

Pd Complex-catalyzed copolymerization of a bicyclic methylenecyclopropane with carbon monoxide to afford a new polyketone †

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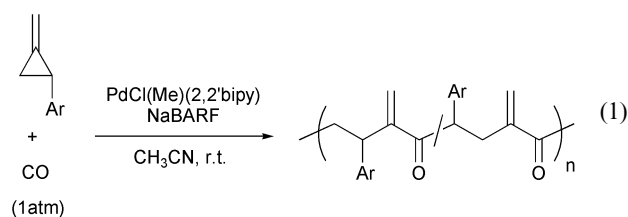
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Alternating copolymerization of 7-methylenebicyclo[4,1,0]heptane with CO in thf is promoted by catalysts prepared from Pd complexes, PdCl(Me)L (L = chelating diimine or diamine), and NaBARF (BARF = [B{C₆H₃(CF₃)₂-3,5}4][−]), to produce the polyketone containing enone and 1,2-cyclohexane units. The Pd complexes with Schiff-base type diimines, 2,9-disubstituted 1,10-phenanthroline, and tmeh are effective as catalysts to afford the polyketone containing mainly the *cis*-1,2-disubstituted cyclohexane ring. Polymerization in thf using Schiff-base diimine as the ligand for Pd produces product with a narrow molecular weight distribution ($M_w/M_n = 1.10$ – 1.19). The increase in molecular weight during polymerization and polymer growth caused by addition of new monomer indicates living polymerization. The reaction catalyzed by cationic Pd complexes with 2,2'-bipy and phen, prepared from NaBARF and PdCl(Me)L (L = 2,2'-bipy, phen) in CH₃CN, produces polymer that contains both *trans*- and *cis*-disubstituted cyclohexane rings in almost equal amounts. Heating of the polymer with *cis*-disubstituted cyclohexane in the presence of sodium *o*-chlorophenolate induces epimerization of the polymer into thermodynamically more stable polyketones with *trans*-disubstituted cyclohexane.

Introduction

Pd Complexes with chelating ligands catalyze the alternating copolymerization of alkenes with CO to produce the corresponding polyketones.^{1,2} Both Pd complexes with Schiff-base type diimine ligands and those with 2,2'-bipy promote the copolymerization. A recent study of the copolymerization of styrene with CO revealed higher activity of the 2,2'-bipy-coordinated Pd complex than the complex with bisoxazoline ligand.³ Pd Complexes with several P-donors such as phosphine/phosphite catalyze the copolymerization of styrene with CO to produce the chiral polyketone.⁴ Pd Complexes with phosphine/sulfonate catalyze the copolymerization of ethylene with CO giving the polyketone containing partial oligoethylene units.^{5,6}

Recently, we reported the ring-opening copolymerization of 2-aryl-1-methylenecyclopropane with CO promoted by Pd complexes with 2,2'-bipy [eqn. (1)].⁷



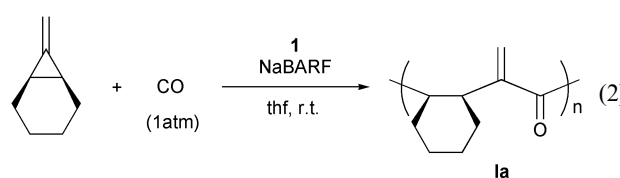
Although the produced polyketone is composed of alternating enone and $-\text{CH}_2-\text{CH}(\text{Ar})-$ groups, it is a mixture of the structural units with head-to-tail or head-to-head linkages. Analogous ring-opening copolymerization of the monomer with a symmetrical structure would be free from the above head-to-tail issue of the produced polymer. In this paper we report on the Pd complex-catalyzed copolymerization of 7-methylenebicyclo[4,1,0]heptane with CO to produce the polyketone with cyclohexane rings in the polymer chain. The stereochemistry of the polymerization varies depending on the ligand bonded to the Pd center as well as reaction conditions.

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Results and discussion

Polymerization

Typically, the catalyst is prepared by addition of NaBARF (BARF = [B{C₆H₃(CF₃)₂-3,5}4][−]) to a thf solution of PdCl(Me)L (**1**: L = {C₆H₃[CH(CH₃)₂]-2,6}-N=C-C₁₀H₆-C=N-{C₆H₃[CH(CH₃)₂]-2,6}) followed by introduction of CO, which leads to a bright yellow solution. The solution probably contains a mixture of the cationic Pd complexes [Pd(R)(X)-L]⁺BARF[−] (R = Me or COMe; X = thf or CO) which are in equilibrium under a CO atmosphere. Addition of 7-methylenebicyclo[4,1,0]heptane to the solution initiates ring-opening copolymerization of the substrate with CO to produce polyketone $-\text{[C(=CH}_2\text{)-CO-C}_6\text{H}_{10}\text{]}_n-$ (**1a**) [eqn. (2)].



The ¹H NMR spectrum of **1a** [Fig. 1(a)] contains the signals of two =CH₂ hydrogens (δ 5.55 and 5.74) and those of two CH hydrogens of the six-membered ring (δ 2.66 and 3.52). The ¹³C{¹H} NMR spectrum [Fig. 1(b)] also exhibits the signals at δ 124.7 and 150.4 which are attributed to =CH₂ and quaternary carbons of the enone group, respectively. The signals at δ 37.8 and 40.8 are assigned to two CH carbons of the cyclohexane ring based on DEPT measurements. The four peaks of the CH₂ carbons of the cyclohexane ring are observed at δ 21.0, 25.7, 26.0 and 28.8. The appearance of a single NMR signal for each hydrogen or carbon clearly indicates that the polymer is composed of a single repeating unit that contains an alternating enone unit bonded with high regularity. Comparison of the NMR spectra of **1a** with those of a model compound, 1-acetyl-2-(2-propenyl)cyclohexane, whose cyclohexane ring is substituted by vinylidene and carbonyl groups, revealed the stereochemical structure of **1a**. *cis*-1-Acetyl-2-(2-propenyl)cyclohexane shows the ¹³C{¹H} NMR signals of CH₂ carbons of the cyclohexane ring at δ 22.4, 24.4, 26.5, 26.6, which are

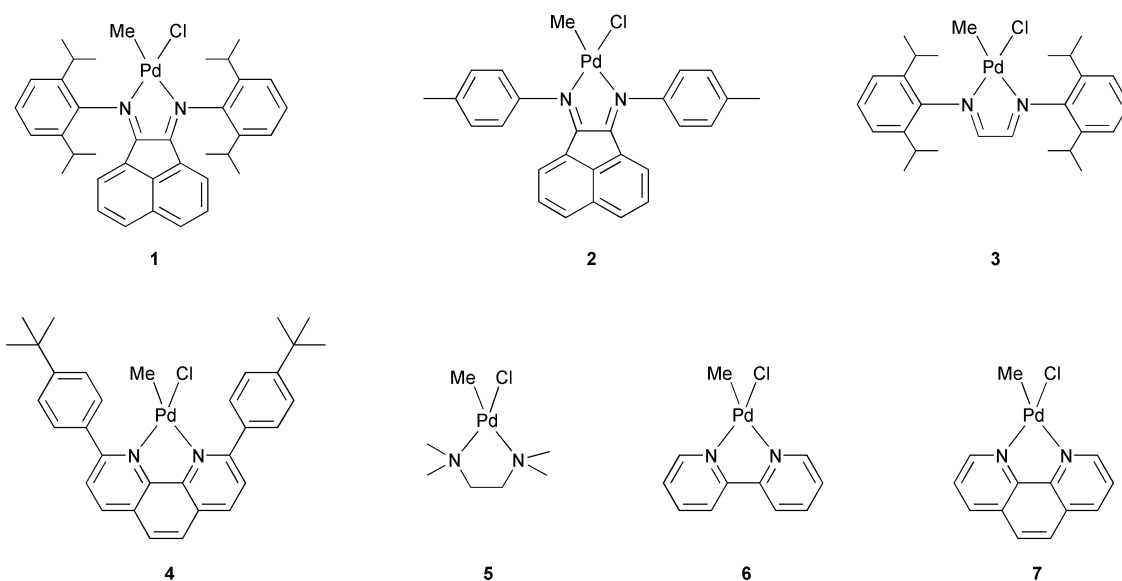


Chart 1 The chelating N-donor ligands used in this study.

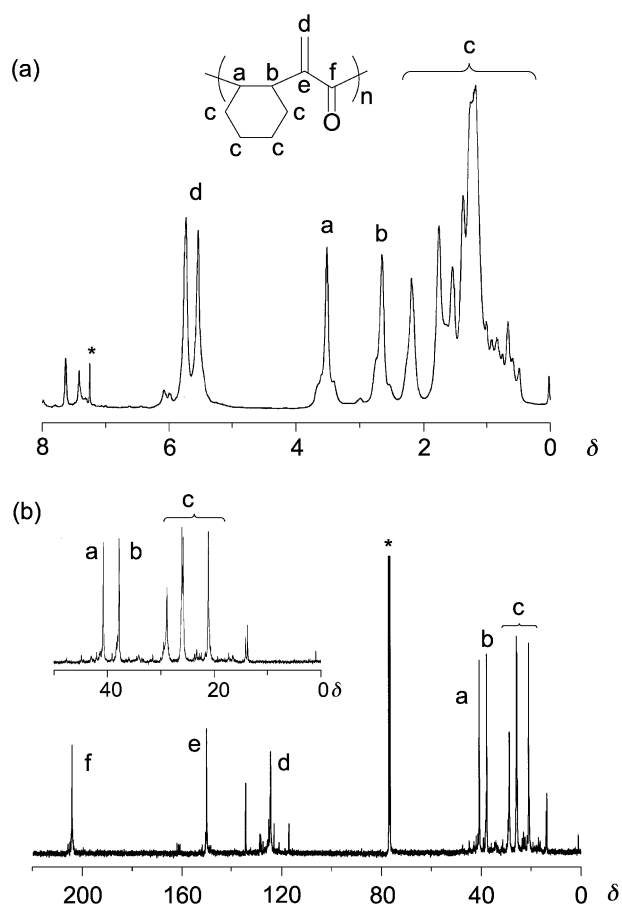


Fig. 1 (a) ^1H and (b) $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of **Ia** in CDCl_3 at 25°C . **Ia** was prepared by polymerization in thf under CO (1 atm) catalyzed by **1**/NaBARF ([Pd] = 25 mM, [monomer]/[Pd] = 100) in thf at room temperature (Table 1, run 2). Peaks with asterisks are due to solvent.

much closer to the peak positions of **Ia** than the *trans* model compound, δ 25.4, 25.9, 29.2, 31.6. Therefore, polymer **Ia** has the *cis*-1,2-disubstituted cyclohexane ring in the structural unit. Minor NMR signals of **Ia** in the spectrum may be assigned to structural units with *trans*-1,2-substituted cyclohexane, which is described in detail later.

Chart 1 summarizes the chelating N-donor ligands used in this study. Table 1 lists the results of the polymerization. Catalysts prepared from the Pd complexes with Schiff-base type

diimine ligands (**1–3**) and NaBARF promote copolymerization of 7-methylenebicyclo[4,1,0]heptane with CO to produce **Ia** (runs 1–9). The reactions in thf under CO (1 atm) for 3–5 h convert the monomer efficiently (70–94% conversion) to produce **Ia** in 48–73% yield. The moderate yield of the polymer product, in spite of the high conversion of monomer, is ascribed to loss of a part of the polymer during purification by reprecipitation. The polymerization with [monomer]/[Pd] = 200 (run 1) forms **Ia** whose yield and molecular weight (73%, $M_n = 29600$, $M_w/M_n = 1.19$) are higher than that obtained from the reaction with [monomer]/[Pd] = 100 (58%, $M_n = 13600$, $M_w/M_n = 1.20$, run 2). Dioxane, acetone and *N*-methylpyrrolidone (nmp) were also used as solvent for the polymerization catalyzed by **3**/NaBARF (runs 7–9). These solvents do not influence the reaction results significantly. The polymerization in CH_3CN (runs 3 and 5) gives **Ia** in lower yield than that catalyzed by the same Pd complexes in thf (runs 2 and 4). Although the cationic palladium complexes, $[\text{PdMe}(\text{solv})\text{L}]^+\text{BARF}^-$, formed in the reaction mixture promote the polymerization, complex **3** catalyzes the polymerization also in the absence of NaBARF (run 10). Copolymerization of 2-aryl-1-methylenecyclopropane with CO, giving the corresponding polyketones, is promoted by $\text{PdCl}(\text{Me})(\text{bipy})$ (**6**) both in the presence and in the absence of NaBARF.⁷ The cationic complex catalyzes the polymerization much more smoothly than the neutral complex; the polyketone formed by the reaction using **6**/NaBARF attains 84% in 3 h, while the reaction catalyzed by **6** requires 66 h to obtain 60% conversion of the monomer. The reactions promoted by cationic and neutral complexes (runs 6 and 10) in this study, however, lead to **Ia** in similar yields. Pd Complexes with 2,9-bis(4-*tert*-butylphenyl)-1,10-phenanthroline (**4**) and tmen (**5**) also bring about the copolymerization (runs 11 and 12).

The polymerization by Pd complexes with diimine ligands (**2**, **3**) and tmen ligand (**5**) affords the copolymer with $M_w/M_n = 1.10$ – 1.11 which is indicative of living polymerization (Table 1, runs 4, 6 and 12). Since narrow polydispersity of the product, isolated in moderate yields, does not necessarily indicate living polymerization, the following experiments were conducted to confirm the living nature of the polymerization. Fig. 2 plots the increase in molecular weight of the product with narrow distribution ($M_w/M_n = 1.10$ – 1.24) during the copolymerization promoted by **2**/NaBARF. The molecular weights of **Ia** are close to those calculated from the ratio of the consumed monomer to the Pd complex (dashed line in Fig. 2). At the initial stage of the polymerization, the polydispersity of the product is close to 1.2, which decreases to 1.1 during the reaction. The reactions with

Table 1 Copolymerization of 7-methylenebicyclo[4,1,0]heptane with CO^a

Run	Catalyst	Solvent	Time/h	Conversion ^b (%)	Product			
					Polyketone ^c (<i>cis</i> : <i>trans</i>)	Yield (%)	M_n^d	M_w/M_n^d
1	1	thf	3	92	Ia (98 : 2)	73	29600	1.19
2	1	thf	3	93	Ia (91 : 9)	58	13600	1.20
3	1	CH ₃ CN	3	—	Ia (94 : 6)	30	15700	1.55
4	2	thf	5	70	Ia (97 : 3)	55	9800	1.10
5	2	CH ₃ CN	3	—	Ia (94 : 6)	40	9200	1.14
6	3	thf	3	94	Ia (81 : 19)	48	13900	1.11
7	3	dioxane	3	95	Ia (89 : 11)	33	10600	1.34
8	3	acetone	3	80	Ia (88 : 12)	47	11800	1.21
9	3	nmp	3	96	Ia (81 : 19)	49	13500	1.22
10 ^e	3	thf	3	96	Ia (91 : 9)	44	16900	1.22
11	4	thf	3	96	Ia (95 : 5)	35	22300	1.43
12	5	thf	3	95	Ia (93 : 7)	44	10700	1.11
13	6	thf	3	92	Ib (91 : 9)	52	6500	1.34
14	6	CH ₃ CN	3	—	Ic (51 : 49)	64	6500	1.40
15 ^f	6	CH ₂ Cl ₂	3	—	Ic (34 : 66)	76	4300	1.81
16	6	CH ₂ Cl ₂	3	—	Ic (72 : 28)	65	19000	1.48
17	7	CH ₃ CN	2	—	Ic (59 : 41)	72	7100	1.23

^a Polymerization was initiated by Pd cationic complex prepared *in situ* from PdCl(Me)(L) and NaBARF in the solvent used in the polymerization. Polymerization conditions: [monomer]/[Pd] = 200 (run 1) and 100 (runs 2–17), [Pd] = 25 mM, CO pressure = 1 atm. ^b Determined by ¹H NMR. ^c *cis/trans* ratios determined by ¹H NMR are shown in parentheses. ^d Determined by GPC based on polystyrene standard. ^e In the absence of NaBARF. ^f The cationic Pd complex was prepared in CH₃CN.

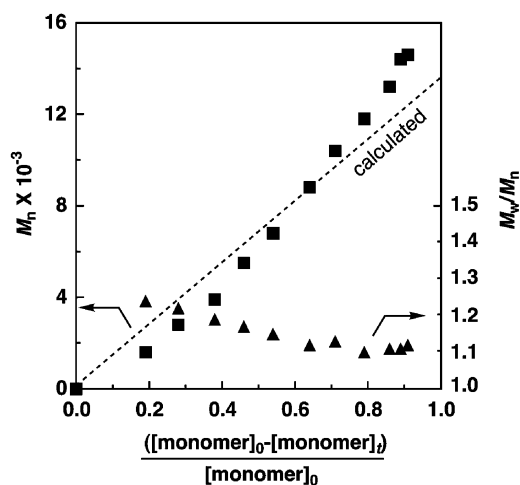


Fig. 2 Relationship between monomer conversion and molecular weight of the polyketone. Polymerization was catalyzed by **2**/NaBARF ([Pd] = 25 mM, [monomer]/[Pd] = 100) in thf at room temperature. A small portion of the reaction mixture was periodically removed for ¹H NMR and GPC analysis.

the [monomer]/[Pd] = 50, 100, and 200, produce **Ia** with molecular weights (M_n) of 3200, 10700, and 29600, respectively. The stability of the living polymer was examined by the polymer growth caused by addition of new monomer. Copolymerization promoted by **5**/NaBARF with [monomer]/[**5**] = 50 for 3 h at 0 °C causes complete consumption of the monomer and formation of the polymer with M_n = 3200 (M_w/M_n = 1.26). Addition of new monomer ([monomer]/[**5**] = 100) and reaction for an additional 6 h led to further growth of the polymer with M_n = 16000 (M_w/M_n = 1.11).

DSC measurement of **Ia** (run 1 in Table 1) shows no T_m throughout the range between 30 to 250 °C, although it shows T_g at 136 °C, which is higher than that of ethylene–CO (5–15 °C)⁸ and styrene–CO copolymers (100–110 °C).⁹ The high T_g value is presumably owing to the rigid cyclohexane ring in the main chain and well-controlled stereoregularity.

Complex **6** also catalyzes the copolymerization of 7-methylenebicyclo[4,1,0]heptane with CO to produce the polyketone with different stereochemical structures depending on the polymerization conditions. The polymerization in thf (Table 1, run 13) produces polyketone **Ib** with lower molecular weight

(M_n = 6500) than **Ia** obtained by the reaction catalyzed by **1–5** under similar conditions (runs 2, 4, 6, 11 and 12). The ¹³C{¹H} NMR spectrum of **Ib** exhibits signals at δ 124.7 and 150.4, which are assigned to =CH₂ and C= carbons, respectively. The CH₂ carbon signals at similar positions (δ 21.1, 25.8, 26.2 and 29.1) to those of **Ia** indicate that the cyclohexane ring of **Ib** has *cis* form similarly to **Ia**. The CH carbon signals of **Ib**, however, are observed as four peaks at δ 38.1, 39.1, 40.7 and 42.0 [Fig. 3(b)]. Two of the four distinct signals are assigned to the

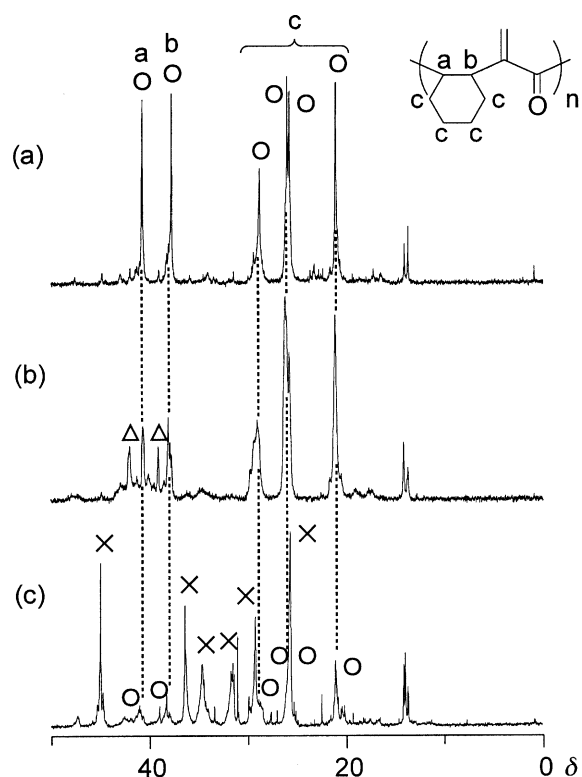
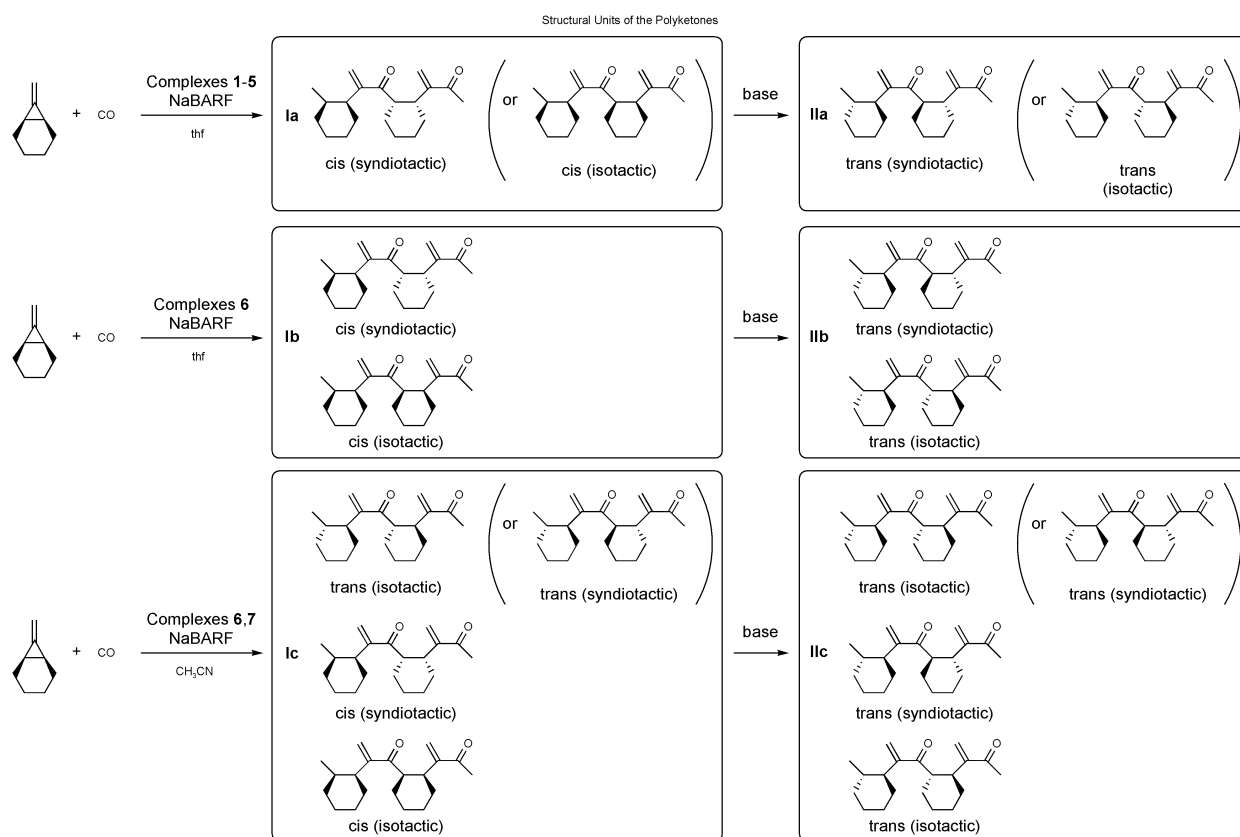


Fig. 3 ¹³C{¹H} NMR spectra (cyclohexane carbon region) of (a) **Ia** (Table 1, run 2), (b) **Ib** (Table 1, run 13), and (c) **Ic** (Table 1, run 15) in CDCl₃ at 25 °C. The copolyketones were prepared under CO (1 atm) in the presence of (a) **1**/NaBARF or (b, c) **6**/NaBARF prepared in CH₃CN ([Pd] = 25 mM, [monomer]/[Pd] = 100) in (a, b) thf or (c) CH₂Cl₂ at room temperature.



structure in **Ia** from the similarity of peak positions. The signals at δ 39.1 and 42.0 [peaks with triangles in Fig. 3(b)] as well as a broad peak in the range δ 39–43 of **Ib** are not observed or observed as quite small signals in the spectrum of **Ia**. The different peak patterns of the CH carbon signals between **Ia** and **Ib** suggests a difference in the tacticity of polymers with *cis*-substituted cyclohexane rings; **Ia** has a single tacticity, isotactic or syndiotactic, shown in Scheme 1, whereas **Ib** contains a mixture of isotactic and syndiotactic diads. Two pairs of the signals can be attributed to the syndiotactic and isotactic diads, while a low broadened peak due to the structural units with other tacticities is observed. The present NMR data do not provide sufficient evidence to assign the signals of **Ib** to an isotactic diad or syndiotactic diad or to clarify whether **Ia** contains isotactic or syndiotactic structural units.

The polymerization promoted by **6**/NaBARF in CH_3CN or that promoted by the catalyst formed in CH_3CN produces polyketone **Ic** (Table 1, runs 14 and 15) which exhibits signals for $=\text{CH}_2$ and C= carbons at lower magnetic field positions, δ 121.4 and 152.1, than the corresponding peaks of **Ia** and **Ib**. The spectrum of **Ic** (run 15) shows the signals for cyclohexane carbons at different positions from those of **Ia** and **Ib** [Fig. 3(c)]. Large and sharp NMR signals (δ 25.7, 29.2, 31.5, 34.7, 36.4 and 45.0) are observed [peaks with cross marks in Fig. 3(c)] in addition to those of **Ia** in small intensities [peaks with circles in Fig. 3(c)]. The former signals are assigned to the CH_2 and CH carbons of *trans*-1,2-disubstituted cyclohexane. The ratios between *cis* and *trans* structures of **Ib** (runs 14 and 15) are determined as 51 : 49 and 34 : 66, respectively, based on the ^1H NMR peak area ratios. The reaction which does not use CH_3CN , both in preparation of the catalyst and in the polymerization, produces **Ic** with a lower content of the unit with *trans*-1,2-disubstituted cyclohexane (28%). PdCl(Me)(phen) (**7**) also initiates the copolymerization to give **Ic** with *cis/trans* = 59 : 41 (Table 1, run 17). Although polyketones **Ia** and **Ib** are mainly composed of the *cis*-1,2-disubstituted cyclohexane repeating unit, the $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of the polymers contain small signals at similar positions to those of **Ic**, indicating

that the *trans*-1,2-disubstituted cyclohexane is also a minor component. As listed in Table 1, **Ia** and **Ib**, prepared from the reaction catalyzed by **1**, **2** and **4–6**, contain less than 10% *trans*-1,2-disubstituted cyclohexane (runs 1–5, 11 and 12), while **Ia** from the reaction catalyzed by **3** has a slightly higher *trans*-1,2-disubstituted cyclohexane content (9–19%, runs 6–10).

Fig. 4 shows plots of the monomer consumption in the reaction promoted by **3**/NaBARF, as well as linear first-order plots of the copolymerization. Scheme 2a depicts the pathway proposed for the copolymerization of 2-aryl-1-methylenecyclopropane with CO promoted by the Pd complexes, giving the corresponding polyketones, which involves the sequential reactions: (i) 1,2-insertion of the C=C double bond of 2-aryl-1-methylenecyclopropane into the Pd–acyl bond, (ii) cleavage of the cyclopropane ring at the growing polymer end by β -alkyl activation, and (iii) insertion of CO into the Pd–alkyl bond to regenerate the acylpalladium species.⁷ The analogous reaction pathway for the copolymerization of 7-methylenebicyclo[4.1.0]-

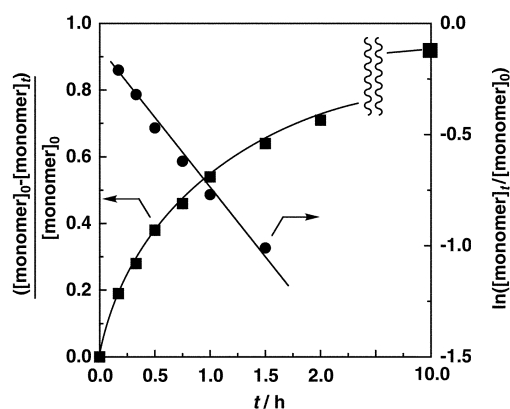
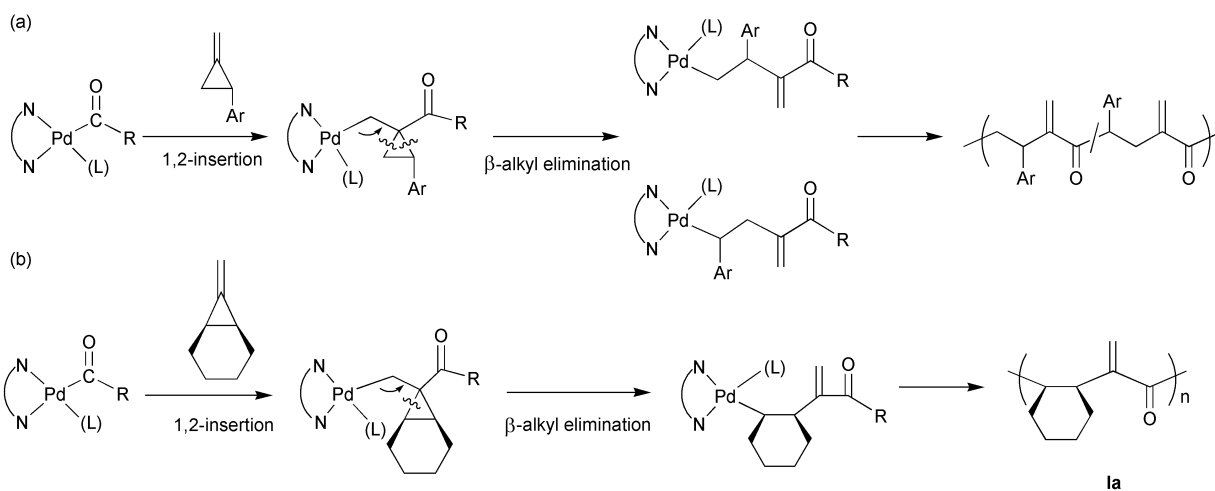


Fig. 4 Time-conversion curve and first-order kinetics plots of the copolymerization of 7-methylenebicyclo[4.1.0]heptane with CO (1 atm) catalyzed by **2**/NaBARF ([Pd] = 25 mM, [monomer]/[Pd] = 100) in thf at room temperature.



Scheme 2

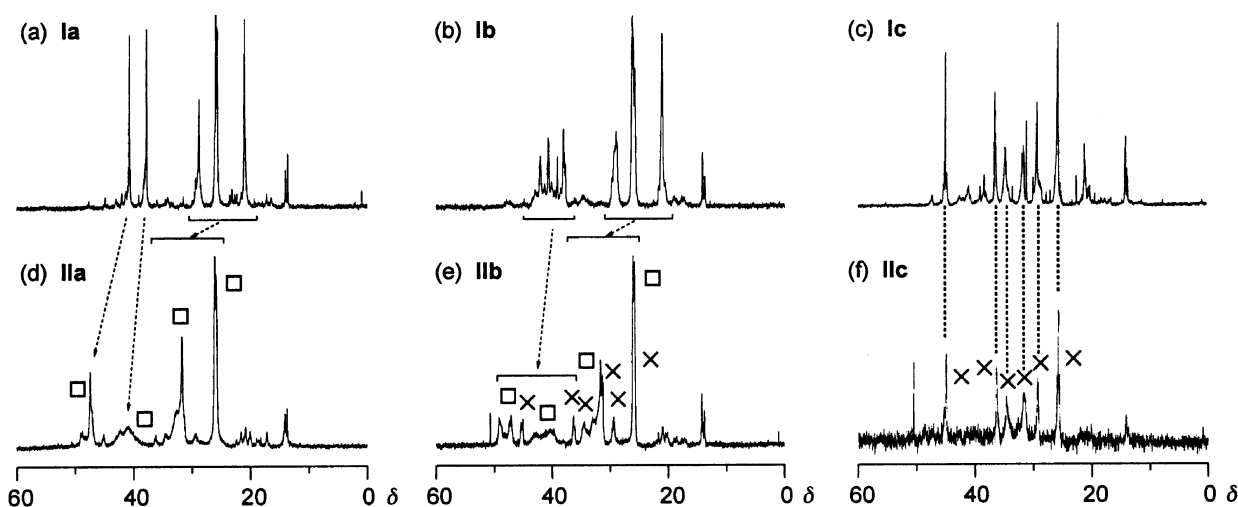


Fig. 5 $^{13}\text{C}\{^1\text{H}\}$ NMR spectra (cyclohexane region) of (a) **Ia** (Table 1, run 2), (b) **Ib** (Table 1, run 13), (c) **Ic** (Table 1, run 15), (d) **IIa** obtained from epimerization of **Ia**, (e) **IIb** obtained from epimerization of **Ib**, and (f) **IIc** obtained from epimerization of **Ic**. In CDCl_3 at 25°C .

heptane with CO in this study is shown in Scheme 2b. The first-order kinetics of the copolymerization to concentration of the monomer indicates that the rate determining step resides in the insertion of the C=C double bond of 7-methylenebicyclo[4,1,0]heptane into the Pd-acyl bond of the growing polymer.

Structure of the polymers and ligands 1–7

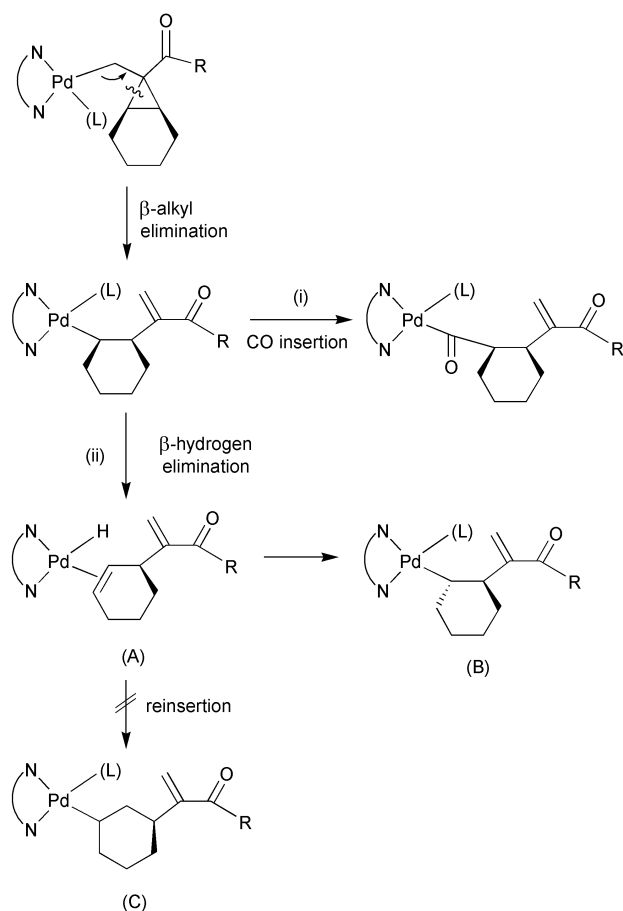
cis-1-Acetyl-2-(2-vinyl)-cyclohexane undergoes base-promoted epimerization to produce the thermodynamically more stable *trans* isomer via inversion of the CH carbon adjacent to the carbonyl group.¹⁰ Isotactic polyketone synthesized from styrene and CO was also reported to be transformed to the atactic polymer.^{9,11} Scheme 1 depicts the structures of the above polyketones and that of the polymers expected from similar epimerization of them. The polymers with *cis*-isotactic and those with *cis*-syndiotactic linkages would be converted to the *trans*-isotactic and *trans*-syndiotactic polymers, respectively. Base-promoted epimerization of the polymers **Ia** and **Ib** containing mainly the *cis*-1,2-disubstituted cyclohexane ring, was conducted by heating them in an *o*-chlorophenol solutions of sodium *o*-chlorophenolate for 24 h at 100°C . Fig. 5 compares the NMR spectra (cyclohexane carbon region) of **Ia** and **Ib** with the respective products of the base-promoted epimerization, **IIa** and **IIb**. The CH carbon signals of **IIa** at δ 47.4 and 40.9 and a part of the CH_2 carbon signal at δ 25.9 and 26.1 [Fig. 5(d)] are observed at lower magnetic field positions than the corresponding signals of **Ia**. The spectrum of **IIb** in Fig. 5(e) contains the peaks observed in the spectrum of **IIa** [peaks

marked with squares in Fig. 5(d)] and the peaks of **IIc** [Fig. 5(f), peaks marked with crosses]. The peaks for **IIc** [Fig. 5(f)] are at lower magnetic field positions than the corresponding peaks of **Ia** and **Ib** [Fig. 5(a) and (b)] except that at δ 36.3 which is at a higher magnetic field position than the CH carbon signals of **Ia** and **Ib** (δ 38–42). Since the cyclohexane carbon signals of *cis*-1-acetyl-2-(2-propenyl)cyclohexane appear at higher field than those of the *trans* isomer (*vide supra*), the above shift of the $^{13}\text{C}\{^1\text{H}\}$ NMR peaks of **Ia** and **Ib** caused by the base-promoted reaction reasonably suggests the *cis* to *trans* isomerization of the structural unit. Heating of **Ic** with base causes no significant change of the NMR signals except disappearance of the small signals at the same position as **Ia** and **Ib**. Polymers **IIa** and **IIc** with *trans* cyclohexane rings show different NMR patterns from each other due to their different tacticities. Polyketone **IIb**, obtained by the epimerization of **Ib**, shows the signals of both **IIa** and **IIc** which can be attributed to the syndiotactic and isotactic diads of the structural units with *trans*-1,2-disubstituted cyclohexane. **IIb** includes ^{13}C NMR signals due to both of the diads.

Scheme 1 summarizes the structures of the polyketones formed by copolymerization of the bicyclic methylenecyclopropane with CO and by the base-promoted epimerization of the formed polyketone. The catalytic reaction promoted by the Pd complexes with bidentate N-ligands produces the polyketone $-\text{C}(\text{=CH}_2)\text{CO}-\text{C}_6\text{H}_{10}-$ with different stereochemical structures, **Ia**, **Ib** and **Ic**, depending on the ligand and the reaction conditions. The reaction using Pd complexes 1–5 and NaBARF in thf leads to **Ia**, having a *cis*-1,2-disubstituted

cyclohexane ring. The NMR spectra indicate the presence of a sole diad with the *cis* structural unit, isotactic or syndiotactic. Catalyst **6**/NaBARF promotes the copolymerization in thf to produce **1b** which lacks regulation in the stereochemistry in the linkage of the structural unit and contains both of the two above diads. Use of CH₃CN in the reactions promoted by **6** and **7** in the presence of NaBARF produces **1c** that contains the repeating unit with *trans*-1,2-disubstituted cyclohexane ring (*trans/cis* = ca. 1 : 1), whereas the reaction using **1** and **2** in CH₃CN leads to polymerization with a high content of the *cis*-cyclohexane containing unit (94%). Low stereoselectivity of the reaction catalyzed by **6**/NaBARF in thf can be attributed to less severe steric hindrance of the bipy ligand than **1–5**/NaBARF which have bulky substituents at the nitrogen atom or at the carbon attached to the nitrogen of the ligand. The reactions by **6**/NaBARF and **7**/NaBARF in CH₃CN are accompanied by formation of the *trans* cyclohexane containing structural unit. The linkage of the structural units of **1a** and **1b** reflects the structure of their respective products **11a** and **11b** by epimerization, **11a** and **1a** have a single tacticity, while **11b** and **1b** contain two (or more) diads in the polymer.

The polyketones **1a** and **1b** contain a small portion of the structural unit with *trans*-1,2-substituted cyclohexene. It is attributed to inversion of the asymmetric carbon at the growing polymer end rather than that of the polymer chain. Scheme 3 depicts a possible pathway for the formation of the polymer unit having *trans*-1,2-cyclohexane ring. The *cis* polymer unit is formed by insertion of CO into the bond between Pd and the cyclohexyl ligand with *cis* geometry [(i) in Scheme 3]. β -Hydrogen elimination of the cyclohexyl ligand prior to the CO insertion (ii) would form a hydridopalladium complex (A) with a π -coordinated cyclohexene group. The complexes may undergo elimination of the polymer with the cyclohexene terminal group to cause chain transfer or reinsertion of the C=C double bond into the Pd–H bond to generate the palladium species



Scheme 3

with a *trans*-1,2-disubstituted cyclohexyl group (B) or with a 1,3-disubstituted cyclohexyl group (C). The COSY NMR spectrum of the polymers, **1a**, **1b** and **1c**, clearly indicates the absence of the structural unit with a 1,3-cyclohexene ring. These experimental results can be rationalized by assuming that intermediate (A) undergoes insertion of the C=C double bond to give (B) rather than (C) with the 1,3-disubstituted cyclohexane ring maybe due to interaction of the enone group of the polymer end with the Pd center of (A).

Formation of the structural unit with a *trans* six-membered ring is enhanced by CH₃CN solvent in the reaction using **6**/NaBARF. Recently we compared the stability of cationic arylpalladium complexes with bipy ligands and found that CH₃CN stabilizes the complex more significantly than ligating thf or acetone.¹² The complexes in thf undergo intermolecular aryl ligand coupling *via* rapid generation of the reactive three-coordinated species *via* dissociation of the solvent. Also in this copolymerization, the solvent coordinates competitively with CO or with the C=C bond of the monomer. The CH₃CN ligand of [PdR(NCCH₃)(L)]⁺ species in the reaction mixture block or retard the replacement of CH₃CN by CO and subsequent insertion of CO into the Pd–C bond. It facilitates β -hydrogen elimination of the cyclohexyl ligand by suppressing the insertion of CO into the Pd–C bond.

In summary, 7-methylenebicyclo[4,1,0]heptane undergoes smooth alternating copolymerization with CO in spite of its sterically bulky structure. Many chelating nitrogen ligands have been employed. The structure of these ligands as well as solvent used significantly influence the stereochemistry of the product. The bulky six-membered ring of the growing polymer end and the substituents of the ligands regulate insertion of the monomer into the Pd–acyl bond to form the *cis*-polyketone with a single tacticity in thf. Tacticity of the polyketone is retained before and after the base-promoted epimerization.

Experimental

General method

Dry CH₃CN and CH₂Cl₂ were used as received. thf was distilled over benzophenone ketyl under Ar. 7-Methylenebicyclo[4,1,0]heptane was prepared by a previously reported procedure.¹³ Diimine ligands,¹⁴ 2,9-bis-(4-*tert*-butylphenyl)-1,10-phenanthroline,¹⁵ PdCl(Me)L¹⁶ and NaBARF¹⁷ were prepared according to the previously reported procedures.

NMR (¹H and ¹³C) spectra were recorded on a Varian Mercury 300 or JEOL JNM-500 spectrometer. The peaks were referenced to CHCl₃ in the CDCl₃ solvent (δ_{H} 7.26) for ¹H and CDCl₃ (δ_{C} 77.0) for ¹³C. Gel permeation chromatography (GPC) was performed at 40 °C on a TOSOH HLC-8020 high-speed liquid chromatograph system equipped with a differential refractometer detector and a variable-wavelength UV-vis detector, using thf as eluent at a flow rate of 0.6 cm³ min⁻¹ with TSKgel SuperHM-L and SuperHM-M columns. The molecular weights were calibrated based on polystyrene standards. DSC was recorded on a Seiko DSC6200R.

Polymerization

Typically, to a 25 cm³ Schlenk flask containing a thf solution (2 cm³) of Pd complex **5** (0.025 mmol, 6.8 mg) was added NaBARF (0.030 mmol, 26.6 mg) under Ar. After stirring for several minutes, the resulting suspension was degassed, flushed with CO (1 atm), and stirred for 10–15 min at room temperature. The color of the mixture changed from pale yellow to bright yellow. 7-Methylenebicyclo[4,1,0]heptane (5.0 mmol, 0.54 g) was added with a syringe. The reaction mixture was stirred under CO (1 atm) for 3 h at room temperature. The products were diluted with CHCl₃ (2 cm³) and poured into a large amount of methanol (ca. 200 cm³). A white solid formed was collected and dried *in vacuo* at 25 °C to give **1a** (0.5 g, 73%

yield). Analogous reaction with [monomer]/[Pd] = 100 produces **1a** in 58%. δ_{H} (CDCl₃): 0.5–2.2 (8H, m, CH₂), 2.66 [1H, s, CH–C(=CH₂)], 3.52 [1H, s, CH–C(=O)], 5.55 (1H, s, C=CH₂), and 5.74 (1H, s, C=CH₂). δ_{C} (CDCl₃): 21.0, 25.7, 26.0, 28.8 (CH₂), 37.8, 40.8 (CH), 124.7 (=CH₂), 150.4 (C=), and 204.5 (C=O).

Copolymerizations under other conditions (Table 1) were carried out analogously. The reaction using **6**/NaBARF in thf gave **1b**. δ_{H} (CDCl₃): 0.7–2.2 (8H, m, CH₂), 2.56, 2.66, 3.52, 3.68 (2H, m, CH), 5.57, 5.63, and 5.77 (2H, s, C=CH₂). δ_{C} (CDCl₃): 21.1, 25.8, 26.2, 29.1 (CH₂), 38.1, 39.1, 40.7, 42.0 (CH), 124.7 (=CH₂), 150.4 (C=), and 204.2 (C=O).

Copolymerization using **6**/NaBARF was performed in CH₂Cl₂ by using the catalyst prepared in CH₃CN or performed in CH₃CN. **1c**: δ_{H} (CDCl₃): 0.7–2.2 (8H, m, CH₂), 2.66, 2.81, 3.10, 3.66 (2H, m, CH), 5.50, 5.66, 5.71, 5.77, 5.96, 6.03 (2H, m, C=CH₂). δ_{C} (CDCl₃): 21.0, 22.4, 25.7, 29.2, 31.0, 31.5, 34.7 (CH₂), 36.4, 38.3, 41.0, 44.8, 45.0 (CH), 121.4 (=CH₂), 152.1 (C=), and 204.9 (C=O).

Base-promoted epimerization of polyketones

Typically, to a 50 cm³ Schlenk flask containing an *o*-chlorophenol solution (12.5 cm³) of **1a** (1 g) was added an *o*-chlorophenol solution of sodium *o*-chlorophenolate [prepared *in situ* from Na (0.023 g) and *o*-chlorophenol (12.5 cm³)] under Ar. After stirring at 100 °C for 24 h, the reaction mixture was poured into a large amount of methanol. A white solid formed which was collected, washed successively with methanol, water, and methanol, in this order, and dried *in vacuo* to give **11a** (50% yield). ¹³C{¹H} NMR (CDCl₃): δ 25.9, 26.1, 31.7 (CH₂), 40.9, 47.4 (CH), 123.4 (=CH₂), 151.0 (C=), and 203.8 (C=O).

The epimerization of **1b** and **1c** was performed similarly to produce **11b** and **11c**, respectively.

11b (46% yield). δ_{C} (CDCl₃): 25.9, 26.1, 29.4, 31.3, 31.7, 33.0, 34.4, 36.3 (CH₂), 40.3, 41.2, 45.4, 47.1 49.2 (CH), 121.6, 123.8 (=CH₂), 151.1, 151.6, 152.2 (C=), 204.1, and 205.1 (C=O).

11c (63% yield). δ_{C} (CDCl₃): 25.7, 29.3, 31.7, 34.6 (CH₂), 36.3, 45.0 (CH), 121.7 (=CH₂), 151.7, 152.1 (C=), and 205.2 (C=O).

Preparation of *cis*-1-acetyl-2-(2-propenyl)cyclohexane

cis-1-Acetyl-2-(2-propenyl)cyclohexane was prepared according to a similar method reported for the preparation of *cis*-1-acetyl-2-(2-vinyl)cyclohexane.¹⁸

To a 300 cm³ round-bottomed flask containing Mg (1.7 g, 70 mmol), 1,2-dibromoethane (0.03 cm³) and thf (45 cm³) was added a thf solution (30 cm³) of 2-bromopropene (8.4 g, 70 mmol) dropwise under Ar below 40 °C. After cooling at –30 °C, addition of CuBr·Me₂S (0.99 g, 4.8 mmol), Me₂S (7.5 cm³), and then dropwise addition of a thf solution (150 cm³) of 1-(2-propenyl)cyclohexene (6.2 g, 50 mmol) to the reaction mixture was followed by stirring at –30 °C for 40 min and warming to –5 °C. The reaction was quenched by addition of NH₄Cl and HCl, followed by neutralization with NaHCO₃, and extracted with ether. Evaporation of the solvent and distillation gave *cis*-1-acetyl-2-(2-propenyl)cyclohexane (94% yield, 7.6 g) (bp 73 °C, 0.3 mmHg). δ_{H} (CDCl₃): 0.7–1.9 (8H, m, CH₂), 1.61 [3H, s, C(=C)CH₃], 1.94 [3H, s, C(=O)CH₃], 2.17 [1H, m, CHC(=CH₂)], 2.78 [1H, m, CHC(=O)], 4.53 (1H, s, =CH₂), and 4.66 (1H, s, =CH₂). δ_{C} (CDCl₃): 22.4, 24.4, 26.5, 26.5 (CH₂), 22.6 [CH₃ (2-propenyl)], 30.1 [CH₃ (acetyl)], 44.5 [CH–C(=CH₂)], 49.9 [CH–C(=O)], 110.9 (=CH₂), 146.2 (C=), and 210.6 (C=O).

Preparation of *trans*-1-acetyl-2-(2-propenyl)cyclohexane

trans-1-Acetyl-2-(2-propenyl)cyclohexane was prepared according to a reported procedure for the preparation of *trans*-1-acetyl-2-(2-vinyl)cyclohexane.¹⁰

To a 300 cm³ round-bottomed flask containing KOH (0.28 g, 5 mmol) and ethanol (85 cm³) was added *cis*-1-acetyl-2-(2-propenyl)cyclohexane (1.9 g, 11 mmol). After heating the mixture under reflux for 1 h, the reaction mixture was poured

into water (100 cm³) and neutralized with HCl (aq). The organic fraction was extracted with CH₂Cl₂, flushed through alumina, and evaporated to give *trans*-1-acetyl-2-(2-propenyl)cyclohexane in 94% yield (1.8 g). δ_{H} (CDCl₃): 0.9–1.8 (8H, m, CH₂), 1.62 [3H, s, C(=C)CH₃], 2.00 [3H, s, C(=O)CH₃], 2.14 [1H, m, CHC(=CH₂)], 2.46 [1H, m, CHC(=O)], 4.60 (1H, s, =CH₂), and 4.63 (1H, s, =CH₂). δ_{C} (CDCl₃): 25.4, 25.9, 29.2, 31.6 (CH₂), 20.2 [CH₃ (2-propenyl)], 28.3 [CH₃ (acetyl)], 47.3 [CH–C(=CH₂)], 55.3 [CH–C(=O)], 110.4 (=CH₂), 148.2 (C=), and 212.0 (C=O).

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