

Rhodium-Catalyzed Polymerization of 3,3-Diarylcyclopropenes Involving a 1,4-Rhodium Migration

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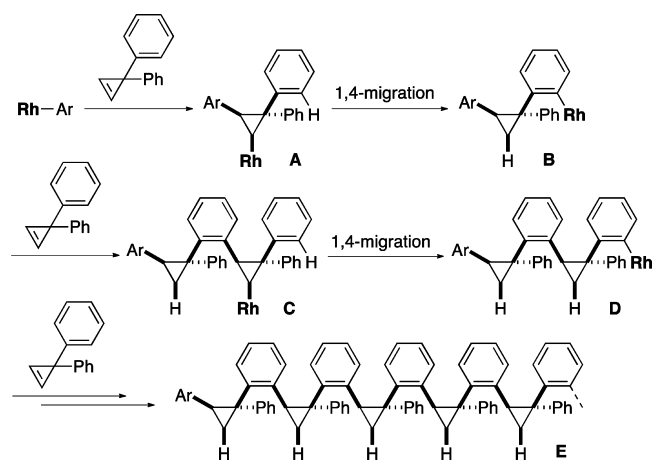
Supporting Information

ABSTRACT: A new mode of metal-catalyzed polymerization reaction has been developed by exploiting the ability of 1,4-rhodium migration of an organorhodium(I) species. Specifically, it has been demonstrated that 3,3-diarylcyclopropenes undergo polymerization through an insertion–1,4-rhodium migration sequence by using an arylrhodium(I) initiator/catalyst to give poly(cyclopropylene-*o*-phenylene)s, which are difficult to synthesize by conventional polymerization methods.

Rhodium-catalyzed carbon–carbon bond forming reactions through insertion of a carbon–carbon or carbon–heteroatom unsaturated bond into a carbon–rhodium bond of organorhodium(I) complexes constitute powerful synthetic tools in modern organic chemistry,¹ and this mode of carbon–carbon bond formation has been successfully applied to the polymerization of arylacetylenes with high catalytic activity.² In addition to this simple insertion (carborhodation) process, rhodium(I) complexes are also known to undergo intramolecular 1,4-rhodium migration from an alkyl-³ or alkenylrhodium⁴ species to an arylrhodium species. This process can quickly add molecular complexity to organic compounds through a C–H bond functionalization and has been effectively utilized in various small molecule syntheses since the first report by Miura et al. in 2000.^{3a,5} Unfortunately, however, this attractive feature of rhodium(I) complexes has never been exploited in the polymerization chemistry despite its potential utility for synthesizing a variety of new types of polymers that are currently inaccessible. Here, we describe the first polymerization reaction involving a 1,4-rhodium migration in the context of a rhodium-catalyzed polymerization of 3,3-diarylcyclopropenes through an insertion–1,4-rhodium migration sequence to give a new class of polymers, poly(cyclopropylene-*o*-phenylene)s, with high efficiency.

Cyclopropenes are highly reactive cyclic alkenes due to their ring strains,⁶ but aside from spontaneous polymerization of unsubstituted cyclopropene,⁷ only a limited number of reports have been made on the use of cyclopropenes as monomers for polymerization reactions in a controlled manner, such as a palladium-catalyzed insertion-polymerization of 3,3-dialkylcyclopropenes⁸ and a molybdenum- or ruthenium-catalyzed ring-opening metathesis polymerization of 3,3-disubstituted cyclopropenes.^{9,10} Under these circumstances, we envisioned that a new type of polymerization process composed of arylrhodation and 1,4-rhodium migration could be realized by the use of

Scheme 1. Schematic Representation of Rhodium-Catalyzed Polymerization of 3,3-Diphenylcyclopropene via 1,4-Rhodium Migration to Yield a Poly(cyclopropylene-*o*-phenylene)

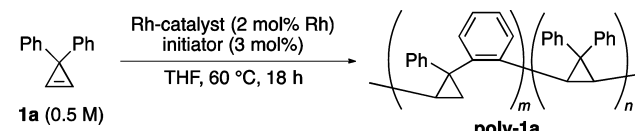


3,3-diarylcyclopropenes as monomers in the presence of a rhodium catalyst (Scheme 1). Thus, a catalytic amount of arylrhodium(I) complex undergoes alkene insertion of a 3,3-diarylcyclopropene to give cyclopropylrhodium(I) intermediate A. Instead of the direct insertion of another molecule of 3,3-diarylcyclopropene, intramolecular 1,4-rhodium migration would lead to arylrhodium(I) species B.¹¹ This then repeats the alkene insertion (arylrhodation)–1,4-rhodium migration sequence to give poly(cyclopropylene-*o*-phenylene) E as the final product.

In an initial investigation, we employed 3,3-diphenylcyclopropene (**1a**: 1.00 mmol) as the monomer and attempted a polymerization reaction in the presence of $[\text{RhCl}(\text{cod})]_2$ (2 mol % Rh) as a catalyst without any initiator in THF (2.0 mL) at 60 °C. Under these conditions, only 7% yield of the polymer was obtained after precipitation from hexane/ CH_2Cl_2 (Table 1, entry 1). In contrast, by using Ph_4BNa (3 mol %) as the initiator, which is known to generate phenylrhodium(I) species by the reaction with $[\text{RhCl}(\text{cod})]_2$,¹² the polymerization smoothly took place under otherwise the same conditions to give **poly-1a** in 83% yield (entry 2). The number-averaged molecular weight (M_n) was calculated to be 6400 g mol^{-1} with PDI of 1.9 using size-exclusion chromatography against a

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Table 1. Rhodium-Catalyzed Polymerization of **1a**: Effect of Catalysts and Initiators


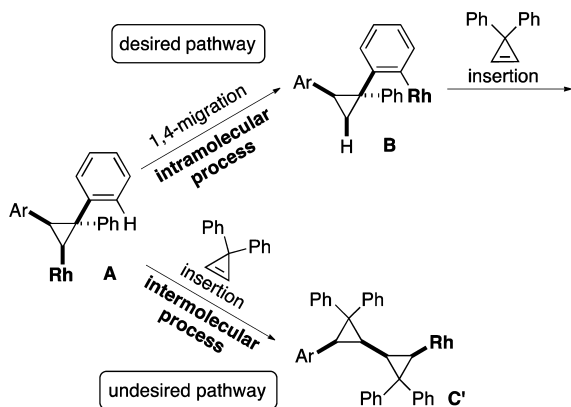
entry	Rh-catalyst	initiator	yield of poly-1a (%)	<i>m/n</i> ^a	<i>M_n</i> (g mol ⁻¹) ^b	<i>M_w</i> / <i>M_n</i> ^b
1	[RhCl(cod)] ₂	none	7	nd ^c	4800	1.2
2	[RhCl(cod)] ₂	Ph ₄ BNa	83	73/27	6400	1.9
3	[RhCl(nbd)] ₂	Ph ₄ BNa	62	58/42	2200	1.5
4	[Rh(OH)(cod)] ₂	Ph ₄ BNa	86	70/30	7000	2.0
5	[Rh(OH)(cod)] ₂	PhB(OH) ₂	78	70/30	5200	2.5
6	[Rh(OH)(cod)] ₂	3,5-Me ₂ C ₆ H ₃ B(OH) ₂	84	78/22	7900	2.0
7	[Rh(OH)(cod)] ₂ /PPh ₃ ^d	3,5-Me ₂ C ₆ H ₃ B(OH) ₂	23	52/48	2600	1.7
8	[Rh(OH)(binap)] ₂	3,5-Me ₂ C ₆ H ₃ B(OH) ₂	4	nd ^c	900	1.1

^aDetermined by ¹H NMR. ^bDetermined using size-exclusion chromatography against a polystyrene standard. ^cnd = not determined. ^dRh/PPh₃ = 1/2.

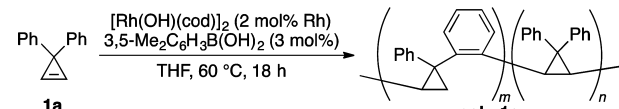
polystyrene standard, and the degree of 1,4-rhodium migration during the polymerization was deduced to be 73% (*m/n* = 73/27) by its ¹H NMR spectrum (vide infra). The use of [RhCl(nbd)]₂¹³ instead of [RhCl(cod)]₂ gave **poly-1a** in a lower yield, molecular weight, and the degree of 1,4-rhodium migration (entry 3), whereas the use of [Rh(OH)(cod)]₂ gave almost the same result as that with [RhCl(cod)]₂ (entry 4). The polymerization was similarly well catalyzed by [Rh(OH)(cod)]₂/PhB(OH)₂, which is also known to generate a phenylrhodium(I),¹⁴ to give **poly-1a** in 78% yield with *m/n* = 70/30 (entry 5). A somewhat better result was obtained by changing the initiator from PhB(OH)₂ to 3,5-Me₂C₆H₃B(OH)₂ (84% yield, *m/n* = 78/22, *M_n* 7900 g mol⁻¹; entry 6). In comparison, the use of rhodium/phosphine catalysts instead of rhodium/diene catalysts significantly lowered the polymerization efficiency (entries 7 and 8).

In the present polymerization, the ideal reaction sequence is a complete alternation of the insertion of cyclopropene **1a** and the successive 1,4-rhodium migration as illustrated in Scheme 1. Under the conditions described in Table 1, however, the direct insertion of **1a** to a cyclopropylrhodium intermediate competes with the desired 1,4-rhodium migration (e.g., *m/n* = 78/22 for entry 5). As shown in Scheme 2, because the 1,4-rhodium

Scheme 2. 1,4-Rhodium Migration vs Direct Insertion from a Cyclopropylrhodium Intermediate



migration (A → B) is an intramolecular process whereas the insertion of **1a** (A → C') is an intermolecular one, we decided to control these two processes by changing the initial concentration of **1a**. As expected, we found that the degree

Table 2. Rhodium-Catalyzed Polymerization of **1a**: Effect of Concentrations


entry	[1a] ₀ (M)	yield of poly-1a (%)	<i>m/n</i> ^a	<i>M_n</i> (g mol ⁻¹) ^b	<i>M_w</i> / <i>M_n</i> ^b
1	0.50	84	78/22	7900	2.0
2	0.17	91	82/18	9000	1.7
3	0.05	81	87/13	8700	1.6
4	0.02	83	90/10	8000	1.5

^aDetermined by ¹H NMR. ^bDetermined using size-exclusion chromatography against a polystyrene standard.

of 1,4-rhodium migration could be improved by lowering the initial concentration of **1a** as compiled in Table 2, and up to 90% was realized at 0.02 M concentration (1.00 mmol of **1a** in 50 mL of THF; entry 4). It is remarkable that the polymerization smoothly proceeds at this low monomer concentration to give **poly-1a** in 83% yield with *M_n* of 8000 g mol⁻¹. The ¹H NMR spectrum of **poly-1a** thus obtained is shown in Figure 1a. A broad peak from 8.5 to 4.7 ppm corresponds to the proton signals on the aromatic rings and a broad peak from 4.3 to -0.3 ppm corresponds to the proton signals on the cyclopropane rings.¹⁵ The area ratio of these two broad peaks is calculated to be 3.13/1 (excluding the CHCl₃ residual peak), which can deduce the degree of 1,4-rhodium migration as 90%, based on the theoretical area ratios of 3/1 for the ideal polymer (9H for aromatic and 3H for aliphatic) and 5/1 for the complete direct-insertion polymer (10H for aromatic and 2H for aliphatic). It is also worth pointing out that the **poly-1a** obtained in the present insertion-1,4-rhodium migration polymerization shows high solubility (>100 mg/mL) at room temperature in various common organic solvents such as benzene, toluene, chlorobenzene, THF, DMF, CH₂Cl₂, and CHCl₃. This is in stark contrast to the poly(cyclopropene)s obtained by simple addition polymerization under palladium catalysis, most of which are known to show poor solubility.^{8,16}

To further confirm the involvement of 1,4-rhodium migration in the present polymerization, we employed 1,2-bisdeuterio-3,3-diphenylcyclopropene (**1a-d₂**) as the monomer as shown in eq 1, and **poly(1a-d₂)** was obtained in 82% yield with *M_n* of 9000 g mol⁻¹. According to the ¹H NMR spectrum in Figure 1b,

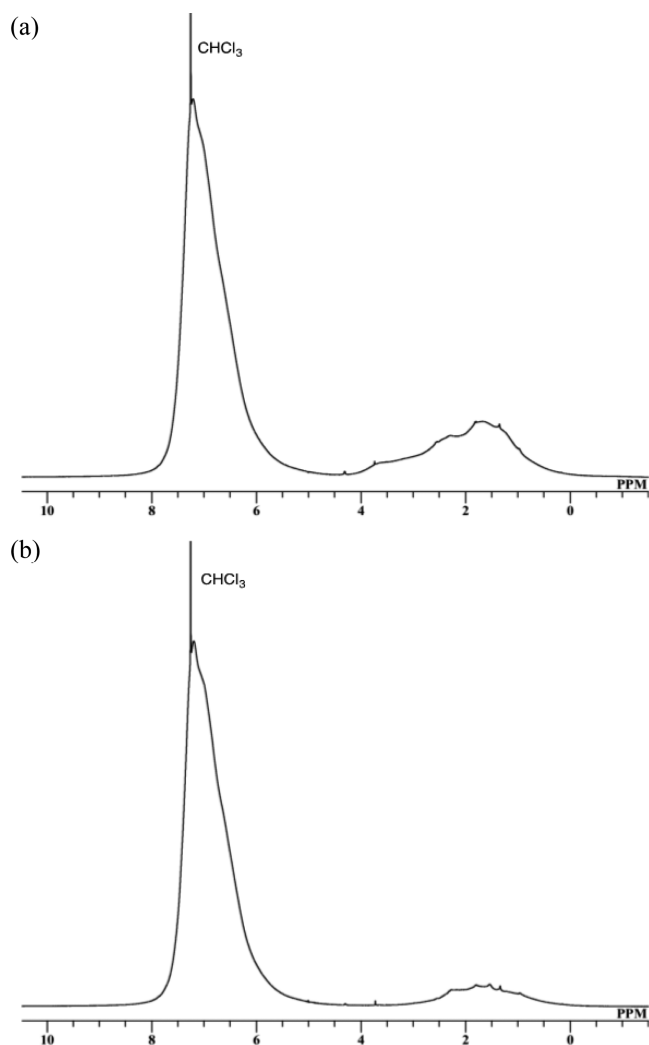
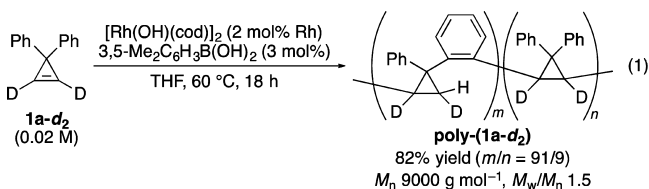


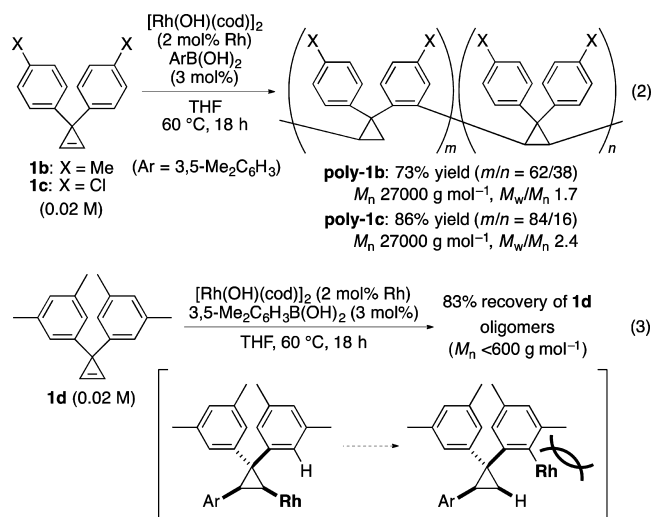
Figure 1. (a) ^1H NMR spectrum of **poly-1a** obtained in Table 2, entry 4 (in dry CDCl_3). (b) ^1H NMR spectrum of **poly(1a- d_2)** obtained in eq 1 (in dry CDCl_3).

the area ratio of the aromatic peak and the aliphatic peak is 9.96/1. If the polymerization takes place without 1,4-rhodium migration, no peaks should appear in the aliphatic region, and the polymerization with perfect 1,4-rhodium migration should provide the area ratio of 9/1. This result therefore supports the insertion–1,4-rhodium migration sequence for the present polymerization, and the degree of 1,4-rhodium migration is calculated to be 91%, which is consistent with the result obtained using nondeuterated monomer **1a** in Table 2, entry 4.



We have also applied this polymerization reaction to other 3,3-diarylcyclopropenes. For example, monomers having substituents at the *para*-positions of the aryl groups such as **1b** ($X = \text{Me}$) and **1c** ($X = \text{Cl}$) can also undergo polymerization efficiently to give **poly-1b** and **poly-1c** in high yields with higher M_n of 27000 g mol^{-1} , although the degree of 1,4-

rhodium migration becomes somewhat lower (eq 2).¹⁷ In contrast to these *para*-substituted 3,3-diarylcyclopropenes, 3,3-bis(3,5-dimethylphenyl)cyclopropene (**1d**) is not suitable as a monomer presumably due to the presence of *meta*-substituents on the phenyl groups, which are known to retard the 1,4-rhodium migration toward the *ortho*-position adjacent to them (eq 3).^{3a,i,4c,f} This also indirectly supports that 1,4-rhodium migration is the key process for the present polymerization reaction.



In summary, we have developed a new mode of metal-catalyzed polymerization reaction by exploiting the ability of 1,4-rhodium migration of an organorhodium(I) species. Specifically, it has been demonstrated that 3,3-diarylcyclopropenes undergo polymerization through an insertion–1,4-rhodium migration sequence by using an arylrhodium(I) initiator/catalyst generated *in situ* to give poly(cyclopropylene-*o*-phenylene)s, which are inaccessible by conventional chain-growth polymerization methods.¹⁸ Future studies will be directed toward further improvement of this new type of polymerization reaction including the development of a catalyst system for the control of tacticity.

■ ASSOCIATED CONTENT

📄 Supporting Information

Experimental procedures and compound characterization data (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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(15) Broad signals in the ¹H NMR spectrum may be due to the lack of tacticity control in the present polymerization. For more discussions on the polymer structure, see the SI.

(16) We confirmed that a polymerization of 3,3-diphenylcyclopropene under the palladium-catalyzed conditions described in ref 8a gave a highly insoluble polymer.

(17) We also conducted a polymerization of 3,3-bis(4-chlorophenyl)cyclopropene-1-¹³C (**1c-¹³C**) to gain further structural insights. See the SI for details.

(18) Even for step-growth polymerization, the preparation of monomers such as 1-halo-2-(2-metallocyclopropyl)benzenes or 1-metallo-2-(2-halocyclopropyl)benzenes would be required.