



Synthesis of a nanocar with organometallic wheels

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ABSTRACT

A new class of nanovehicles incorporating *trans*-alkynyl(dppe)₂ruthenium-based wheels is reported. A four-wheeled nanocar and a three-wheeled trimer were synthesized for future studies at the single molecule level.

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A current trend in physical and biological sciences is the pursuit of miniaturized machinery.¹ To achieve this goal, two complementary strategies have been developed. The first is the 'top-down' approach which consists of the miniaturization of existing objects following microscale technologies. However, this approach is reaching some physical limits due to the incompatibility of such technology with the nanometer scale. The opposite approach, known as the 'bottom-up' strategy, starts from atoms and molecules and follows a monumentalization² strategy consisting of the association of different modular functional units through the formation of covalent bonds within only one molecule. In this strategy, the development of molecular machines and nanocarriers is crucial to control the transport processes at the atomic level.³ In combination with imaging tools such as scanning tunneling microscopy (STM),⁴ our group has developed individually accessible nanocars, each bearing a chassis, axles and wheels for a restricted rolling motion on a metallic surface.^{5,6}

The first generation of nanocars used C₆₀ fullerene-based wheels and were studied at the single molecular level.⁵ Studies by STM demonstrated a thermally-driven directional motion on a gold surface.^{5a,b} However, due to the photoactive nature of the fullerenes and the low solubility of the resulting nanocars, a second generation of nanovehicles using *p*-carborane wheels has been synthesized.⁶ These *p*-carborane wheels produce more soluble nanovehicles and are not photoactive, which is crucial for light-powered nanocars.^{6a,e}

In the quest for new molecular wheels, octahedral 18-electron *trans*-alkynylbis(1,2-bis-(diphenylphosphino) ethane)ruthenium(II) complexes⁷ (Fig. 1) appeared to be good candidates, as the low rotation barrier around the alkyne bond might allow a free rotation while the bulky phosphine ligands could act as a tire to interact with metallic surfaces. Good physisorption on metallic surfaces, which has been demonstrated to be crucial for a rolling

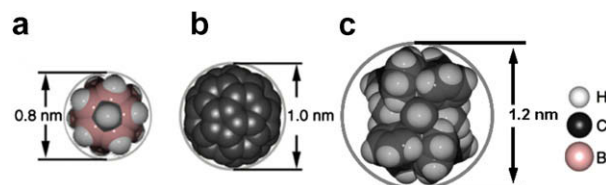


Figure 1. Relative size and space-filling of (a) *p*-carborane, (b) C₆₀ fullerene, and (c) *trans*-[Ru(C≡CH)₂(dppe)₂] wheels.

motion of the wheels,^{4b,5a,8} should be provided by the diphenylphosphine groups. Furthermore, the overall wheel size of ~1.2 nm should allow imaging by STM, and the large *Z* value of the ruthenium atoms should open new possibilities of imaging by transmission electron microscopy (TEM). In this Letter we report the synthesis of a new nanocar (**1**) with organometallic wheels based on a *trans*-alkynyl ruthenium complex. In order to provide evidence for a rolling mechanism, the synthesis of its trimer analogue (**2**), which should be restricted to a pivoting motion as we showed for the C₆₀-wheeled trimer,^{5a} is also presented.

The synthesis of nanocar **1** (Fig. 2) was initially considered via a convergent route consisting of the synthesis of a full axle with the ruthenium wheels followed by a final coupling with the inner core. However, the final palladium-catalyzed coupling failed probably due to the steric hindrance of the bulky ruthenium wheels as seen in the CPK model (Fig. 2b). A new route based on a modular strategy similar to the one used for the fullerene based nanocars⁵ was thus considered. The chassis bearing four alkyne groups was first synthesized using Sonogashira coupling reactions followed by a coordination of the four ruthenium wheels in a final step. In order to increase the solubility of the nanocars, four propoxy groups were added to the inner core.

The synthesis (Scheme 1) started with a double Sonogashira coupling reaction between the bis-terminal-alkyne **3** and the aryl iodide **4**,⁶ followed by deprotection to yield **5**. The axles were further extended by a phenylacetylene unit to allow the coordination

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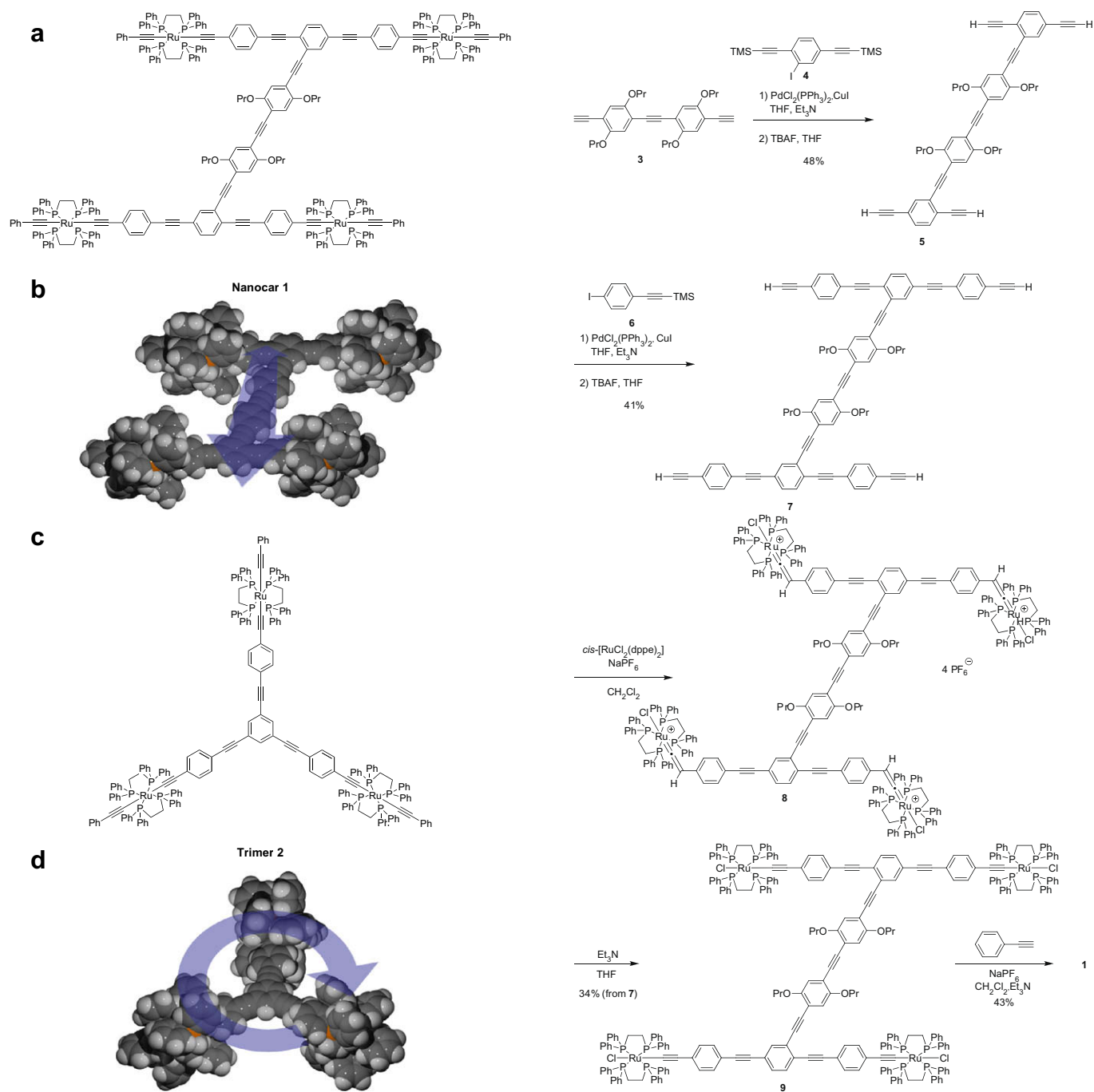
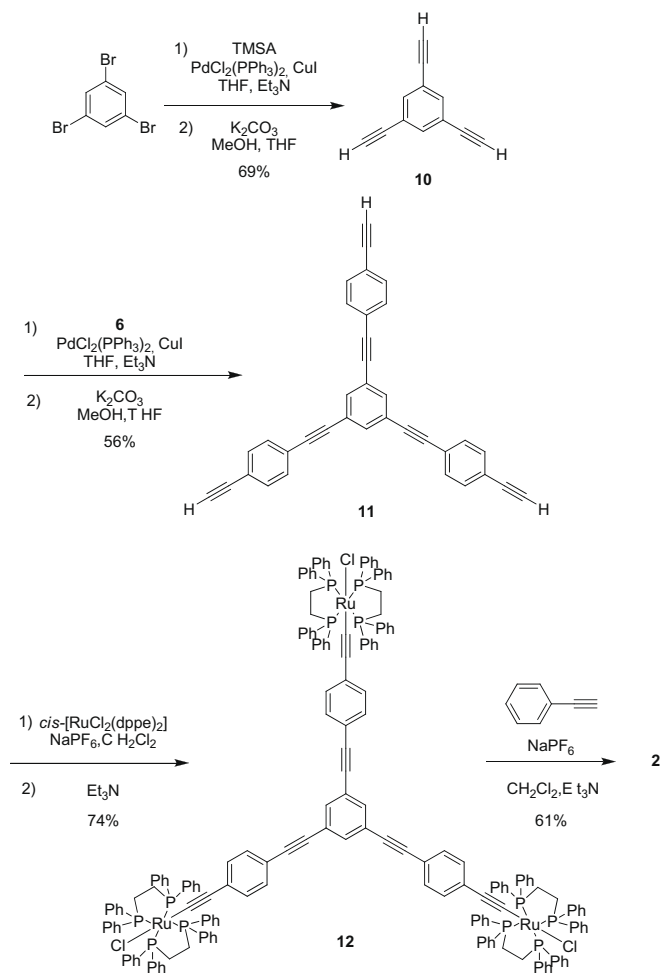


Figure 2. Nanocar (a, b) and trimer (c, d) with ruthenium wheels and their CPK model geometry optimized with SPARTAN. The blue arrow represents the expected motion of the molecule on a surface.

of the bulky ruthenium wheels by a quadruple Sonogashira coupling reaction between **5** and **6**. After deprotection with TBAF, the chassis **7** was obtained in a moderate yield. The activation of the four terminal alkynes of **6** was realized with the bulky 16-electron species $[\text{RuCl}(\text{dppe})_2]\text{PF}_6$, generated in situ from $\text{cis}[\text{RuCl}_2(\text{dppe})_2]$ ⁹ in the presence of NaPF_6 at room temperature. This reaction led to the intermediate tetra(vinylideneruthenium(II)) complex **8**, as it has been shown for linear monovinylidene complexes.¹⁰ The remaining chloride of the vinylidene complex being less reactive to further substitution, dissymmetric ruthenium complexes can be selectively obtained. The crude vinylidene intermediate **8** was subsequently deprotonated with triethyl-

amine to give the nanocar precursor **9** in a 34% yield from **7**. Since the remaining chloride ligands are potentially reactive upon deposition onto metallic surfaces, the wheels were capped with phenylacetylene moieties. The ligand exchange reaction required heating of **9** at 35 °C in the presence of phenylacetylene and triethylamine to give nanocar **1**. The intermediate tetravinylidene complex leading to **1** was not isolated, since a disubstitution could not occur. The complexation reactions can be monitored by ^{31}P NMR with a clear shift of the signals corresponding to the phosphine ligands from 49.2 ppm for **9** to 53.6 ppm for **1**. The *trans* geometry of the complexes was confirmed by the observation of only one singlet in the ^{31}P NMR spectrum since a *cis* geometry would give two signals.

Scheme 2. Synthesis of trimer **2**.

In order to demonstrate the rolling versus sliding mechanism, a threefold symmetric trimer model **2** (Fig. 2) was also synthesized. Similar to the fullerene wheeled nanovehicles,^{5a} the three wheel trimer should exhibit a pivoting motion if a rolling mechanism is effective. The synthesis of **2**¹¹ (Scheme 2) is based on a stepwise construction of the inner core followed by a final wheel attachment.

The triangular core was synthesized starting from 1,3,5-tribromobenzene using a Sonogashira coupling reaction with TMSA followed by a deprotection reaction to provide **10**.¹² Compound **10** was further coupled to **6** using a Sonogashira coupling reaction to afford, after deprotection, the inner core **11**. Similarly to the nanocar synthesis, the ruthenium wheels were added by reaction with *cis*-[RuCl₂(dppe)₂] to yield the trichlororuthenium trimer **12**. The chloride ligands were finally exchanged with phenylacetylene to obtain trimer **2**.

As an alternative to STM, it is possible that the optical properties could be exploited to image nanocars on a nonmetallic surface by using confocal fluorescence microscopy,¹³ hence optical studies of the products were done. The UV-vis spectra of nanocar **1** and trimer **2** (Fig. 3a) exhibit metal-to-ligand charge transfer (MLCT) transitions of the ruthenium complexes at 414 and 408 nm, respectively.¹⁴ Both complexes show strong high-energy bands around 330 nm, probably corresponding to π - π^* intra-ligand transitions,^{7d,15} since they are also observed in the chassis **7**. The fluorescence properties of nanocar **1** and trimer **2** were also investigated (Fig. 3b). Both compounds present a fluorescence emission band

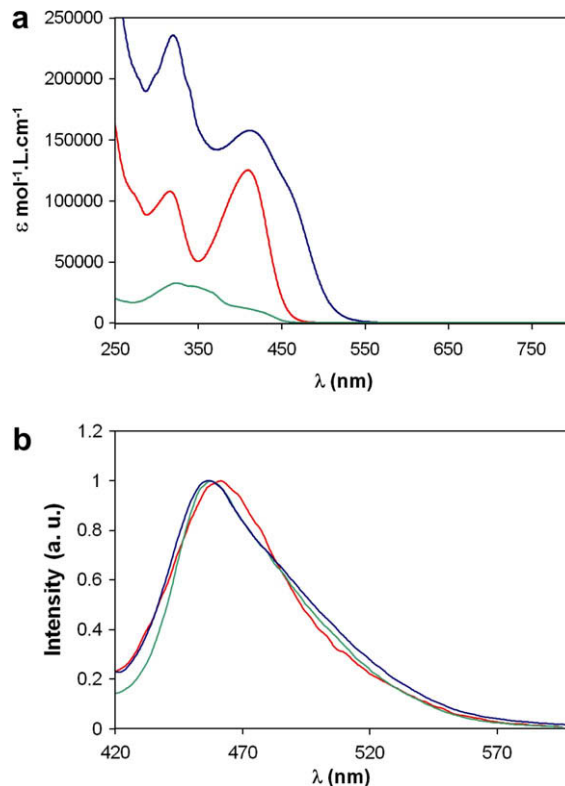


Figure 3. (a) UV-vis spectra of nanocar **1** (blue, top line) and trimer **2** (red, middle line) and **7** (green, bottom line) in CH₂Cl₂. (b) Normalized fluorescence spectra (excitation at 330 nm) of Nanocar **1** (blue) and trimer **2** (red) and **7** (green) in CH₂Cl₂.

around 460 nm (457 nm for **1** and 462 nm for **2**) similar to the one observed for the chassis **7**. This makes the molecules suitable for surface studies using fluorescence.

In summary we have synthesized a new nanocar with ruthenium-based wheels and its threefold symmetric analogue trimer. Studies at the single molecule level of **1** and **2** by STM on metallic surfaces are now in progress.

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Supplementary data

Synthetic procedures, ¹H NMR, ¹³C NMR, IR, and mass spectra or elemental analysis of compounds **1–9** and **12** are available. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2009.01.042.

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