A star-shaped ruthenium complex with five ferrocenyl-terminated arms bridged by *trans*-platinum fragments†

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We present the synthesis of the new heteropolytopic penta(4-ethynylphenyl)cyclopentadiene ligand, its complexation through the Cp ring to ruthenium tris(indazolyl)borate and through the terminal alkyne groups to five ferrocenyl ethynyl platinum units, yielding an undecanuclear heterotrimetallic complex.

With increasing interest in the unique chemical and physical properties possessed by metal complexes, the development of novel functionalized nanosized materials incorporating transition metal complexes is a promising area of research. In the last few years, there has been a growing interest in the design of star-shaped molecules incorporating different metal centres.[1] Their magnetic[2] or multi-redox properties have yielded molecules which have found applications in the fields of catalysis,[3] artificial photosynthesis[4] and sensors.[5] However, they have not been extensively studied due to synthetic difficulties.

Polyalkyne compounds are particularly well-suited as rigid building blocks for such supramolecular assemblies.[6] Hexaethynylbenzene and its derivatives have received extensive attention over the last two decades, starting with the pioneering work performed by Vollhardt *et al.*[7] The analogous five-membered (pentaethynyl)cyclopentadiene has been prepared and coordinated to a manganese tricarbonyl fragment by Bunz *et al.*,[8] and it has been shown recently by Rubin *et al.* to have the remarkable property, for a free ligand, to exist as a radical that can be easily oxidized to the corresponding antiaromatic cation.[9] However, nothing is known about the synthesis, reactivity and stability of penta(*para*-ethynylphenyl)cyclopentadiene, in which the *para*-phenylene units are intercalated between the Cp ring and the alkyne functions.

We present here the synthesis of the new TIPS-protected penta(4-ethynylphenyl)cyclopentadiene ligand (**4**) (TIPS = tri(isopropyl)silyl). Following a stepwise approach, its polytopicity allowed us to obtain star-shaped molecule **1** (Fig. 1) by complexation through the Cp ring to a ruthenium tris(indazolyl)borate fragment and to five ferrocenyl ethynyl platinum units through the terminal alkyne groups. This star-shaped molecule is the heart of our electrically-triggered rotary motor project,[10] in which the ferrocenes will act as electroactive units for reversible redox cycles. To favour charge localization on a ferrocene unit, it is preferable to break the conjugation between the electroactive groups. For this purpose, *trans*-bis(alkynyl) bis(trialkylphosphine)platinum(II) complexes, although moderately insulating,[11] have been selected for a combination of reasons: (i) the rigidity and linearity of the assembly are maintained, (ii) the electroneutrality of the molecule is preserved, essential for its deposition on a surface, and (iii) the diameter of the molecule is significantly increased (from 2 to 3 nm), favourable for future near-field microscopy studies. Moreover, the preparation of platinum acetylide complexes with rigid alkynyl backbones has been described by Stang *et al.* and Takahashi *et al.* for use in the formation of organometallic dendrimers that 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.[12] A modular strategy was followed in order to prepare separately the different metallic building blocks and to assemble them step-by-step around the penta(4-ethynylphenyl)cyclopentadiene ligand.

Starting from the previously described 1-bromo-1,2,3,4,5-penta(*para*-bromophenyl)cyclopentadiene (**3**),[13] compound **4** was prepared in a remarkable 81% isolated yield by a quintuple coupling with mono-TIPS-protected acetylene (Scheme 1).‡ At this stage, it is preferable to keep the alkyne functions protected in order to coordinate selectively the cyclopentadienyl (Cp) ring. This also allows us to vary the nature of the metals coordinated to the two different types of binding sites offered by this polytopic ligand. By following Connelly and Manners' methodology, which uses a brominated Cp with $Ru_3(CO)_{12}$,[14] a bromine atom was introduced back at the 1-position of the Cp ring by means of ^{n}BuLi and *N*-bromosuccinimide (NBS) at a low temperature to yield compound **5**. Ruthenium was subsequently coordinated, giving

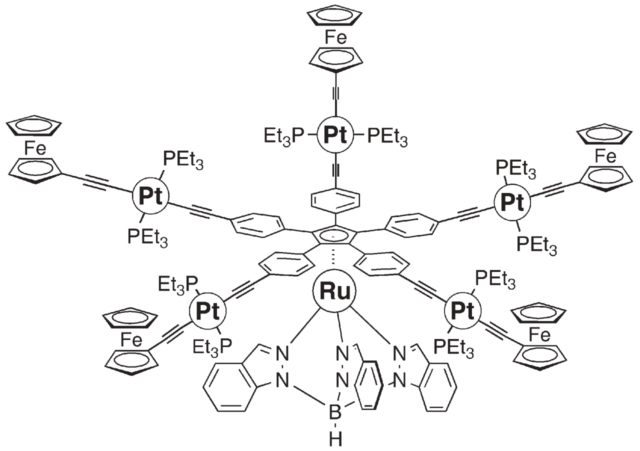

Fig. 1 Chemical structure of **1**, an undecanuclear heterotrimetallic complex.

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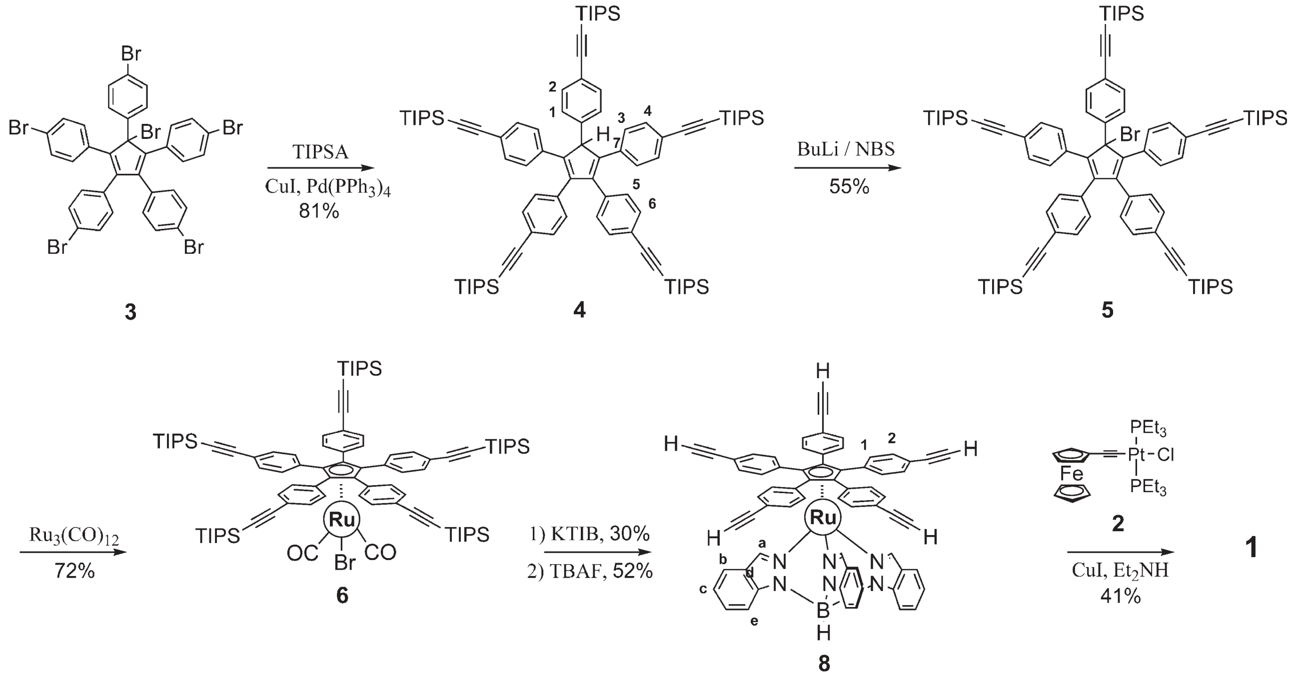

Scheme 1 Synthetic route followed to yield the heterotrimetallic undecanuclear complex **1**.

complex **6** in a 72% yield after chromatography. By reacting **6** with potassium tris(indazolyl)borate (KTIB), complex **7**, incorporating a tripodal ligand derived from the scorpionate family,[15] was formed, together with another unidentified complex of similar polarity that was hardly separable by chromatography. An analytically pure sample of **7** could be obtained in 30% yield after a second chromatographic purification, although the yield of the reaction was clearly higher. Finally the TIPS protecting groups were removed by an overnight reaction with tetrabutylammonium fluoride (TBAF) to yield the desired complex **8**, bearing five free acetylene groups, now available for coordination. The problem of purifying complex **7** could be avoided by performing the TIB complexation and TIPS deprotection in a one-pot fashion, with a 37% overall yield.

Ethynylferrocenyl platinum fragment **2** was prepared starting from *trans*-dichlorobis(triethylphosphine)platinum(II) by the substitution of one chloride ligand for a ferrocenylethynyl group.[16] It was achieved by heating *trans*-Pt(PEt$_3$)$_2$Cl$_2$ with ethynylferrocene for 36 h in the presence of diethylamine. Complex **2** was obtained in 74% yield after chromatography by using conventional heating to reflux. The yield of this step could be improved to 86% by using microwave irradiation (300 W) at 113 °C in a sealed tube for 15 min. The five ferrocene–platinum units were subsequently introduced by a quintuple coupling of chloro-platinum complex **2** with complex **8**, yielding the desired heterotrimetallic complex **1** in 41% isolated yield after column chromatography (SiO$_2$, cyclohexane/Et$_2$O (0–20%)), corresponding to a yield of 84% per coupling.§

^{1}H NMR spectroscopy clearly showed an AA′BB′ pattern for the phenyl groups attached to the central Cp ring and an integration of 45 protons for the signals of the ferrocene units. Free rotation of the Cp ligand was observed down to −90 °C. The *trans* geometry around the platinum-diphosphino centres was confirmed by ^{31}P NMR[17] and ^{195}Pt NMR[18] spectroscopy from the $^1J_{\text{P–Pt}}$ coupling constant. For complex **1**, the value of the coupling constant was found to be 2374 Hz, corresponding to a *trans* geometry; a *cis* coupling constant is usually much larger (about 3500 Hz).[17] The presence of the five ethynylferrocene units was also confirmed by mass spectrometry. Oxidation of the five iron centres occurs simultaneously at a potential of 0.31 V/SCE, followed by oxidation of the ruthenium centre at 0.60 V (Fig. 2). These values are lower than the potentials measured for ethynyl ferrocene, which presents an oxidation wave at 0.59 V/SCE, showing the electron-rich character of the diphosphinoplatinum fragments that are able to stabilize the Fe(III) oxidation state. It must be noted that the platinum centres were not oxidized within the potential window used (−1.8 to +1.5 V/SCE in dichloromethane). In addition, preparative electrolysis of **1** was performed on a platinum grid, first to oxidize the ferrocene sites, then to oxidize the ruthenium site. After back reduction, the starting material was recovered unchanged, showing the robustness of the molecule towards oxidation. Finally, after performing a partial oxidation of the ferrocene sites, no intervalence transition between Fe(II) and Fe(III) was observed, thus confirming the absence of

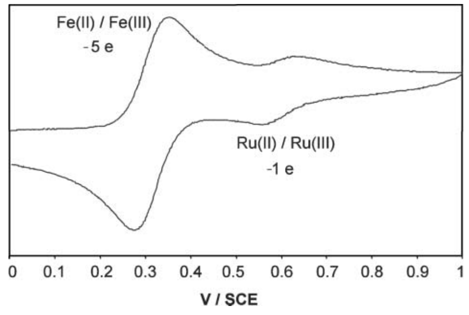

Fig. 2 Cyclic voltammogram of **1** (CH$_2$Cl$_2$, ^{n}Bu$_4$NPF$_6$, Pt working and counter electrode). All waves were reversible. The sweep rate was 100 mV s^{-1}.

measurable electronic communication between the electroactive ferrocene units.

We have reported the synthesis of the new TIPS-protected penta(4-ethynylphenyl)cyclopentadiene (**4**). This versatile ligand is well suited to giving access to a large variety of heteropolynuclear complexes due to its polytopicity. Its coordination takes place step-by-step, in our case binding the Cp ring first and then the five alkyne functions. However, the reverse approach could be more appropriate for other types of metals. We prepared a heterotrimetallic undecanuclear star-shaped complex built around a ruthenium centre by following a building block strategy. The final step was a quintuple complexation of the terminal alkyne groups by platinum fragments, occurring with a 41% isolated yield. Electrochemical measurements showed the oxidation processes were independent for each metal. We are now exploring the possibility of using this star-shaped heterotrimetallic complex as the prototype for an electron-fuelled rotary motor.

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Notes and references

‡ **4**: MS: (DCI/NH_3) 1349 $[MH]^+$, 1381 $[M + 2NH_3]^+$. High resolution LSI: calc. $[M]^+ = 1346.8706$ ($C_{90}H_{126}Si_5$), found = 1346.8787 (100% $[M]^+$). ^1H NMR (250 MHz, CD_2Cl_2): δ 7.34 (d, 6 H, $J = 8$ Hz, H_2–H_6), 7.21 (d, 4 H, $J = 8$ Hz, H_4), 7.17 (d, 2 H, $J = 8$ Hz, H_1), 7.02 (d, 4 H, $J = 8$ Hz, H_5), 6.96 (d, 4 H, $J = 8$ Hz, H_3), 5.16 (s, 1 H, H_7) and 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 and 11.26.

§ **1**: MS: (ES^+) 2113 $[M]^{2+}$ and 1409 $[M]^{3+}$. MALDI-TOF: 4226.2 $[M]^+$ (calc. 4226.98). ^1H NMR (500 MHz, CD_2Cl_2): δ 8.04 (d, 3 H, $J = 6.8$ Hz, H_e), 8.02 (s, 3 H, H_a), 7.45 (d, 3 H, $J = 8.7$ Hz, H_b), 7.38 (m, 3 H, H_c), 7.25 (d, 10 H, $J = 8.5$ Hz, H_1), 7.03 (t, 3 H, $J = 7.6$ Hz, H_d), 6.97 (d, 10 H, $J = 8.5$ Hz, H_2), 4.22 (t, 10 H, $J = 1.8$ Hz, subst. Cp), 4.15 (s, 25 H, Cp), 4.07 (t, 10 H, $J = 1.8$ Hz, subst. Cp), 2.17 (m, 60 H, CH_2) and 1.22 (m, 90 H, CH_3). ^{13}C NMR (125 MHz, CD_2Cl_2): δ 143.37, 140.31, 133.24, 130.92, 129.61, 127.69, 126.01, 123.06, 120.03, 119.98, 111.36, 109.21, 108.78, 104.86, 102.62, 87.52, 72.95, 70.09, 69.31, 66.97, 16.23 and 8.15. ^{31}P NMR (200 MHz, CD_2Cl_2): δ 11.30 (s, $^1J_{^{31}P-^{195}Pt} = 2374$ Hz). ^{195}Pt NMR (500 MHz, CD_2Cl_2): δ −4742. UV-vis (CH_2Cl_2; λ_{max}/nm (ε/mol^{-1} L cm^{-1})): 264 (225000), 306 (169200), 359 (58000) and 436 (10400). CV (CH_2Cl_2, $^n Bu_4NPF_6$) $E_{Fe(II)-Fe(III)}$ (V/SCE) = +0.31 rev. (5 e); $E_{Ru(II)-Ru(III)}$ (V/SCE) = +0.60 rev. (1 e) (sweep rate = 100 mV s^{-1}).

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