

Toward Chemical Propulsion: Synthesis of ROMP-Propelled Nanocars

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In the current trend of miniaturization of devices, science and engineering on the nanoscale offers new possibilities for the design and synthesis of functional materials.¹ In contrast to the “top-down” approach that is currently reaching its limits, nanoscale engineering is also driven by a “bottom-up” approach. Nanomachines are promising new entities that are designed to exhibit controlled mechanical motion resembling their macroscopic analogues.^{2–4} Among the most important tasks for molecular machines is the directed motion and transport of nanocargo.

We have recently developed a family of nanovehicles that resemble their macroscopic analogues, with the goal of transporting nanocargo in a controlled manner on surfaces.^{5,6} These so-called nanocars are composed of a chassis connected to axles terminated by molecular wheels. The first-generation nanocar bearing C₆₀ wheels showed thermally activated translational motion and pivoting on a gold surface.^{7,8} The translational motion occurred perpendicular to the axles. The directionality of the translation was possible due to the rolling action of the molecular wheels. However, in order to obtain unidirectional motion, the nanocar must consume energy from an external source since latent thermal energy only leads to two-dimensional Brownian motion.² The goal of the present work is to synthesize a nanomachine that can convert energy inputs into controlled unidirectional motion on a surface. In the first examples of such control, the electric field gradient of a scanning tunneling microscope tip was successfully used to attract a nanocar in a forward-rolling motion.⁷ Also, a nanocar incorporating a light-powered Feri-nga motor⁹ and a diazobenzene-based

ABSTRACT The synthesis and ring-opening metathesis polymerization (ROMP) activity of two nanocars functionalized with an olefin metathesis catalyst is reported. The nanocars were attached to a Hoveyda–Grubbs first- or second-generation metathesis catalyst *via* a benzylidene moiety. The catalytic activity of these nanocars toward ROMP of 1,5-cyclooctadiene was similar to that of their parent catalysts. The activity of the Hoveyda–Grubbs first-generation catalyst-functionalized nanocar was further tested with polymerization of norbornene. Hence, the prospect is heightened for a ROMP process to propel nanocars across a surface by providing the translational force.

KEYWORDS: nanomachines · nanocars · Grubbs catalyst · ring-opening metathesis polymerization

nanoworm¹⁰ have already been described. However, investigation of other sources of energy, such as the thrust that can be developed from the energy released during a chemical reaction, would permit the synthesis of a family of nanovehicles that can be operated using various stimuli. For example, biological nanomachines such as myosin or ATP synthase commonly use the energy liberated by a chemical reaction (generally the hydrolysis of ATP) to bias Brownian motion into unidirectional motion. Alternatively, artificial chemically powered nanomotors working in solution have recently been described.¹¹ These nanomotors are bimetallic nanorods that use the catalytic dismutation of hydrogen peroxide for propulsion in solution. Inspired both by nature and artificial systems, in this work, we have investigated the functionalization of *p*-carborane-wheeled nanocars with Ru-based metathesis catalysts for potential propelling by a ring-opening metathesis polymerization (ROMP). Three main methods have been previously explored to attach a metathesis catalyst to a support.¹² Permanent binding can be achieved by exchange of the anionic ligands or *via* modification of the N-heterocyclic carbene (NHC)

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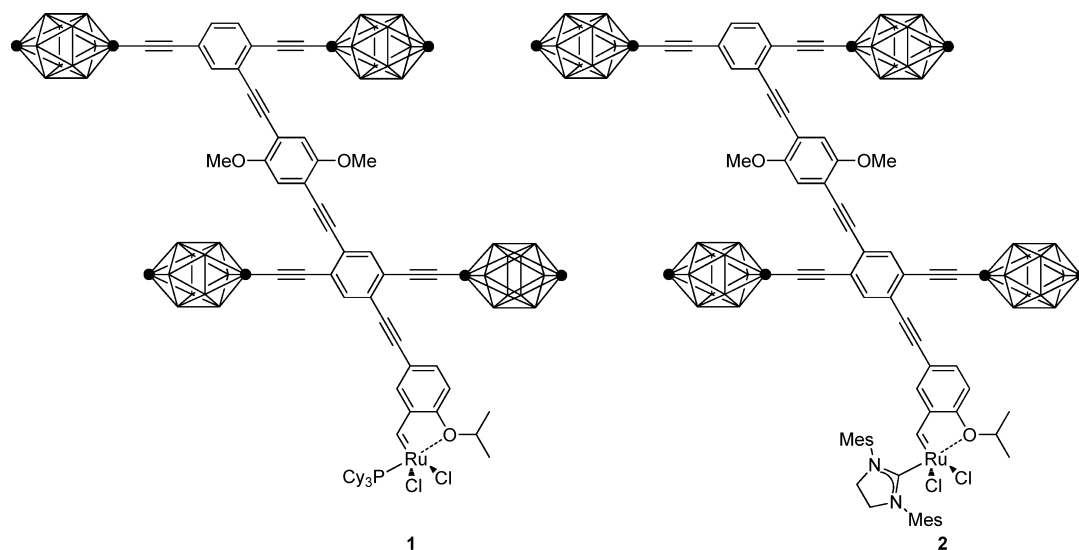


Figure 1. Ru-based metathesis catalyst nanocars **1** and **2**. Every vertex of the carborane wheel is BH except the darkened sites, where the outer (*para*) is CH and the inner (*ipso*) is alkynyl-substituted C.

ligand, whereas temporary attachment can be accomplished by a benzylidene moiety. In this report, we present the synthesis and catalytic activity toward ROMP of two modified Hoveyda–Grubbs metathesis catalysts, **1** and **2**, bound to a carborane-wheeled nanocar by a benzylidene moiety (Figure 1). By feeding the nanocar with a cyclic strained alkene such as norbornene, a ROMP should occur on the surface and the energy liberated might provide the thrust to propel the nanocar (Figure 2).

RESULTS AND DISCUSSION

The syntheses of nanocars **1** and **2** are based on a modular approach using a styryl-substituted nanocar as a common intermediate. To synthesize the precursor of the isopropoxy styryl fragment, 5-iodosalicylaldehyde was alkylated with 2-iodopropane in the presence of Cs_2CO_3 to give **3**. A Sonogashira coupling between iodide **3** and trimethylsilylacetylene (TMSA) gave protected alkyne **4** which, after deprotection with K_2CO_3 in MeOH, afforded **5** (Scheme 1).

The nanocar moiety was first assembled by a statistical coupling between alkyne **6**¹³ and axle **7**.¹³ Coupling of the resultant iodide nanocar **8** with alkyne **5** afforded aldehyde nanocar **9** in good yield. Finally, styryl-

substituted nanocar **10** was obtained by olefination of aldehyde **9** under conventional Wittig conditions (Scheme 2).

With styryl-substituted nanocar **10** in hand, we proceeded to the preparation of the catalysts using a ligand exchange procedure (Scheme 3).¹⁴ Nanocar **10** was treated with Grubbs first-generation **11**¹⁵ or second-generation catalyst **12**¹⁶ in CH_2Cl_2 at 40 °C for 2 h in presence of CuCl as a phosphine scavenger. ¹H NMR analysis of the crude reaction indicated the formation of only one benzylidene-containing species. The other major compound in the mixture was unreacted nanocar **10**. After chromatographic purification on silica gel, phosphine-containing complex **1** was obtained in 63% yield whereas NHC-substituted complex **2** was obtained in 53% yield. Although the complexes were stored in a glovebox, they were both air- and moisture-stable. A catalyst solution prepared in CDCl_3 under ambient conditions did not show changes by ¹H NMR after 3 days.

NMR spectroscopic data were consistent with a typical Hoveyda–Grubbs Ru complex.¹⁷ The alkylidene proton in the phosphine-containing complex **1** was observed in the ¹H spectrum as a doublet at 17.40 ppm with $J_{\text{PH}} = 4.4$ Hz, whereas the benzylidene carbene ¹³C signal was observed at 277.4 ppm. The presence of the phosphine ligand was confirmed by the ³¹P NMR signal

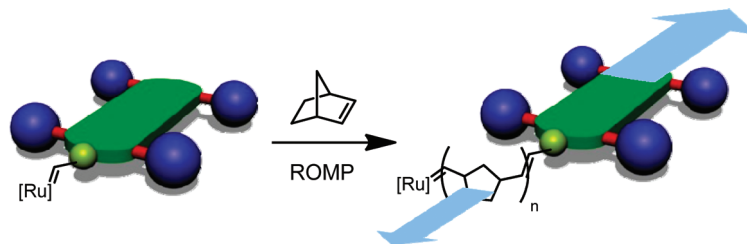
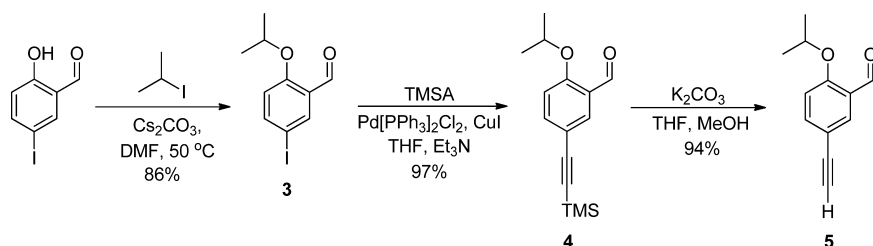


Figure 2. Proposed propulsion scheme for a nanocar composed of four wheels (blue) connected to a chassis (green) by two axles (red) and bearing a ruthenium-based ROMP catalyst. By addition of norbornene, a ROMP should occur at the ruthenium site, leading to a polymer growth on one end of the nanocar. In the process, the energy liberated might propel the nanocar. Concurrently, the ruthenium catalyst and the nanocar will move away from each other (blue arrows).

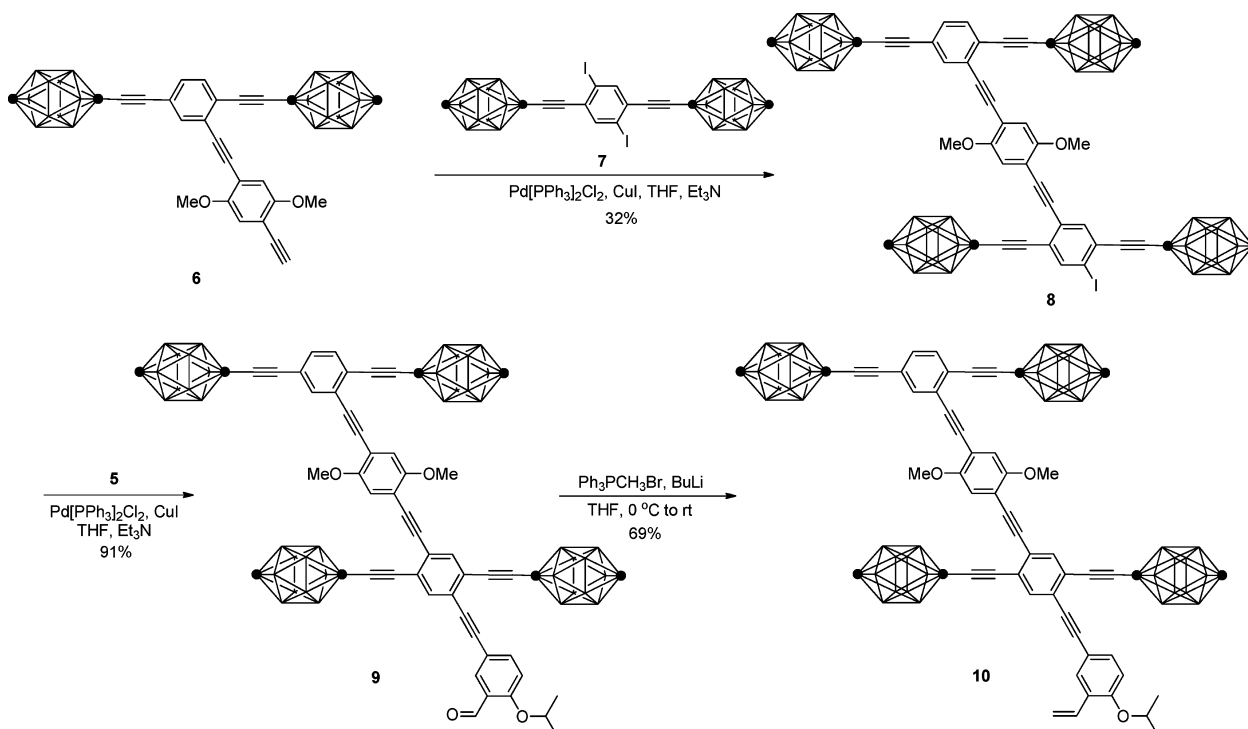


Scheme 1. Synthesis of isopropoxy benzaldehyde **5**.

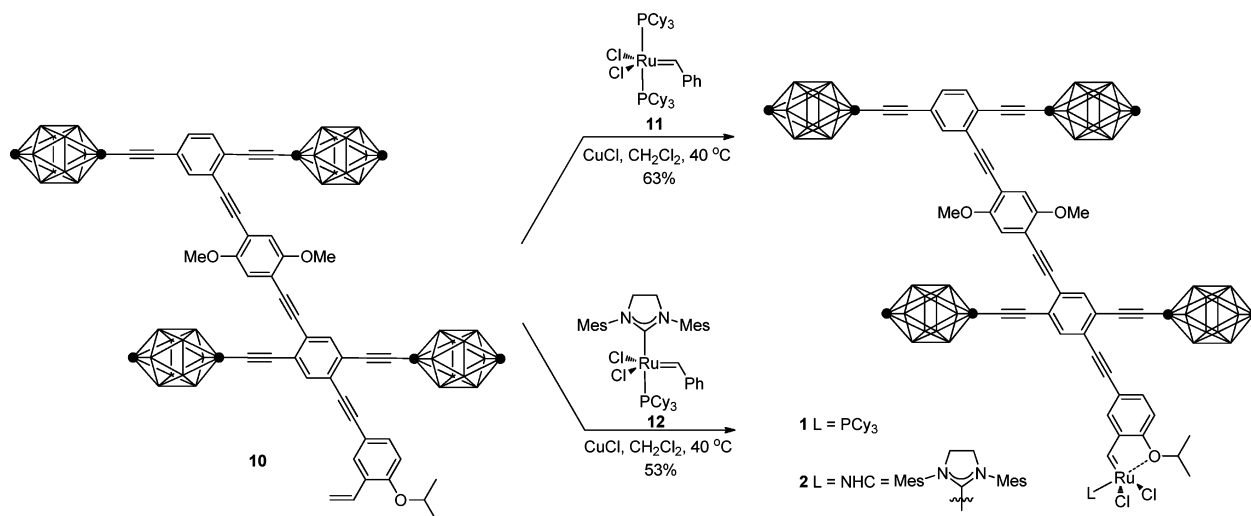
observed at 60.16 ppm. In the case of the NHC-substituted complex **2**, the benzylidene proton was observed in the ^1H spectrum as a broad singlet at 16.61 ppm and the benzylidene carbene ^{13}C resonated at 295.0 ppm. The isopropoxy methine protons were observed at 5.33 and 4.96 ppm for **1** and **2**, respectively.

The catalytic activity of **1** and **2** toward ROMP of 1,5-cyclooctadiene (cod) was tested according to the standard procedure developed by Grubbs (Figure 3).^{18,19} In that system, cod was selected partially due to its relatively slow polymerization rate, compared to more highly strained cyclic olefins such as norbornene, which facilitates monitoring of the reaction by NMR spectroscopy. Only 5% conversion was observed using the phosphine-containing complex **1** as catalyst during the 60 min that the reaction was monitored. Low activity was expected for **1**, however, given that its parent Hoveyda–Grubbs catalyst **13** exhibits 4% conversion under those conditions. On the other hand, nearly complete conversion was observed with the NHC-substituted complex **2** when the first spectrum was taken at 3 min. This complex had comparable activity to its parent catalyst **14**.

The activation of oxygen-chelated ruthenium catalysts by electron-withdrawing groups has been well-established.²⁰ One of the most prominent examples is the nitro-substituted complex **15** (Table 1) reported by Grela and co-workers. The catalytic activity of **15** toward a variety of olefin metathesis processes is remarkably higher than that of **14**.²¹ They reasoned that the electron-withdrawing nitro group would weaken the *i*PrO \rightarrow Ru chelation and therefore facilitate initiation of the catalytic cycle. Comparison of NMR data between **15** and its parent catalyst **14** further supports their conclusion (Table 1). The *i*PrO methine proton (H_a) and carbon (C_a) of **15** are shifted downfield compared to **14**, whereas the benzylidene carbene carbon (C_b) and proton (H_b) are shifted upfield. Similarly, the *i*PrO carbon and proton signals of NHC-substituted nanocar **2** are shifted downfield, whereas its benzylidene carbene carbon is shifted upfield, although the benzylidene proton is shifted downfield. Therefore, it is possible that the sp-linked nanocar chassis slightly decreases the availability of the isopropoxy-ether lone pair to bind the ruthenium and thereby might cause a subtle enhancement of the catalytic activity of **2** with respect to **14**,



Scheme 2. Synthesis of styryl-substituted nanocar **10**.



Scheme 3. Final assembly of nanocars **1** and **2**.

though the data obtained are too close to make any conclusive assessments.

Due to the low conversion observed with *cod*, the catalytic activity of phosphine-containing nanocar **1** toward ROMP was also tested with a more reactive substrate (Scheme 4). With norbornene, a highly viscous mixture was obtained within a few minutes, indicating a high degree of polymerization. According to the ratio of the integrals of the vinyl protons in the ring-opened polynorbornene, the polymer obtained was, as expected, predominantly *trans* (84%).

These results show that both norbornene and 1,5-cyclooctadiene might be usable as chemical fuels for the ROMP-propelled motion of nanocars **1** and **2** on a surface. Designing the imaging reaction chamber remains a challenge, however.

We further tried, unsuccessfully, to prepare the nanocar such that the Ru catalyst would remain permanently bound to the nanocar during and after polymerization. See Scheme S1 (Supporting Information) for

that attempted protocol. We also prepared a norbornene-containing nanocar as a ROMP generation site (Scheme S2), though the possibility of mixed polymer products precludes us from investigating that further.

CONCLUSION

In summary, we have synthesized potentially chemically powered nanocars based on olefin metathesis catalysts. We demonstrated that stable yet highly active modified Hoveyda–Grubbs catalyst nanocars **1** and **2** can be prepared using a ligand exchange process on the benzylidene moiety. Their high activity toward ROMP in solution makes them good candidates for surface-initiated ROMP that will permit evaluation of polymer growth to propel the motion of the nanocar. Studies of ROMP reactions on a surface are currently underway to assess their potential in chemically powered propulsion.

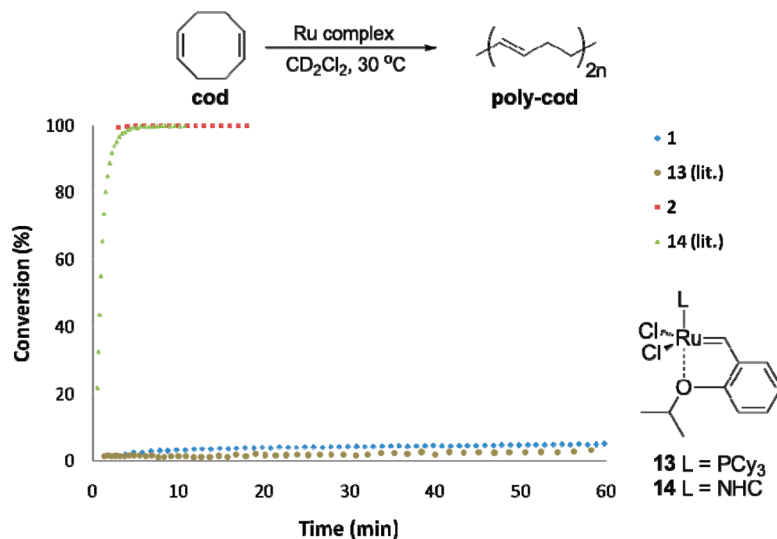


Figure 3. ROMP activity of **1** and **2** versus their unsubstituted analogues **13** and **14**.

TABLE 1. Comparison of NMR Data of Complexes **2**, **14**, and **15**

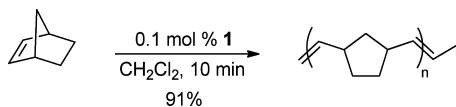
cmpd	δ (ppm) in CDCl ₃			
	C _a	H _a	C _b	H _b
2	76.2	4.96	295.0	16.61
14	74.9	4.89	296.8	16.56
15	77.6	4.98	291.2	16.47

2 X = Nanocar moiety
14 X = H
15 X = NO₂

METHODS

Synthesis of Nanocar Catalyst 1. A 10 mL round-bottom flask equipped with a stir bar and condenser was charged with Ru complex **11** (11.5 mg, 13.9 μ mol) and CuCl (4.0 mg, 40.0 μ mol). Then CH₂Cl₂ (0.5 mL) was added, immediately followed by addition of a solution of nanocar **10** (15.0 mg, 12.6 μ mol) in CH₂Cl₂ (2.5 mL). The resulting solution was stirred at 40 °C for 2 h. The solvent was removed in vacuum, and the residue was purified (Geduran silica gel, see General Methods in the Supporting Information, 40% then 70% CH₂Cl₂ in hexanes) to afford **1** as a brownish solid (14.0 mg, 63%). Five milligrams of starting material **10** was recovered: FTIR (neat) 3059, 2928, 2852, 2611, 2361, 1688, 1594, 1504, 1450, 1411, 1386, 1262, 1221, 1181, 1101, 1063, 1043, 1008 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 17.40 (d, 1H, $J_{\text{PH}} = 4.4$ Hz), 7.91 (d, 1H, $J = 2.0$ Hz), 7.79 (dd, 1H, $J_1 = 8.6$ Hz, $J_2 = 2.0$ Hz), 7.50 (s, 1H), 7.48 (d, 1H, $J = 1.0$ Hz), 7.46 (s, 1H), 7.23 (d, 1H, $J = 8.0$ Hz), 7.13 (m, 2H), 7.07 (d, 2H, $J = 3.0$ Hz), 5.33 (septet, 1H, $J = 6.0$ Hz), 4.00 (s, 6H), 3.20–1.70 (br m, 83H); ¹³C NMR (126 MHz, CDCl₃) δ 277.4, 154.29, 154.26, 153.4, 144.0, 135.9, 135.7, 135.5, 132.9, 132.5, 132.3, 131.2, 126.7, 126.1, 125.8, 125.7, 125.6, 124.04, 123.96, 123.93, 122.2, 117.2, 115.8, 113.8, 113.7, 113.4, 94.9, 92.4, 92.2, 92.1, 91.3, 91.2, 90.9, 88.0, 86.7, 78.1, 78.0, 77.8, 76.7, 71.7, 69.7, 69.5, 69.3, 60.5, 56.6, 36.1, 35.9, 30.3, 29.9, 28.0, 27.9, 26.4, 22.4, 22.2; ³¹P NMR (202 MHz, CDCl₃) δ 60.16 (s). It was not possible to obtain mass spectrometry characterization of this compound; MALDI-TOF, ESI, and EI methods were attempted.

Synthesis of Nanocar Catalyst 2. A 10 mL round-bottomed flask equipped with a stir bar and condenser was charged with Ru complex **12** (7.5 mg, 8.8 μ mol) and CuCl (4.0 mg, 40.4 μ mol). Then CH₂Cl₂ (0.5 mL) was added, immediately followed by addition of a solution of nanocar **10** (10.0 mg, 8.0 μ mol) in CH₂Cl₂ (2.5 mL). The resulting solution was stirred at 40 °C for 2 h. The solvent was removed in vacuum, and the residue was purified (Geduran silica gel, see General Methods in the Supporting Information, 40% then 60% CH₂Cl₂ in hexanes) to afford **2** as an olive-green solid (7.0 mg, 53%). One milligram of starting material **10** was recovered: FTIR (neat) 3054, 2966, 2924, 2856, 2611, 2210, 1950, 1725, 1593, 1488, 1463, 1412, 1385, 1262, 1220, 1162, 1134, 1102, 1063, 1040 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 16.61 (s, 1H), 7.70 (dd, 1H, $J_1 = 8.5$ Hz, $J_2 = 2.0$ Hz), 7.49 (s, 1H), 7.48 (d, 1H, $J = 1.0$ Hz), 7.42 (s, 1H), 7.23 (d, 1H, $J = 8.5$ Hz), 7.15 (dd, 1H, $J_1 = 8.5$ Hz, $J_2 = 2.0$ Hz), 7.11–7.07 (m, 7H), 6.86 (d, 1H, $J = 9.0$ Hz), 4.96 (septet, 1H, $J = 6.0$ Hz), 4.19 (s, 4H), 4.00 (s, 6H), 3.20–1.70 (br m, 62H), 1.31 (d, 6H, $J = 6.0$ Hz); ¹³C NMR (126 MHz, CDCl₃) δ 295.0, 210.6, 154.3, 153.0, 145.4, 139.3, 135.8, 135.6, 133.2, 132.4, 131.2, 129.7, 126.7, 126.0, 125.64, 125.55, 124.14, 124.07, 123.9, 122.2, 117.0, 115.8, 113.7, 113.4, 95.1, 92.4, 92.24, 92.18, 91.5, 91.3, 91.2, 91.0, 88.0, 86.1, 78.1, 78.0, 77.8, 76.2, 69.7, 69.5, 69.3, 60.6, 60.5, 56.7, 51.8, 29.9, 21.3. It was not possible to obtain mass spectrometry characterization of this compound. MALDI-TOF, ESI, and EI methods were tried.

Scheme 4. ROMP of norbornene catalyzed by **1**.

ROMP of 1,5-Cyclooctadiene.¹⁸ CD₂Cl₂ was freeze/pump/thawed three times. *cis,cis*-1,5-Cyclooctadiene was distilled over CaH₂ immediately prior the polymerization reaction. As reported by Grubbs,¹⁸ in our experience, aged cyclooctadiene gave considerably lower rates. ¹H NMR spectra were collected at 500 MHz. Inside a glovebox, an NMR tube with a septum/screw cap was charged with catalyst solution (0.40 μ mol) and CD₂Cl₂ to give a total volume of 0.80 mL. The solution was equilibrated at 30 °C in the NMR probe. The sample was then ejected to add *cis,cis*-1,5-cyclooctadiene (50 μ L, 0.40 mmol) via syringe. A series of spectra were collected over an appropriate period of time. The degree of conversion to polymer was determined by comparing the ratio of the integrals of the methylene protons in the starting material, δ 2.36 (m) with those in the product, δ 2.09 br (m), δ 2.04 (br m). The integration that **1** and **2** exhibit in this region was neglected since a 1000:1 ratio of *cis,cis*-1,5-cyclooctadiene/catalyst was used.

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Supporting Information Available: Detailed experimental procedures, characterization of compounds **1–5** and **8–10**, tables of ROMP results, and two alternative synthetic approaches investigated to prepare ROMP-propelled nanocars. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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