ORGANIC
LETTERS

2008
Vol. 10, No. 2
229−232

Synthesis of a Nanocar with an Angled Chassis. Toward Circling Movement

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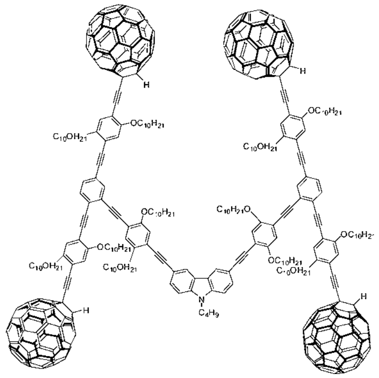
Received October 31, 2007

ABSTRACT



Nanocars with an angled chassis have been synthesized and imaged using scanning tunneling microscopy. These angled chassis nanocars were designed to further our understanding of the directional control and surface-rolling capabilities of this class of nanomachines. The alkylated carbazole inner core might enable the molecular scaffold to produce circular rolling motions of the nanovehicles on surfaces.

Recent advancements in imaging techniques such as scanning tunneling microscopy (STM) have allowed organic chemists to expand the field of molecular machinery from the more traditional solution-based machines[1] to the design and synthesis of molecular machines that are individually addressable or controllable.[2] Of particular importance for our group is the synthesis and manipulation of nanocars that demonstrate a restricted rolling motion, rather than random sliding motion, on surfaces such as gold.[3] With complementary results from other research groups also showing wheel-like rolling motions,[4] there is a basis for extension of the field to produce more complex functionalized molecular vehicles with varying properties.[5] Reported here is the design and synthesis of a nanocar with an angled carbazole chassis to further develop our understanding of directional movement on gold surfaces.

As illustrated in Figure 1, the angled nanocar **1** was designed to combine the directional movements of two existing fullerene surface-rolling molecules: the nanocar, which rolls in directions perpendicular to the axles, and the

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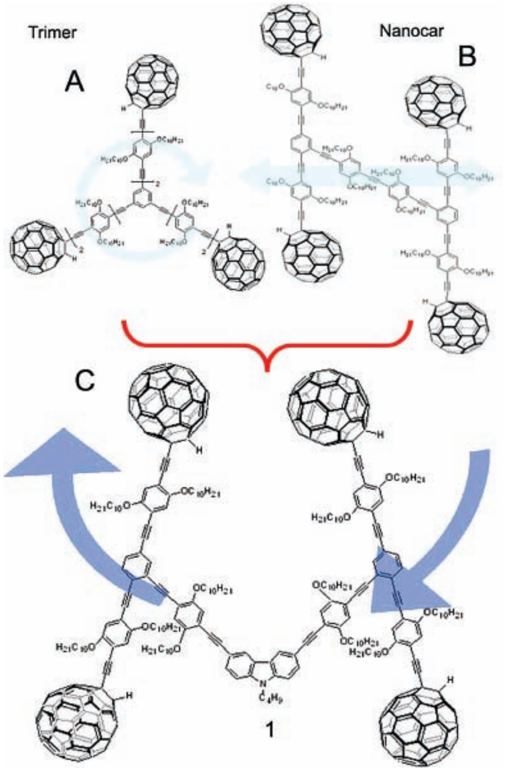
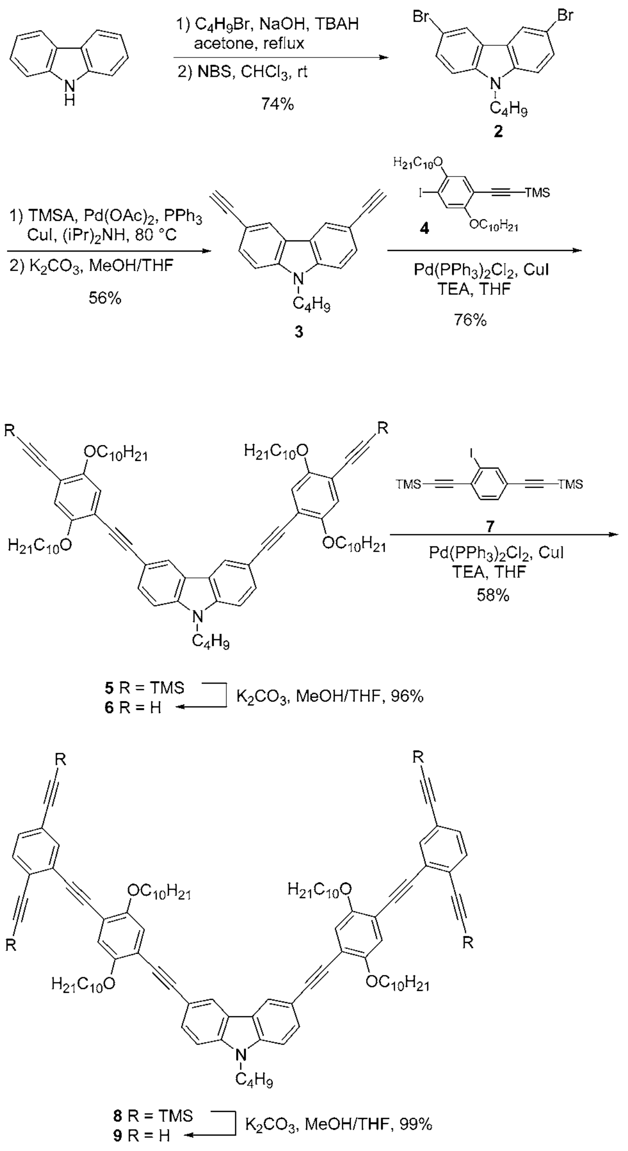


Figure 1. The trimer molecule (A) and nanocar (B) motions (light blue arrows) have already been observed by STM.[3] (C) The fullerene-wheeled angled chassis nanocar should undergo circular motion rather than the pivoting as in A and translation as in B.

Scheme 1. Synthesis of Chassis **9**[a]



[a] TBAH = tetrabutylammonium hydroxide; TMSA = trimethylsilylacetylene.

trimer, which rotates on the surface around an interior axis without any translational motion.[3] The angled chassis created by the carbazole provides a new dimension in molecular design to study additional structure-based directional control on the surface of gold.

The synthesis of **1** (Scheme 2) begins with four straightforward steps attaching two terminal alkynes to the carbazole inner core **3**.[6] The product was then coupled via a Sonogashira reaction with **4**,[3,7] an alkoxy-functionalized axle used in fullerene-wheeled nanocars to ameliorate the insolubility of fullerenes. After deprotection of the alkynes in **5**, another Sonogashira coupling between **6** and **7**[5] afforded the protected form of the chassis **8**. Removal of the TMS protecting groups afforded the chassis **9** (Scheme 1).

By a stepwise synthesis, the axles were elongated to afford compound **10**, followed by the removal of TMS protecting groups to afford compound **11** in two steps. Four fullerene wheels were successfully coupled via the in situ ethynylation method[3,7] using excess lithium hexamethyldisilazide (LHMDS) in THF in the presence of excess C_{60} to complete the synthesis of the angled nanocar **1**.

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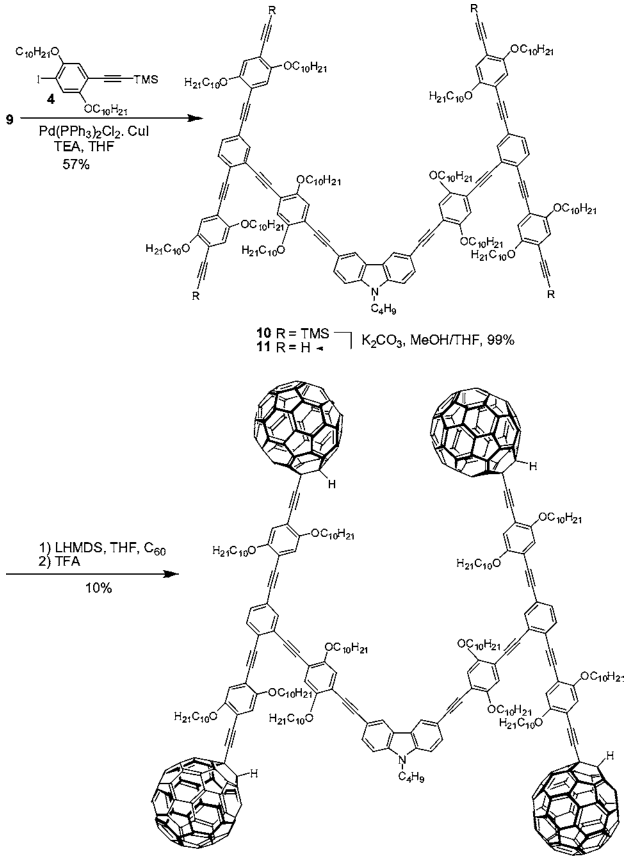
Scheme 2. Synthesis of Angled Nanocar **1**



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With the addition of the axles and the *N*-alkylated carbazole, the tetrafullerene (**1**) proved to be sufficiently soluble for definitive characterization by ^{1}H NMR, ^{13}C NMR, and mass spectrometric analysis.[8]

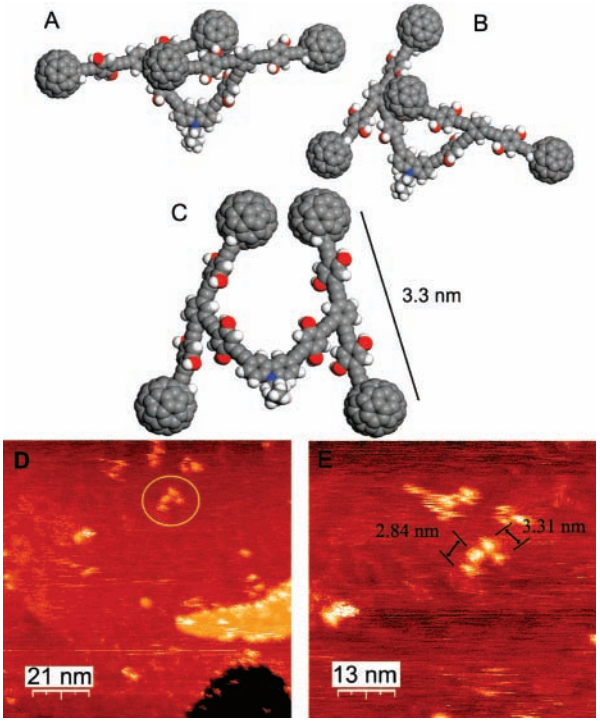

Figure 2. (A−C) Three models of possible conformations of **1** represented by material studios (MS) modeling. (D) STM[10] image of **1** shown in A (bias voltage = −0.71 V, tunneling current = 7 pA). (E) Higher resolution view of **1**, same tunneling parameters.

Our next step was to image the angled nanocar (Figure 2). STM imaging of the molecule revealed that a large variety

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(8) **Angled Nanocar 1.** To an oven-dried 500 mL round-bottom flask equipped with a magnetic stir bar were added **11** (0.075 g, 0.0250 mmol) and C_{60} (0.200 g, 0.278 mmol). After adding THF (250 mL), the mixture was sonicated for 3 h (general purpose sonicator). To the greenish-brown suspension formed after sonication was added LHMDS (1.00 mL, 1.00 mmol) dropwise at room temperature over 1 h. As the reaction progressed, the mixture turned into a deep greenish-black solution. During the addition of LHMDS, small aliquots from the reaction were extracted and quenched with trifluoroacetic acid (TFA), dried, and redissolved in CS_2 for TLC analysis (developed in a mixture of CS_2, CH_2Cl_2, and hexanes 2:1:1). Completion of the reaction was confirmed by the disappearance of the starting materials. Upon completion, the reaction was quenched with TFA to give a brownish slurry. Excess TFA and solvent were then removed in vacuo to afford a crude product that was dissolved in CS_2 and directly loaded onto a column. The column was eluted with CS_2/CH_2Cl_2 (100:1) to remove unreacted C_{60}, followed by CS_2/CH_2Cl_2 (1:1) for complete removal of trace C_{60} and elution of product. The product was further purified using another flash column with graduated elution of CS_2/CH_2Cl_2/hexanes (4:1:3 then 2:1:1). A third column with elution (2:1:1) was used to complete the purification to afford **1** (0.015 g, 10%): FTIR 2950, 2922, 2851, 2207, 2151, 1591, 1501, 1461, 1410, 1382, 1277, 1215, 1015, 843, 732, 662 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 8.27 (dd, 2H, $J = 1.51$ Hz, $J = 0.5$ Hz), 7.67 (dd, 2H, $J = 8.46$ Hz, $J = 1.57$ Hz), 7.38 (d, 2H, $J = 8.58$ Hz) (aromatic H on 3,6-disubstituted carbazole ring), 7.76 (dd, 2H, $J = 1.66$ Hz, $J = 0.59$ Hz), 7.54 (dd, 2H, $J = 8.01$ Hz, $J = 0.5$ Hz), 7.48 (dd, 2H, $J = 8.03$ Hz, $J = 1.66$ Hz) (aromatic H on 1,2,4-trisubstituted phenyl ring), 7.29 (s, 2H), 7.13 (s, 2H), 7.07 (s, 2H), 7.04 (s, 2H), 6.96 (s, 2H), 6.94 (s, 2H) (six aromatic H on the three types of tetrasubstituted phenyl rings), 7.18 (s, 4H) (the fullerene C-H), 4.32 (t, 2H) (the carbazole $N-CH_2-$), 4.17 (t, 2H, $J = 6.05$ Hz), 4.15 (t, 2H, $J = 6.63$ Hz), 4.03 (t, 2H, $J = 6.55$ Hz), 3.97 (t, 2H, $J = 6.53$ Hz), 3.86 (t, 2H, $J = 6.33$ Hz), 3.74 (t, 2H, $J = 6.24$ Hz) (the six $-OCH_2-$ groups), 2.0−1.1 (m, 196H) (other decyl and carbazole CH_2 groups), 0.99 (t, 3H, $J = 7.35$ Hz) (the carbazole CH_3), 0.87−0.81 (m, 36H) (six different decyl CH_3 groups); ^{13}C NMR (126 MHz $CDCl_3$) δ 154.6, 154.3, 153.84, 153.76, 153.6, 153.4 (six different signals from aryloxy C), 151.7, 151.5, 147.7, 147.5, 146.8, 146.52, 146.50, 146.34, 146.33, 145.9, 145.8, 145.7, 145.56, 145.55, 145.5, 144.8, 144.6, 143.3, 142.71, 142.68, 142.24, 142.16, 142.1, 142.0, 141.8, 141.7, 140.5, 140.4, 136.2, 135.3 (30 different fullerene sp^{2} signals; the two slightly different fullerene environments cannot be differentiated), 134.4, 131.6, 130.8, 130.0, 124.0, 108.9 (six different C−H groups on the 3,6-disubstituted carbazole and 1,2,4-trisubstituted phenyl rings, the last signal is C-1 of carbazole), 143.1, 126.5, 125.9, 123.2, 122.6, one signal in the cluster of seven signals from 115.14 to 113.27 (six different substituted C on the 3,6-disubstituted carbazole and the 1,2,4-trisubstituted phenyl rings, the first signal is C-8a/C-9a of carbazole), 117.6, 117.4, 117.2, 117.09, 117.08, 116.8 (six different C−H groups on three types of tetrasubstituted phenyl rings), 115.1, 114.4, 114.3, 114.2, 114.0, 113.5, 113.3 (six of these seven signals are from six different alkyne-substituted C on three types of tetrasubstituted phenyl rings), 101.2, 100.2, 97.8, 96.5, 94.4, 93.7, 92.7, 92.3, 91.1, 88.2, 84.5, 80.2 (the 12 different alkyne C; lack of symmetry in the trisubstituted phenyl ring results in the three groups with two alkynes giving 3 × 4 = 12 well-resolved alkynyl signals), 70.1, 69.9, 69.8, 69.6, 69.5, 69.3 (the six different $-OCH_2-$ C), 62.0 (fullerene C−H signal), 55.6 (fullerene sp^{3} quaternary C), 43.2 ($N-CH_2-$ broad signal detected only in the DEPT-135 ^{13}C experiment because of its increased sensitivity), 31.97, 31.96 (×2), 31.9, (four signals for six C-8 decyl C), 31.1 ($N-CH_2-\mathbf{C}H_2-$) 30.0, 29.85, 29.83, 29.76, 29.74, 29.714, 29.708, 29.70, 29.65, 29.643, 29.64, 29.636, 29.49, 29.47, 29.44, 29.43, 29.42, 29.41, 29.39, 29.35, 29.3 (numerous signals for six sets of C-3 through C-7 decyl C), 26.6, 26.23, 26.19, 26.16, 26.1, 26.0 (the six different $-OCH_2-\mathbf{C}H_2-$ C), 22.8, 22.74, 22.71, 22.69 (four signals for the six C-9 decyl C), 20.6 ($N-CH_2-CH_2-\mathbf{C}H_2-$), 14.20, 14.18, 14.1 (three signals for the six C-10 decyl C), 13.9 ($N-CH_2-CH_2-CH_2-\mathbf{C}H_3$); MALDI-TOF MS *m*/*z* (silver nitrate as the matrix) calcd for $C_{448}H_{289}NO_{12}$ 5873, found 5873.

of final conformations were possible when adsorbed onto the gold surface. The source of this result is revealed by molecular modeling and appears to be due to the inherent structural flexibility of **1** (Figure 2A−C).[9] Preliminary results indicate a random distribution of different conformations on the gold surfaces with no preference for any particular conformation. Examples of conformations imaged are shown in Figure 2D, with a higher resolution image shown in Figure 2E.[10]

In summary, we have successfully synthesized a new version of a nanocar wherein the angled architecture of the chassis might provide circling directional control for surface-rolling nanomachines. Since the prevalence of conformation C (Figure 2C) is low, imaging of these nanocars in circular motion has been slowed. However, further work is underway, and results will be presented in the near future.

Acknowledgment. We thank the Welch Foundation, C-1489, American Honda Motor Co., the NSF NIRT (ECCS-0708765), and the NSF Penn State MRSEC for financial support. The NSF, CHEM 0075728, provided partial funding for the 400 MHz NMR. We thank Drs. I. Chester of FAR Research, Inc., and R. Awartari of Petra Research, Inc., for providing trimethylsilylacetylene.

Supporting Information Available: Experimental details as well as spectroscopic data (FTIR, ^{1}H NMR, ^{13}C NMR, and mass spectrometric analysis) for nanocar **1** and compounds **5**, **6**, and **8**−**11**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(9) Relative energies were calculated using PC Spartan (molecular mechanics), A: 4732.18 kcal/mol, B: 4734.16 kcal/mol, C: 4744.10 kcal/mol. Lower energies were observed for A and B because of fullerene−fullerene and fullerene−phenyl $\pi-\pi$ stabilization.

(10) **Sample Preparation and Data Collection for STM Study.** The toluene solution of **1** (5 μM) was dosed in high vacuum using a fast-actuating, small orifice solenoid valve[11,12] onto argon-sputtered and annealed Au(111) on mica substrates and was imaged using an RHK variable-temperature UHV-STM. The dosing technique was chosen over sublimation in vacuum, as it appeared in thermal decomposition studies using a thermogravimetric analyzer in our previous work that **1** was thermally sensitive.[3]

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