Rh-catalyzed intermolecular and enantioselective [4 + 2] cycloaddition of 1,3-dienes with dimethyl acetylenedicarboxylate

Takanori Shibata,* Daisuke Fujiwara and Kohei Endo

Received 19th November 2007, Accepted 22nd November 2007
First published as an Advance Article on the web 11th December 2007
DOI: 10.1039/b717914f

A Rh-BINAP complex catalyzed an intermolecular and enantioselective [4 + 2] cycloaddition of 1-monosubstituted, 1,1- or 1,2-disubstituted buta-1,3-dienes with dimethyl acetylenedicarboxylate to give chiral cyclohexa-1,4-dienes.

Introduction

The [4 + 2] cycloaddition of 1,3-dienes with alkenes or alkynes is widely recognized as a powerful synthetic tool for the construction of 6-membered ring systems. In particular, the development of Lewis acid-catalyzed enantioselective Diels–Alder reactions of dienes with dienophiles, possessing heteroatom(s) as coordination site(s), has been one of main topics in organic synthesis, and various efficient chiral Lewis acids have been reported in both intermolecular and intramolecular reactions.[1] On the contrary, transition metal-catalyzed [4 + 2] cycloaddition is another approach. For instance, in 1983, iron complex-catalyzed intermolecular [4 + 2] cycloadditions of 1,3-dienes with alkynes were reported.[2] Rh complexes have also shown themselves to be efficient catalysts.[3] Since 1989, intramolecular [4 + 2] cycloadditions of dienynes have been comprehensively studied using Ni[4] and Rh catalysts.[5] Enantioselective cycloadditions have also been realized using chiral Rh[6] and Ir catalysts.[7] However, an example of intermolecular and enantioselective cycloaddition has been reported using a chiral cobalt catalyst, where a reaction of only a 1-boron functionalized-3-methylbuta-1,3-diene and trimethylsilylacetylene was disclosed.[8]

We disclose here the Rh-catalyzed intermolecular and enantioselective [4 + 2] cycloaddition of substituted buta-1,3-dienes and dimethyl acetylenedicarboxylate (DMAD).[9]

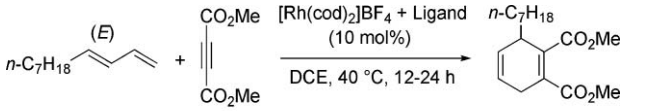
Results and discussion

We chose the reaction of 1-alkyl-substituted (*E*)-buta-1,3-diene **1a** and DMAD as a model reaction, and examined several chiral phosphorus ligands in cationic Rh complexes, which are already known as efficient catalysts in [4 + 2] cycloadditions (Table 1).[3] BINAP derivatives were appropriate ligands, and cyclohexa-1,4-diene **3aa** was obtained in moderate ee (Table 1, entries 1–3). A Rh-BDPP complex gave the product in good yield, yet with lower ee (Table 1, entry 4), and CHIRAPHOS and Me-DUPHOS were unsuitable ligands (Table 1, entries 6 and 7).

When an isolated Rh-BINAP complex was used as the chiral catalyst, the enantioselectivity exceeded 80% (Table 2, entry 1). Under the same reaction conditions, we next examined several alkynes as coupling partners (Table 2, entries 2–6). When 3-hexyne-2,5-dione (**2b**), namely an alkynyl diketone, was used in place of an alkynyl diester, the reaction gave a complex mixture.[10] Product **3ab** could not be completely purified but its ee was comparable with that of DMAD (Table 2, entry 2). In contrast, in the case of 1,4-diphenyl-2-butyne-1,4-dione (**2c**), the corresponding cycloadduct **3ac** was obtained in good yield but the ee was very poor (Table 2, entry 3). [4 + 2] Cycloadducts could not be detected in the reaction with *N*,*N*,*N*′,*N*′-tetramethyl acetylenedicarboxamide (**2d**) under the same reaction conditions (Table 2, entry 4). Alkynyl monoesters did not give the corresponding [4 + 2] cycloadducts at all (Table 2, entries 5 and 6). These results imply that the oxygen atom of the carbonyl moiety is important for the induction of high enantioselectivity, and that two electron-withdrawing groups are indispensable for the cross-coupling of 1,3-dienes and alkynes.[11]

Various 1-substituted buta-1,3-dienes were submitted to the reaction with DMAD (Table 3). (*E*)- and (*Z*)-penta-1,3-diene clearly showed different reactivities (Table 3, entries 1 and 2). That is, it took only 4 h for the complete consumption of DMAD, and the highest ee of 94% was achieved by the opposite enantiomer **3ba**. It is noteworthy that both enantiomers were selectively obtained from the choice of diene geometry using the same chiral catalyst. When a phenyl group was introduced, the ee decreased (Table 3,

Table 1 Screening of chiral ligands in Rh-catalyzed intermolecular [4 + 2] cycloadditions



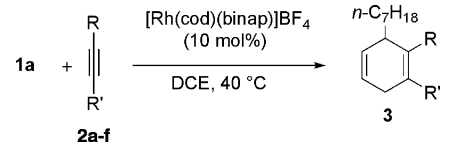
1a 2a 3aa

Entry[a]	Ligand[b]	Yield of **3aa** (%)	ee (%)
1	(*S*)-BINAP	64	67
2	(*S*)-Tol-BINAP	62	69
3	(*S*)-xylyl-BINAP	37	72
4	(*S*)-BDPP	72	45
5	(*S*)-NORPHOS	32	22
6	(*S*)-CHIRAPHOS	<5	9
7	(*S*,*S*)-Me-DUPHOS	Trace	—

[a] Diene **1a**/DMAD = 3 : 1. [b] Tol-BINAP: 2,2′-bis(di-*p*-tolylphosphino)-1,1′-binaphthyl, xylyl-BINAP: 2,2′-bis(di(3,5-xylyl)phosphino)-1,1′-binaphthyl, BDPP: 2,4-bis(diphenylphosphino)pentane, NORPHOS: 2,3-bis(diphenylphosphino)bicyclo[2.2.1]hept-5-ene, CHIRAPHOS: 2,3-bis(diphenylphosphino)butane, Me-DUPHOS: 1,2-bis(2,5-dimethylphospholano)benzene.

Department of Chemistry and Biochemistry, School of Advanced Science and Engineering, Waseda University, 3-4-1, Okubo, Shinjuku, Tokyo, 169-8555, Japan. E-mail: tshibata@waseda.jp; Fax: +81 352868098

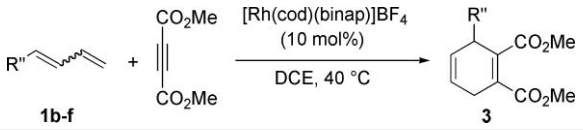
Table 2 Screening of alkynes in Rh-catalyzed intermolecular [4 + 2] cycloadditions



Entry[a]	R	R′	Alkyne	Yield (%)	ee (%)
1	CO_2Me	CO_2Me	**2a**	65 (**3aa**)	82
2	C(O)Me	C(O)Me	**2b**	*ca.* 30 (**3ab**)	78
3	C(O)Ph	C(O)Ph	**2c**	69 (**3ac**)	7
4	$C(O)NMe_2$	$C(O)NMe_2$	**2d**	—	—
5	CO_2Me	Me	**2e**	—	—
6	CO_2Me	Ph	**2f**	—	—

[a] Diene **1a**/alkyne = 3 : 1.

Table 3 Intermolecular [4 + 2] cycloaddition of various 1,3-dienes with DMAD

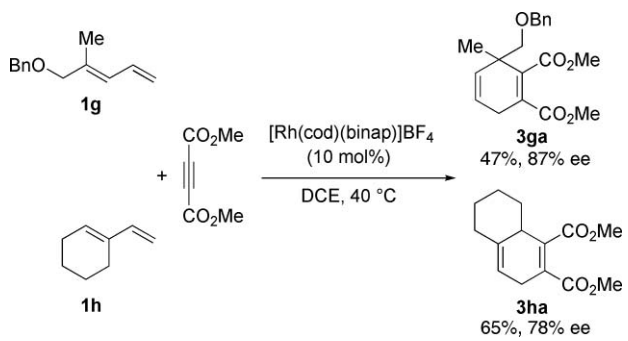


Entry[a]	R″	Diene[b]	Time/h	Yield (%)	ee (%)
1	Me	**1b-*E***	24	51 (**3ba**)	78
2	Me	**1b-*Z*** [c]	4	51 (**3ba**)	−94
3	Ph	**1c**	24	65 (**3ca**)	65
4	$BnO(CH_2)_2$	**1d**	24	54 (**3da**)	89
5	$TBSO(CH_2)_2$	**1e**	24	62 (**3ea**)	84
6	$MeTsN(CH_2)_2$	**1f**	24	66 (**3fa**)	89

[a] Diene **1**/alkyne = 3 : 1. [b] (*E*)-1,3-Dienes were used, except entry 2. [c] (*Z*)-1,3-Diene was used.

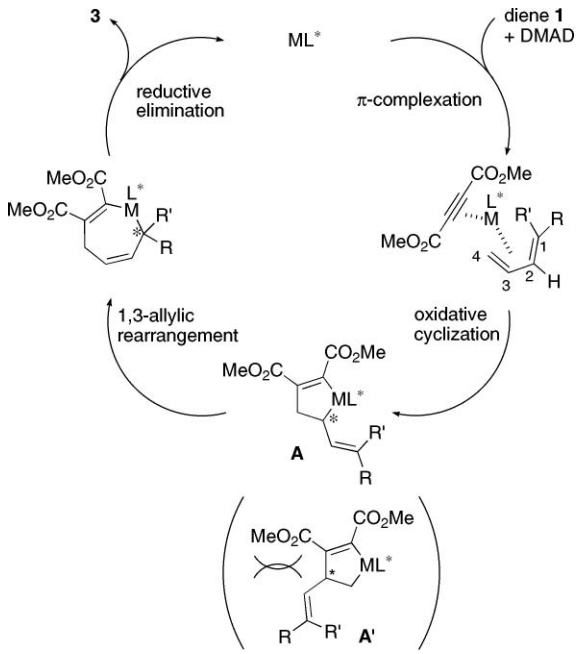
entry 3). Functionalized 1,3-dienes **1d–1f**, with an oxygen or nitrogen atom, were also tolerable, and the corresponding products were obtained in relatively high ee (Table 3, entries 4–6).

We further examined 1,1-disubstituted buta-1,3-diene **1g** under the same reaction conditions and obtained cyclohexa-1,4-diene **3ga**, with a quaternary carbon stereocenter, in good ee (Scheme 1). 1,2-Disubstituted buta-1,3-diene **1h** was also a good substrate, and bicyclic compound **3ha** was obtained.

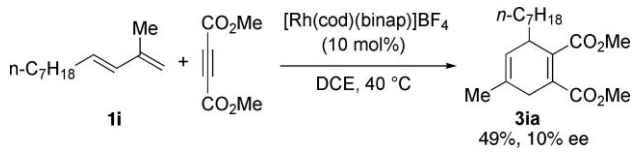


Scheme 1

Scheme 2 shows a proposed mechanism for our intermolecular [4 + 2] cycloadditions. π-Complexation of a diene and an alkyne to the chiral rhodium complex forms the beginning of the reaction. The 3,4-position of a 1-substituted-1,3-diene is an *exo* olefin and less sterically hindered than the 1,2-position. Therefore, oxidative coupling proceeds between the 3,4-position of the diene and DMAD. Metallacyclopentene **A** would therefore be preferentially obtained because of steric repulsion between the methoxycarbonyl and alkenyl groups in **A**′. A following 1,3-allylic rearrangement and reductive elimination then give the cyclohexa-1,4-diene. When a (*Z*)-1,3-diene (R′ is not hydrogen) is used, the 1,3-allylic rearrangement would probably proceed readily because of steric repulsion between R′ and the ligand at the metal center. The enantioselectivity is determined at the oxidative coupling step, and the steric discrimination of a large alkenyl group and a small hydrogen would induce high enantioselectivity. In practice, when hydrogen is replaced by a methyl group at the 3-position, the ee drastically decreases (Scheme 3).



Scheme 2



Scheme 3

Conclusion

We have developed an intermolecular and enantioselective [4 + 2] cycloaddition. The chiral Rh complex-catalyzed reaction of 1-monosubstituted, and 1,1- and 1,2-substituted 1,3-dienes with DMAD gave cyclohexa-1,4-dienes in good to high ee.

Experimental

General

Anhydrous 1,2-dichloroethane (DCE) is commercially available. It was dried over molecular sieves 4A (MS 4A) and de-gassed by argon bubbling before use. All reactions were conducted under an argon atmosphere. IR spectra were recorded with a Horiba FT730 spectrophotometer. NMR spectra were measured with JEOL AL-400 and Lambda500 spectrometers using tetramethylsilane as an internal standard and $CDCl_3$ as a solvent. Mass spectra were measured with a JEOL JMS-SX102A instrument. Optical rotations were measured with a Jasco DIP-1000 polarimeter.

Typical experimental procedure (Table 3)

[Rh(cod)(binap)]BF_4 (9.2 mg, 0.010 mmol) was stirred in CH_2Cl_2 (1.0 mL) at room temperature under an atmosphere of argon. The flask was purged with hydrogen gas and the solution stirred for a further 30 min. After the solvent and hydrogen had been excluded under reduced pressure, argon gas was introduced. DCE (0.1 mL) was added to the flask, followed by a DCE solution (0.4 mL) of 1,3-diene **1** (0.30 mmol) and DMAD (14.2 mg, 0.1 mmol), and the mixture was stirred at 40 °C for 24 h. The solvent was removed under reduced pressure and the resulting crude products were purified by thin-layer chromatography to give pure cycloadduct **3**. The ee was determined by HPLC analysis using a chiral column.

Dimethyl 3-heptylcyclohexa-1,4-diene-1,2-dicarboxylate (3aa)

Colorless oil. IR (CH_2Cl_2): 2927, 1730 and 1257 cm^{-1}; ^1H NMR: δ 0.87 (t, $J = 6.8$ Hz, 3H), 1.21–1.33 (m, 10H), 1.41–1.58 (m, 2H), 2.85–3.06 (m, 2H), 3.19–3.28 (m, 1H), 3.76 (s, 3H), 3.79 (s, 3H), 5.64–5.70 (m, 1H) and 5.72–5.78 (m, 1H); ^{13}C NMR: δ 14.1, 22.6, 25.2, 27.1, 29.1, 29.6, 31.8, 33.9, 37.5, 52.1, 52.1, 122.5, 127.2, 129.9, 139.8, 167.6 and 169.4; HRMS (FAB, positive): $[M + H]^+$ found m/z 295.1911, calc. for $C_{17}H_{27}O_4$ 295.1909; $[\alpha]_D^{22} = 62.04$ (c 0.21 in $CHCl_3$, 82% ee). The ee was determined by HPLC analysis using Daicel Chiralpak AS-H (eluent 1% 2-propanol in hexane, flow rate: 0.5 mL min^{-1}, retention time: 12 min for the major isomer and 14 min for the minor isomer).

3-Heptyl-1,2-bis(phenylcarbonyl)cyclohexa-1,4-diene (3ac)

Colorless oil. IR (CH_2Cl_2): 2927, 1658 and 1265 cm^{-1}; ^1H NMR: δ 0.85 (t, $J = 7.0$ Hz, 3H), 1.12–1.57 (m, 12H), 2.89–2.97 (m, 1H), 3.32–3.39 (m, 1H), 3.58 (s, 1H), 5.88–5.92 (m, 2H) and 7.25–7.52 (m, 10H); ^{13}C NMR: δ 14.1, 22.6, 26.0, 29.0, 29.1, 29.5, 31.7, 34.7, 38.2, 122.7, 128.2, 128.3, 128.5, 129.1, 129.2, 133.0, 133.1, 136.8, 137.6, 138.2, 142.0, 198.4 and 198.5; HRMS (FAB, positive): $[M + H]^+$ found m/z 387.2362, calc. for $C_{27}H_{31}O_2$ 387.2324; $[\alpha]_D^{21} = 36.28$ (c 1.18 in $CHCl_3$, 7% ee). The ee was determined by HPLC analysis using Daicel Chiralpak AS-H (eluent: 10% 2-propanol in hexane, flow rate: 0.5 mL min^{-1}, retention time: 8 min for the minor isomer and 9 min for the major isomer).

Dimethyl 3-methylcyclohexa-1,4-diene-1,2-dicarboxylate (3ba)

Colorless oil. IR (CH_2Cl_2): 2952, 1720 and 1255 cm^{-1}; ^1H NMR: δ 1.15 (d, $J = 3.6$ Hz, 3H), 2.84–3.09 (m, 2H), 3.16–3.27 (m, 1H), 3.76 (s, 3H), 3.80 (s, 3H) and 5.60–5.73 (m, 2H); ^{13}C NMR: δ 20.5, 27.0, 32.4, 52.1, 52.2, 121.3, 128.9, 129.4, 140.2, 167.7 and 169.2; HRMS (FAB, positive): $[M + Na]^+$ found m/z 233.0791, calc. for $C_{11}H_{14}O_4Na$ 233.0790; $[\alpha]_D^{24} = 26.27$ (c 0.87 in $CHCl_3$, 78% ee from (E)-penta-1,3-diene). The ee was determined by HPLC analysis using Daicel Chiralpak AS-H (eluent: 1% 2-propanol in hexane, flow rate: 1.0 mL min^{-1}, retention time: 10 min for the minor isomer and 12 min for the major isomer).

Dimethyl 3-phenylcyclohexa-1,4-diene-1,2-dicarboxylate (3ca)

Colorless oil. IR (CH_2Cl_2): 2951, 1724 and 1259 cm^{-1}; ^1H NMR: δ 3.02–3.05 (m, 1H), 3.20–3.23 (m, 1H), 3.53 (s, 3H), 3.77 (s, 3H), 4.37–4.39 (m, 1H), 5.74–5.82 (m, 2H) and 7.18–7.36 (m, 5H); ^{13}C NMR: δ 27.4, 44.1, 51.9, 52.2, 121.2, 127.1, 127.4, 128.4, 128.6, 131.0, 136.9, 141.4, 168.0 and 168.1; HRMS (FAB, positive): $[M + H]^+$ found m/z 273.1147, calc. for $C_{16}H_{17}O_4$ 273.1127; $[\alpha]_D^{22} = 75.45$ (c 1.00 in $CHCl_3$, 65% ee). The ee was determined by HPLC analysis using Daicel Chiralpak AS-H (eluent: 10% 2-propanol in hexane, flow rate: 0.5 mL min^{-1}, retention time: 16 min for the minor isomer and 18 min for the major isomer).

Dimethyl 3-(2-(benzyloxy)ethyl)cyclohexa-1,4-diene-1, 2-dicarboxylate (3da)

Colorless oil. IR (CH_2Cl_2): 2949, 2862, 1722 and 1257 cm^{-1}; ^1H NMR: δ 1.71–1.80 (m, 1H), 1.93–2.01 (m, 1H), 2.86–3.04 (m, 2H), 3.33–3.42 (m, 1H), 3.51 (d, $J = 6.8$ Hz, 1H), 3.53 (d, $J = 6.8$ Hz, 1H), 3.73 (s, 3H), 3.77 (s, 3H), 4.44 (d, $J = 11.8$ Hz, 1H), 4.50 (d, $J = 11.8$ Hz, 1H), 5.71–5.75 (m, 2H) and 7.24–7.37 (m, 5H); ^{13}C NMR: δ 27.2, 33.9, 34.9, 52.2, 67.2, 72.9, 122.6, 126.9, 127.5, 127.6, 128.3, 130.8, 138.4, 138.7, 167.7 and 168.9 (a signal in the aliphatic region was overlapped); HRMS (FAB, positive): $[M + H]^+$ found m/z 331.1581, calc. for $C_{19}H_{23}O_5$ 331.1545; $[\alpha]_D^{22} = 70.29$ (c 0.90 in $CHCl_3$, 89% ee). The ee was determined by HPLC analysis using Daicel Chiralcel OJ-H (eluent: 10% 2-propanol in hexane, flow rate: 1.0 mL min^{-1}, retention time: 20 min for the major isomer and 24 min for the minor isomer).

Dimethyl 3-(2-(tert-butyldimethylsiloxy)ethyl)cyclohexa-1, 4-diene-1,2-dicarboxylate (3ea)

Colorless oil. IR (CH_2Cl_2): 2952, 1728 and 1257 cm^{-1}; ^1H NMR: δ 0.04 (s, 6H), 0.88 (s, 9H), 1.57–1.66 (m, 2H), 1.83–1.91 (m, 1H), 2.87–3.05 (m, 2H), 3.32–3.35 (m 1H), 3.64–3.76 (m, 1H), 3.79 (s, 3H), 3.80 (s, 3H) and 5.75 (s, 2H); ^{13}C NMR: δ −5.4, −5.3, 18.2, 25.9, 27.2, 34.7, 37.1, 52.1, 60.0, 122.4, 126.9, 130.3, 139.3, 167.6 and 169.0; HRMS (FAB, positive): $[M + H]^+$ found m/z 355.1933, calc. for $C_{18}H_{31}O_5Si$ 355.1941; $[\alpha]_D^{25} = 44.63$ (c 1.20 in $CHCl_3$, 84% ee). The ee was determined by HPLC analysis using Daicel Chiralpak AD-H (eluent: 1% 2-propanol in hexane, flow rate: 0.5 mL min^{-1}, retention time: 8 min for the minor isomer and 9 min for the major isomer).

Dimethyl 3-(2-(*N*-methyl-*N*-tosylamino)ethyl)cyclohexa-1, 4-diene-1,2-dicarboxylate (3fa)

Colorless oil. IR (CH_2Cl_2): 2951, 1726 and 1265 cm^{-1}; ^1H NMR: δ 1.62–1.69 (m, 1H), 1.84–1.94 (m, 1H), 2.43 (s, 3H), 2.69 (s, 3H), 2.74–2.80 (m, 1H), 2.95–2.98 (m 2H), 3.26–3.33 (m, 2H), 3.76 (s, 3H), 3.79 (s, 3H), 5.80 (s, 2H), 7.31 (d, $J = 8.0$ Hz, 2H) and 7.64

(d, J = 8.0 Hz, 2H); ^{13}C NMR: δ 21.4, 27.2, 31.6, 34.6, 34.7, 46.7, 52.2, 123.3, 126.1, 127.3, 129.6, 131.4, 134.5, 137.8, 143.2, 167.4 and 168.6 (a signal in the aliphatic region was overlapped); HRMS (FAB, positive): $[M + H]^+$ found m/z 408.1506, calc. for $C_{20}H_{26}O_6NS$ 408.1481; $[a]_D^{24} = 40.67$ (c 0.70 in $CHCl_3$, 89% ee). The ee was determined by HPLC analysis using Daicel Chiralpak AD-H (eluent: 10% 2-propanol in hexane, flow rate: 1.0 mL min^{-1}, retention time: 14 min for the major isomer and 19 min for the minor isomer).

Dimethyl 3-((benzyloxy)methyl)-3-methylcyclohexa-1,4-diene-1,2-dicarboxylate (3ga)

Colorless oil. IR (CH_2Cl_2): 2952, 1726 and 1261 cm^{-1}; ^{1}H NMR: δ 1.19 (s, 3H), 2.99 (s, 2H), 3.30–3.39 (m, 1H), 3.44–3.52 (m, 1H), 3.74 (s, 6H), 4.44–4.58 (m, 2H), 5.50–5.57 (m, 1H), 5.74–5.84 (m, 1H) and 7.20–7.35 (m, 5H); ^{13}C NMR: δ 15.1, 23.7, 27.0, 41.0, 51.9, 52.1, 73.4, 122.4, 127.4, 127.4, 127.5, 128.2, 128.7, 131.3, 138.5, 166.7 and 169.0; HRMS (FAB, positive): $[M + H]^+$ found m/z 331.1544, calc. for $C_{19}H_{23}O_5$ 331.1546. The ee was determined by HPLC analysis using Daicel Chiralpak AS-H (eluent: 5% 2-propanol in hexane, flow rate: 0.5 mL min^{-1}, retention time: 11 min for the major isomer and 12 min for the minor isomer).

Dimethyl bicyclo[4.4.0]deca-1,4-diene-4,5-dicarboxylate (3ha)

Colorless oil. IR (CH_2Cl_2): 2931, 1728 and 1263 cm^{-1}; ^{1}H NMR: δ 1.16–1.52 (m, 3H), 1.82–2.00 (m, 4H), 2.26–2.29 (m, 1H), 2.85–3.03 (m, 3H), 3.75 (s, 3H), 3.79 (s, 3H) and 5.36 (bs, 1H); ^{13}C NMR: δ 26.5, 27.4, 28.0, 33.2, 35.2, 40.1, 52.1, 52.1, 113.9, 128.7, 137.0, 139.6, 167.7 and 169.5; HRMS (FAB, positive): $[M + H]^+$ found m/z 251.1302, calc. for $C_{14}H_{19}O_4$ 251.1283; $[a]_D^{21} = 12.36$ (c 1.68 in $CHCl_3$, 78% ee). The ee was determined by HPLC analysis using Daicel Chiralpak AS-H (eluent: 10% 2-propanol in hexane, flow rate: 0.5 mL min^{-1}, retention time: 12 min for the minor isomer and 16 min for the major isomer).

Dimethyl 3-heptyl-5-methylcyclohexa-1,4-diene-1,2-dicarboxylate (3ia)

Colorless oil. IR (CH_2Cl_2): 2927, 1728 and 1259 cm^{-1}; ^{1}H NMR: δ 0.81–0.93 (m, 3H), 1.16–1.64 (m, 12H), 1.74 (s, 3H), 2.71–2.99 (m, 2H), 3.16–3.29 (m, 1H), 3.76 (s, 3H), 3.79 (s, 3H) and 5.37 (s, 1H); ^{13}C NMR: δ 14.1, 22.6, 22.6, 25.3, 29.2, 29.7, 31.8, 31.8, 34.1, 38.7, 52.0, 52.1, 121.6, 129.7, 129.9, 140.2, 167.5 and 169.5; HRMS (FAB, positive): $[M + H]^+$ found m/z 309.2066, calc. for $C_{18}H_{29}O_4$ 309.2066; $[a]_D^{22} = -4{,}71$ (c 0.90 in $CHCl_3$, 10% ee). The ee was determined by HPLC analysis using Daicel Chiralpak AS-H (eluent: 5% 2-propanol in hexane, flow rate: 0.5 mL min^{-1}, retention time: 8 min for the major isomer and 12 min for the minor isomer).

Acknowledgements

We thank Prof. P. A. Evans (University of Liverpool, UK) for his helpful advice on the synthesis of N,N,N',N'-tetramethyl acetylenedicarboxamide. We also thank Ai Kawachi (Waseda University, Japan) for her experimental assistance. This research was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

Notes and references

1 Recent selected reviews: (*a*) D. Carmona, M. P. Lamata and L. A. Oro, *Coord. Chem. Rev.*, 2000, **200–202**, 717; (*b*) Y. Hayashi, *Cycloaddition in Organic Synthesis*, ed. S. Kobayashi and K. A. Jørgensen, Wiley-VCH, Weinheim, 2001, pp. 5; (*c*) E. J. Corey, *Angew. Chem., Int. Ed.*, 2002, **41**, 1650.
2 H. T. Dieck and R. Diercks, *Angew. Chem., Int. Ed. Engl.*, 1983, **22**, 778.
3 (*a*) I. Matsuda, M. Shibata, S. Sato and Y. Izumi, *Tetrahedron Lett.*, 1987, **28**, 3361; (*b*) S. J. Paik, S. U. Son and Y. K. Chung, *Org. Lett.*, 1999, **1**, 2045.
4 (*a*) P. A. Wender and T. E. Jenkins, *J. Am. Chem. Soc.*, 1989, **111**, 6432; (*b*) P. A. Wender and T. E. Smith, *J. Org. Chem.*, 1996, **61**, 824; (*c*) K. Kumar and R. S. Jolly, *Tetrahedron Lett.*, 1998, **39**, 3047.
5 (*a*) R. S. Jolly, G. Luedtke, D. Sheehan and T. Livinghouse, *J. Am. Chem. Soc.*, 1990, **112**, 4965; (*b*) P. A. Wender, T. E. Jenkins and S. Suzuki, *J. Am. Chem. Soc.*, 1995, **117**, 1843; (*c*) S. R. Gilbertson and G. S. Hoge, *Tetrahedron Lett.*, 1998, **39**, 2075; (*d*) B. Wang, P. Cao and X. Zhang, *Tetrahedron Lett.*, 2000, **41**, 8041; (*e*) D. J. R. O'Mahony, D. B. Belanger and T. Livinghouse, *Org. Biomol. Chem.*, 2003, **1**, 2038; (*f*) D. Motoda, H. Kinoshita, H. Shinokubo and K. Oshima, *Angew. Chem., Int. Ed.*, 2004, **43**, 1860; (*g*) W. J. Yoo, A. Allen, K. Villeneuve and W. Tam, *Org. Lett.*, 2005, **7**, 5853; (*h*) S. I. Lee, S. Y. Park, J. H. Park, I. G. Jung, S. Y. Choi and Y. K. Chung, *J. Org. Chem.*, 2006, **71**, 91; (*i*) A. Saito, T. Ono, A. Takahashi, T. Taguchi and Y. Hanzawa, *Tetrahedron Lett.*, 2006, **47**, 891; (*j*) F. K. Cheung, A. M. Hayes, D. J. Morris and M. Wills, *Org. Biomol. Chem.*, 2007, **5**, 1093.
6 (*a*) L. McKinstry and T. Livinghouse, *Tetrahedron*, 1994, **50**, 6145; (*b*) D. J. R. O'Mahony, D. B. Belanger and T. Livinghouse, *Synlett*, 1998, 443; (*c*) S. T. Gilbertson, G. S. Hoge and D. G. Genov, *J. Org. Chem.*, 1998, **63**, 10077; (*d*) H. Heath, B. Wolfe, T. Livinghouse and S. K. Bae, *Synthesis*, 2001, 2341; (*e*) K. Aikawa, S. Akutagawa and K. Mikami, *J. Am. Chem. Soc.*, 2006, **128**, 12648.
7 T. Shibata, K. Takasaku, Y. Takesue, N. Hirata and K. Takagi, *Synlett*, 2002, 1681.
8 G. Hilt, W. Hess and K. Harms, *Org. Lett.*, 2006, **8**, 3287.
9 Fairly recently, an enantioselective [4 + 2] cycloaddition using a Rh-chiral diene complex was reported that includes two examples of intermolecular reactions: R. Shintani, Y. Sannohe, T. Tsuji and T. Hayashi, *Angew. Chem., Int. Ed.*, 2007, **46**, 7277.
10 The only identified by-product was a [2 + 2 + 2] cycloadduct of two alkynes and diene **1a**.
11 Actually, the reaction of diene **1a** with ethyl 4,4,4-trifluorobut-2-ynoate gave the [4 + 2] cycloadducts, but as an inseparable mixture of regioisomers.