10 (5H, s, Cp), 4.02 (2H, t, J = 2.0 Hz, subst. Cp), 2.16 (1H, s, H alkyne, 2.13 (12H, m, CH_2CH_3), 1.18 (18H, m, CH_2CH_3); ^{13}C NMR: (100 MHz, CD_2Cl_2) δ 104.24; 102.28; 100.61; 94.03; 72.94; 70.08; 69.31; 66.96; 16.05; 8.11; ^{31}P NMR: (160 MHz, $CDCl_3$) δ 10.70 (s, $J_{195_{Pt-P}}$ = 2380 Hz).

η^5-1,2,3,4,5-Penta[4-{*trans*-ethynyl-(ethynylferrocenyl)-bis(triethylphosphine)platinum(II)} phenyl] cyclopentadienyl hydrotris[6-(ethoxycarbonyl) indazol-1-yl]borate ruthenium(II) (8). In a Schlenk tube, η^5-1,2,3,4,5-penta(4-(ethynyl)phenyl)cyclopentadienylhydrotris[6-(ethoxycarbonyl) indazol-1-yl]borate ruthenium(II) (**14**) (16 mg, 0.013 mmol, 1 eq.), THF (2 mL) and diethylamine (1 mL) were degassed under argon during 20 min. *trans*-Chloro-(ferrocenylethynyl)-bis(triethylphosphine)-platinum(II) (**5**) (50 mg, 0.073 mmol, 5.6 eq.) and CuI (5 mg, 0.010 mmol, 2 eq.) were added and the mixture was stirred at room temperature for 8 h. The same amounts of additional CuI and platinum complex were added and the solution was stirred at room temperature overnight. Solvents were removed under reduced pressure and the crude material was column chromatographed (SiO_2, cyclohexane–Et_2O (0–20%)) to give an orange solid (20 mg, 35%). MS: (MALDI-TOF) 4442.4 $[M]^+$ (Calc. 4442.19); ^1H NMR: (500 MHz, C_6D_6) δ 9.24 (s, 3H, H_d), 8.70 (s, 3H, H_a), 8.02 (d, 3H, J = 7.2 Hz, H_c), 7.78 (d, 10H, J = 7.6 Hz, H_o), 7.36 (d, 10H, J = 7.6 Hz, H_m), 6.99 (d, 3H, J = 7.2 Hz, Hb), 4.53 (s broad, 10H, subst. Cp), 4.33 (s, 25H, Cp), 4.1 (q, 6H, J = 6.4 Hz, OCH_2CH_3), 4.12 (s broad, 10 H, subst. Cp), 2.09 (m, 60H, CH_2), 1.43 (t, 9H, J = 6.4 Hz, OCH_2CH_3), 1.22 (m, 90H, CH_3); ^{13}C NMR: (125 MHz, C_6D_6) δ 166.40; 143.55; 140.99; 133.73; 130.32; 125.90; 121.30; 120.30; 113.94; 70.51; 69.61; 67.29; 60.61; 16.57; 8.33; ^{31}P NMR: (200 MHz, C_6D_6) δ 11.30 (s, $J_{195_{Pt-P}}$ = 2393 Hz); ^{195}Pt NMR: (500 MHz, C_6D_6) δ–4745.

1,2,3,4,5-Penta(4-(triisopropylsilylacetylene)phenyl)cyclopentadiene (10). In a Schlenk tube, 1-bromo-1,2,3,4,5-penta(4-bromophenyl)cyclopentadiene (**9**) (300 mg, 0.32 mmol, 1 eq.), TIPSA (1.4 mL, 6.4 mmol, 20 eq.), diisopropylamine (2 mL) and freshly distilled THF (4 mL) were degassed under argon during 20 min. CuI (12 mg, 0.06 mmol, 20 mol%) and $Pd(PPh_3)_4$ (40 mg, 0.03 mmol, 10 mol%) were added and the mixture was heated at 80 °C overnight. The same amounts of additional CuI, TIPSA and Pd^0 were added and the mixture was heated at 80 °C for another 24 h. Solvents were removed under reduced pressure and the crude material was column chromatographed (SiO_2, cyclohexane–CH_2Cl_2 (0–10%)) to give a fluorescent yellow glassy solid (350 mg, 81%). MS: (DCI/NH_3) 1349 $[MH]^+$, 1381 $[M + 2NH_3]^+$; High Resolution LSI Calculated $[M]^+$: 1346.8706 ($C_{90}H_{126}Si_5$) Found: 1346.8687 (100% $[M]^+$). ^1H NMR: (250 MHz, CD_2Cl_2) δ 7.34 (d, 6H, J = 8 Hz, H_{b-f}), 7.21 (d, 4H, J = 8 Hz, H_d), 7.17 (d, 2H, J = 8 Hz, H_a), 7.02 (d, 4H, J = 8 Hz, H_e), 6.96 (d, 4H, J = 8 Hz, H_c), 5.16 (s, 1H, H_g), 1.14 (m, 105 H, TIPS); ^{13}C NMR: (100 MHz, CD_2Cl_2) δ 146.80; 144.11; 137.92; 135.71; 135.23; 132.37; 131.74; 131.49; 129.95; 128.76; 128.30; 122.24; 122.02; 121.74; 106.83; 106.78; 106.72; 91.34; 91.23; 90.57; 62.11; 18.43; 18.39; 11.30; 11.26.

1-Bromo-1,2,3,4,5-penta(4-(triisopropylsilylacetylene)phenyl) cyclopentadiene (11). In a Schlenk tube, 1,2,3,4,5-penta(4-(triisopropylsilylacetylene)phenyl)cyclopentadiene (**10**) (380 mg, 0.28 mmol, 1 eq.) was dissolved in freshly distilled THF (10 mL). ^{n}BuLi (0.28 mmol, 1 eq.) was added dropwise under argon at −78 °C and the mixture was stirred at this temperature for 30 min. NBS (55 mg, 0.30 mmol, 1.1 eq.) was subsequently added and the mixture was stirred at −78 °C for 30 min. The temperature was left to raise slowly to room temperature. Solvents were removed under reduced pressure and the crude material was column chromatographed (SiO_2, cyclohexane) to give an orange glassy solid (220 mg, 55%). MS: (DCI/NH_3) 1427 $[MH]^+$, 1444 $[M + NH_4]^+$; High Resolution LSI Calculated $[M]^+$: 1424.7811 ($C_{90}H_{125}BrSi_5$) Found: 1424.7863 (100% $[M]^+$); ^1H NMR: (500 MHz, $CDCl_3$) δ 7.36 (broad s, 4H, H_{a-b}), 7.28 (d, 4H, J = 8 Hz, H_f), 7.21 (d, 4H, J = 8 Hz, H_d), 6.89 (d, 4H, J = 8 Hz, H_e), 6.88 (d, 4H, J = 8 Hz, H_c), 1.15 (s, 21H, TIPS), 1.14 (s, 42H, TIPS), 1.11 (s, 42H, TIPS); ^{13}C NMR: (125 MHz, $CDCl_3$) δ 148.34; 141.55; 135.27; 134.03; 133.52; 132.32; 131.86; 131.56; 131.4; 130.08; 129.80; 127.36; 123.32; 122.69; 122.51; 106.90; 106.81; 106.37; 91.81; 91.64; 91.51; 75.35; 18.67; 11.32.

Bromo-η^5-1,2,3,4,5-penta[4-(triisopropylsilylacetylene)phenyl] cyclopentadienyl dicarbonyl ruthenium(II) (12). Ruthenium carbonyl (37 mg, 0.058 mmol, 1 eq.) and 1-bromo-1,2,3,4,5-penta (4-(triisopropylsilylacetylene)phenyl)cyclopentadiene (**11**) (250 mg, 0.17 mmol, 3 eq.) were heated under argon at reflux for 2 h in 4 mL of freshly distilled toluene. The solution, initially yellow, rapidly turned to dark green and then to cherry red. Solvents were removed under reduced pressure and the crude material was column chromatographed (SiO_2, cyclohexane–CH_2Cl_2 (0–10%)) to give a yellow solid (200 mg, 72%). MS: (DCI/NH_3) 1618 $[M + 2NH_3]^+$, 1601 $[M + NH_3]^+$, 1563 $[M + 2NH_3 - 2CO]^+$, 1545 $[M + NH_3 - 2CO]^+$, 1528 $[M - 2CO]^+$; High Resolution LSI Calculated $[M]^+$: 1582.6753 ($C_{92}H_{125}BrO_2RuSi_5$) Found: 1582.6791 (100% $[M]^+$); Mp = 180 °C (with decomposition). ^1H NMR: (250 MHz, CD_2Cl_2) δ 7.28 (d, 10H, J = 8.6 Hz, H_o), 7.00 (d, 10H, J = 8.6 Hz, H_m), 1.13 (s, 105H, TIPS); ^{13}C NMR: (100 MHz, CD_2Cl_2) δ 196.17; 132.28; 131.70; 129.36; 123.99; 106.31; 105.99; 92.76; 18.53; 11.43; IR: $\nu_{C=O}$ 2004 (s) and 2048 (s) cm^{-1}.

η^5-1,2,3,4,5-Penta-(4-(triisopropylsilylacetylene)phenyl)cyclopentadienyl hydrotris [6-(ethoxycarbonyl)indazol-1-yl] borate ruthenium(II) (13). Bromo-η^5-1,2,3,4,5-penta(4-(triisopropylsilylacetylene)phenyl)cyclopentadienyl dicarbonyl ruthenium(II) (**12**) (160 mg, 0.1 mmol, 1 eq.) and potassium hydrotris [6-(ethoxycarbonyl)indazol-1-yl]borate (125 mg, 0.2 mmol, 2 eq.) were heated in a sealed tube at 150 °C under microwave irradiation during 10 minutes in a mixture of 2 ml of acetonitrile and 1 ml of DMF. The crude reaction mixture was evaporated under vacuum. The product was adsorbed on silica and purified by column chromatography (SiO_2, cyclohexane–CH_2Cl_2 80%) to a yellow solid (35 mg, 17%). MS: (APCI) 2029 $[M + H]^+$; High Resolution LSI Calculated $[M]+$: 2026.9835 ($C_{120}H_{153}BBrO_2N_6O_6RuSi_5$) Found: 2026.9872 (100% $[M]^+$); ^1H NMR: (250 MHz, CD_2Cl_2) δ 8.76 (s, 3H, H_a), 7.99 (s, 3H, H_d), 7.68 (d, 3H, J = 8.6 Hz, H_c), 7.46 (d, 3H, J = 8.6 Hz, H_b), 7.31 (d, 10H, J = 8.2 Hz, H_o), 7.17 (d, 10H, J = 8.2 Hz, H_m), 4.47 (q, 6H, J = 7.1 Hz, CH_2), 1.48 (t, 9H, J = 7.1 Hz,CH_3), 1.08 (m, 105H, TIPS); ^{13}C NMR: (63 MHz, CD_2Cl_2) δ 166.80; 143.11; 140.84; 133.31; 133.04; 131.04; 129.03; 125.31; 122.78; 121.03; 119.81; 113.86; 106.53; 91.85; 88.53; 61.25; 18.39; 14.25; 11.28.

η^5-1,2,3,4,5-Penta[4-(ethynyl)phenyl]cyclopentadienyl hydrotris [6-(ethoxycarbonyl)indazol-1-yl] borate ruthenium(II) (14). η^5-1,2,3,4,5-Penta-(4-(triisopropylsilylacetylene)phenyl) cyclopentadienyl hydrotris [6-(ethoxycarbonyl)indazol-1-yl] borate ruthenium(II) (**13**) (30 mg, 0.015 mmol, 1 eq.) was dissolved in 2 ml of TBAF 1M in THF (2 mmol, 135 eq.) with 5% of water. The solution was stirred at room temperature overnight and the solvent was evaporated. The crude product was purified by column chromatography (SiO_2, CH_2Cl_2) to give a yellow solid (10 mg, 54%). MS: (APCI) 1246 $[M]^+$; ^1H NMR: (250 MHz, CD_2Cl_2) δ 8.76 (s, 3H, H_a), 7.98 (s, 3H, H_d), 7.68 (d, 3H, J = 8.5 Hz, H_c), 7.44 (d, 3H, J = 8.5 Hz, H_b), 7.31 (d, 10H, J = 8.4 Hz, H_o), 7.17 (d, 10H, J = 8.4 Hz, H_m), 4.47 (q, 6H, J = 7.1 Hz, CH_2), 3.11 (s, 5H, CH), 1.48 (t, 9H, J = 7.1 Hz, CH_3); ^{13}C NMR: (63 MHz, CD_2Cl_2) δ 166.85; 143.19; 140.83; 133.82; 133.43; 131.32; 129.21; 125.38; 121.53; 121.18; 119.85; 113.95; 88.48; 83.04; 78.16; 61.36; 14.32.

Acknowledgements

G. V. thanks the French Ministry of National Education and the Ecole Normale Supérieure of Lyon for a PhD Fellowship. A. C. thanks the French Ministry of National Education and the Institut Universitaire de France for a PhD Fellowship. Dr Christine Lepetit (LCC-CNRS) is gratefully acknowledged for her assistance in the DFT calculations and we also would like to thank CALMIP (Calculation centre, Toulouse, France) for computing facilities. Dr Isabelle M. Dixon is warmly acknowledged for her corrections and comments on this manuscript. Christine Viala is also thanked for technical assistance in the measurement of the NMR spectra.

References

1 Special issue on molecular machines: *Acc. Chem. Res.*, 2001, **34**.

2 (*a*) D. Horinek and J. Michl, *J. Am. Chem. Soc.*, 2003, **125**, 11900; (*b*) H. Jian and J. M. Tour, *J. Org. Chem.*, 2003, **68**, 5091; (*c*) T. R. Kelly, H. De Silva and R. A. Silva, *Nature*, 1999, **401**, 150; (*d*) T. R. Kelly, R. A. Silva, H. De Silva, S. Jasmin and Y. Zhao, *J. Am. Chem. Soc.*, 2000, **122**, 6935; (*e*) N. Koumura, R. W. J. Zijistra, R. A. Van Delden, N. Harada and B. L. Feringa, *Nature*, 1999, **401**, 152; (*f*) D. A. Leigh, J. K. Y. Wong, F. Dehez and F. Zerbetto, *Nature*, 2003, **424**, 174; (*g*) K. Tashiro, K. Konishi and T. Aida, *J. Am. Chem. Soc.*, 2000, **122**, 7921; (*h*) M. K. J. Ter Wiel, R. A. Van Delden, A. Meetsma and B. L. Feringa, *J. Am. Chem. Soc.*, 2003, **125**, 15076; (*i*) M. Ikeda, M. Takeuchi, S. Shinkai, F. Tani, Y. Naruta, S. Sakamoto and K. Yamaguchi, *Chem.-Eur. J.*, 2002, **8**, 5541; (*j*) Z. Dominguez, H. Dang, M. J. Strouse and M. A. Garcia-Garibay, *J. Am. Chem. Soc.*, 2004, **124**, 2398; (*k*) T. Akutagawa, K. Shitagami, S. Nishihara, S. Takeda, T. Hasegawa, T. Nakamura, Y. Hosokoshi, K. Inoue, S. Ikeuchi, Y. Miyazaki and K. Saito, *J. Am. Chem. Soc.*, 2005, **127**, 4397.

3 A. Carella, G. Rapenne and J. P. Launay, *New J. Chem.*, 2005, **29**, 288.

4 G. S. Kottas, L. I. Clarke, D. Horinek and J. Michl, *Chem. Rev.*, 2005, **105**, 1281.

5 (*a*) M. Mayor, C. Von Hanisch, H. B. Weber, J. Reichert and D. Beckmann, *Angew. Chem., Int. Ed.*, 2002, **41**, 1183; (*b*) S. C. Jones, V. Coropceanu, S. Barlow, T. Kinnibrugh, T. Timofeeva, J.-L. Bredas and S. R. Marder, *J. Am. Chem. Soc.*, 2004, **126**, 11782; (*c*) P. Siemsen, U. Gubler, C. Bosshard, P. Gunter and F. Diederich, *Chem.-Eur. J.*, 2001, **7**, 1333.

6 D. Astruc, *Acc. Chem. Res.*, 1997, **30**, 383.

7 (*a*) S. Leininger, P. J. Stang and S. Huang, *Organometallics*, 1998, **17**, 3981; (*b*) N. Ohshiro, F. Takei, K. Onitsuka and S. Takahashi, *J. Organomet. Chem.*, 1998, **569**, 195; (*c*) K. Onitsuka, M. Fujimoto, H. Kitajima, N. Ohshiro, F. Takei and S. Takahashi, *Chem.-Eur. J.*, 2004, **10**, 6433; (*d*) K. Onitsuka, M. Fujimoto, N. Ohshiro and S. Takahashi, *Angew. Chem., Int. Ed.*, 1999, **38**, 689; (*e*) K. Onitsuka, A. Shimizu and S. Takahashi, *Chem. Commun.*, 2003, 280.

8 J. G. Rodriguez, A. Onate, R. M. Martin-Villamil and I. J. Fonseca, *J. Organomet. Chem.*, 1996, **513**, 71.

9 D. Osella, R. Gobetto, C. Nervi, M. Ravera, R. D'Amato and M. V. Russo, *Inorg. Chem. Commun.*, 1998, **1**, 239.

10 C. LeVanda, D. O. Cowan, C. Leitch and K. Bechgaard, *J. Am. Chem. Soc.*, 1974, **96**, 6788.

11 (*a*) N. S. Hush, *Coord. Chem. Rev.*, 1985, **64**, 135; (*b*) A.-C. Ribou, J.-P. Launay, M. L. Sachtleben, H. Li and C. W. Spangler, *Inorg. Chem.*, 1996, **35**, 3735.

12 J. L. Toto, T. T. Toto, C. P. de Melo, B. Kirtman and K. Robins, *J. Chem. Phys.*, 1996, **104**, 8586.

13 (*a*) C. Ho Choi, M. Kertesz and A. Karpfen, *J. Chem. Phys.*, 1997, **107**, 6712; (*b*) D. Jacquemin, E. A. Perpete, I. Ciofini and C. Adamo, *Chem. Phys. Lett.*, 2005, **405**, 376.

14 (*a*) J. T. Lin, J. J. Wu, C.-S. Li, Y. S. Wen and K.-J. Lin, *Organometallics*, 1996, **15**, 5028; (*b*) Z. Yuan, G. Stringer, I. R. Jobe, D. Kreller, K. Scott, L. Koch, N. J. Taylor and T. B. Marder, *J. Organomet. Chem.*, 1993, **452**, 115.

15 Y. Mori, T. Kasai, T. Takesada, H. Komatsu, H. Yamazaki and M.-A. Haga, *Chem. Lett.*, 2001, 996.

16 S. Woitellier, J. P. Launay and C. Joachim, *Chem. Phys.*, 1989, **131**, 481.

17 R. Stowasser and R. Hoffmann, *J. Am. Chem. Soc.*, 1999, **121**, 3414.

18 HyperChem Professional 6, (2002) HyperCube.

19 K. Sonogashira, T. Yatake, Y. Tohda, S. Takahashi and N. Hagihara, *J. Chem. Soc., Chem. Commun.*, 1977, 291.

20 A. O. King, E. Negishi, F. J. Villani, Jr and A. Silveira, Jr, *J. Org. Chem.*, 1978, **43**, 358.

21 R. D'Amato, A. Furlani, M. Colapietro, G. Portalone, M. Casalboni, M. Falconieri and M. V. Russo, *J. Organomet. Chem.*, 2001, **627**, 13.

22 S. O. Grim, R. L. Keiter and W. McFarlane, *Inorg. Chem.*, 1967, **6**, 1133.

23 A. Carella, J. Jaud, G. Rapenne and J.-P. Launay, *Chem. Commun.*, 2003, 2434.

24 G. Vives, A. Carella, J. P. Launay and G. Rapenne, *Chem. Commun.*, 2006, 2283.

25 (*a*) B. Chaudret and F. A. Jalon, *J. Chem. Soc., Chem. Commun.*, 1988, 711; (*b*) J. K. Evju and K. R. Mann, *Organometallics*, 2002, **21**, 993.

26 H. C. L. Abbenhuis, U. Burckhardt, V. Gramlich, A. Martelletti, J. Spencer, I. Steiner and A. Togni, *Organometallics*, 1996, **15**, 1614.

27 N. G. Connelly and I. Manners, *J. Chem. Soc., Dalton Trans.*, 1989, 283.

28 A. Carella, G. Vives, T. Cox, J. Jaud, G. Rapenne and J. P. Launay, *Eur. J. Inorg. Chem.*, 2006, 980.

29 (*a*) S. Trofimenko, *Scorpionates; The Coordination Chemistry of Polypyrazolylborate Ligands*, Imperial College Press, London, 1999; (*b*) A. L. Rheingold, B. S. Haggerty, G. P. A. Yap and S. Trofimenko, *Inorg. Chem.*, 1997, **36**, 5097.

30 A. L. Rieger, G. B. Carpenter and P. H. Rieger, *Organometallics*, 1993, **12**, 842.

31 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, A. G. Baboul, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. G. Johnson, W. Chen, M. W. Wong, J. L. Andres, M. Head-Gordon, E. S. Replogle and J. A. Pople, *GAUSSIAN 98 (Revision A.7)*, Gaussian, Inc., Pittsburgh, PA, 1998.

32 (*a*) P. Boulet, M. Buchs, H. Chermette, C. Daul, E. Furet, F. Gilardoni, F. Rogemond, C. W. Schlaepfer and J. Weber, *J. Phys. Chem. A*, 2001, **105**, 8999; (*b*) M. J. Mayor-Lopez and J. Weber, *Chem. Phys. Lett.*, 1997, **281**, 226.