

Regioselective formation of allylidencyclopropanes from Fischer chromiumcarbene complexes and vinylidencyclopropanes

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(Received September 7, 1993; in revised form November 4, 1993)

Abstract

The reaction of Fischer chromiumcarbene complexes with vinylidencyclopropanes in refluxing benzene proceeds in a highly regioselective fashion to afford allylidencyclopropanes.

Key words: Chromium; Molybdenum; Carbene; Small ring; Nuclear magnetic resonance; Infrared spectroscopy; Mass spectrometry

1. Introduction

The reaction of metal carbene complexes with unsaturated carbon–carbon and carbon–nitrogen bonds appears in important organic processes such as the formation of cyclopropane [1], naphthoquinone [2], indanone [3], α,β -unsaturated enone [4], pyrone [5], β -lactam [6], cyclobutanone [7], furan [8] and cyclopentenone [9], as well as alkene [10] and alkyne [11] polymerization. Recently, limited examples of the coupling reaction of Fischer carbene complexes $[(CO)_5M=C(OEt)Ph]$; $M = Cr, Mo, W$ with allenes were reported to give trimethylenemethane complexes as a major product [12]. However, with the tungstencarbene complex $(CO)_5W=C(H)Ph$, the coupling reaction gave methylenecyclopropanes and methylenecyclopropane complexes [13]. Here we report a novel coupling reaction of Fischer chromiumcarbene complexes **1** with vinylidencyclopropanes **2**, leading to allylidencyclopropanes **3**. The reaction described here is the first

example of a double-bond migration reaction of allenes involving the chromiumcarbene carbon center [14*].

Results and discussion

Table 1 displays a series of examples with three chromiumcarbene complexes **1a–c** and four vinylidencyclopropanes **2a–d** [15] leading to allylidencyclopropanes **3**, which undergo facile Diels–Alder reactions with activated dienophiles [16]. In general, carbene complexes **1a,b** react smoothly with **2** (4 h, 50°C, benzene), while complex **1c** reacts at higher temperature (4 h, 80°C). Without exception, the primary products **3** arise from coupling of the chromium atom with the dimethylmethylene end of the allene. The first two steps in the reaction pathway must be replacement of a coordinated CO ligand with an external allene, followed by metalacyclobutane **4** formation. Noteworthy is that the carbene complexes only react on the less hindered side of the cyclopropane ring ($R^2 = H$, **2b–d**).

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* Reference number with asterisk indicates a note in the list of references.

TABLE 1. Reaction of chromiumcarbene complexes **1** with vinylidencyclopropanes **2**

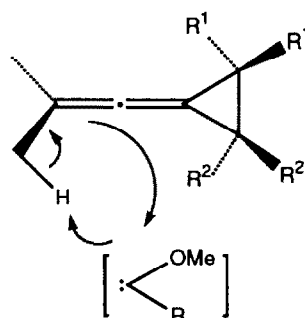
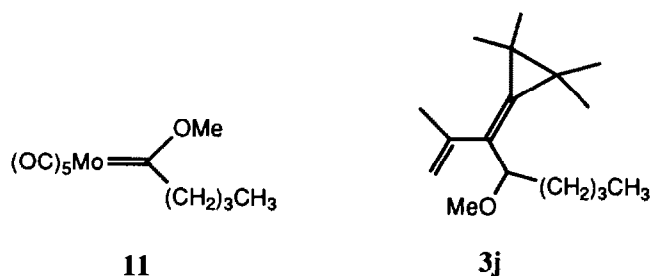
Carbene	Vinylidencyclopropane	Allylidencyclopropane	Yield (%)
$(OC)_5Cr=C(R)OMe$			
(1a) R = Me	(2a)	(3a) R = R ¹ = R ² = Me	63
(1a)		(3b) R = Me, R ¹ = Ph, R ² = H	91
(1a)		(3c) R = Me, R ¹ = cyclohexyl, R ² = H	75
(1b) R = Ph	(2a)	(3d) R = Ph, R ¹ = R ² = Me	81
(1b)	(2b)	(3e) R = R ¹ = Ph, R ² = H	86
(1b)	(2c)	(3f) R = Ph, R ¹ = cyclohexyl, R ² = H	86
(1c) R = <i>o</i> -methoxyphenyl	(2a)	(3g) R = <i>o</i> -methoxyphenyl, R ¹ = R ² = Me	72
(1c)	(2c)	(3h) R = <i>o</i> -methoxyphenyl, R ¹ = cyclohexyl, R ² = H	93
(1b)		(3i) (d.e. ratio = 2:1)	47

The postulated intermediate **4** does not rearrange to trimethylenemethane complexes [12] nor undergo reductive elimination to produce methylenecyclopropanes [13] as reported in the literature. It apparently involves an exocyclic β -hydride elimination to give **5** followed by reductive elimination to give diene **3** (Scheme 1). The reason for the difference is not clear. We assume that the strain present in the cyclopropane moiety and/or the bulky groups (methyl, phenyl or cyclohexyl) on the cyclopropane ring of **4** may force the C–H bond of the methyl group (on the metalocyclobutane ring) to insert into the chromium atom (β -hydride elimination). Thus, β -hydride elimination also occurs on the carbene ligand when R and R² are methyl groups (Scheme 1). The same intermediate **4** (R¹ = R² = R = methyl) can afford α,β -unsaturated ketone **8** as the minor product via **6** and **7** (**3a**/**8** = 5:1). Wienand and Reissig have proposed a similar sequence of β -hy-

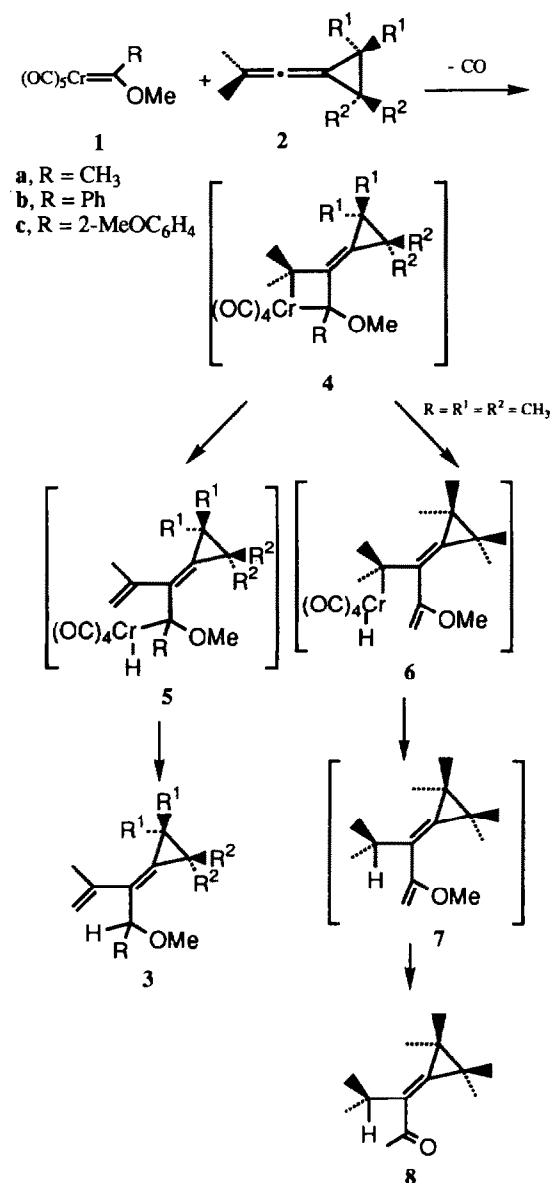
dride elimination of a chromium metallacyclobutane to explain the insertion of the carbene ligand of a Fischer carbene complex into olefinic C–H bonds [17]. In most cases, the carbon–carbon double bond connected to the cyclopropane ring has the (*E*)-configuration (**3b–i**). In some examples, diene rearrangement products (**9** and **10**) are isolated as the minor products (**3g**/**9** = 5:1; **3h**/**10** = 3:2). However, the reaction is not particularly stereoselective as illustrated by the coupling of allene **2d** with the chromiumcarbene complex **1b** to produce **3i** as a mixture of diastereomers in a ratio of 2:1. Moreover, as found for the chromiumcarbene complexes **1**, the reaction of the Fischer molybdenumcarbene complex $(CO)_5Mo=C(OMe)Bu$ (**11**) with allene **2a** follows the same pathway to give **3j** as the major product in 40% yield.

The reaction described here is a formal ene reaction involving Fischer chromiumcarbene complexes (Scheme

2). Further application of the allylidencyclopropanes is underway in our laboratory.



Scheme 2. The 'ene-like' reaction of Fischer chromiumcarbene complexes.



Scheme 1. Proposed reaction pathways for the formation of **3** and **8**.

2. Experimental details

2.1. General

All reactions were run under a nitrogen atmosphere in oven-dried glassware unless otherwise indicated. Anhydrous solvents or reaction mixtures were transferred via an oven-dried syringe or cannula. Benzene was used directly from the commercial source (Merck Chemical Co.). Vinylidenecyclopropanes were synthesized according to the literature procedure [15]. Flash column chromatography was carried out according to the method of Still *et al.* [18] with Merck silica gel (Kieselgel 60, 230–400 mesh) using the indicated solvents. Analytical thin-layer chromatography was performed with Silica gel 60 F₂₅₄ plastic plates of 0.2-mm thickness from Merck. The term 'under nitrogen' implied that the apparatus was evacuated (oil pump) and then filled with nitrogen three times. The term 'short-path distillation (Kugelrohr distillation)' refers to the process in which the entire distillation apparatus (tube closed at one end, held horizontally), with the exception of the collection bulb, was heated slowly in an air bath from 25°C to 150°C under vacuum; the distillate was collected at -78°C. ¹H NMR spectra were obtained with a JEOL-EX 400 (400 MHz) spectrometer. Chemical shift values are expressed in ppm relative to either tetramethylsilane (0.00 ppm) or CHCl₃ (7.26 ppm) as internal standards. ¹³C NMR spectra were recorded using a JEOL-EX 400 (100.4 MHz) spectrometer with CDCl₃ (77.0 ppm) as an internal standard. Infrared (IR) spectra were recorded with a JASCO IR-700 spectrophotometer. Mass spectra were acquired on a JEOL JMS-D 100 spectrometer at an ionization potential of 70 eV and are reported as mass/charge (*m/z*) with percentage relative abundance. High-resolution mass spectra were obtained with an AEI MS-9 double focusing mass spectrometer and a JEOL JMS-HX 110 spectrometer in the Department of Chemistry, Northern Instrument Center, Hsinchu.

2.2. General procedure for coupling of Fischer chromi-umcarbene complexes with vinylidencyclopropanes

Carbene complex **1** and vinylidencyclopropane **2** (1.2–2.0 molar equiv.) in 10 ml of benzene were heated at 50°C (for **1a** or **1b**) or at reflux (for **1c**) under a nitrogen atmosphere in a three-necked round-bottom flask equipped with a water condenser, a thermometer and a glass stopper. After **1** had been consumed completely (monitored by TLC), the reaction mixture was diluted with 100 ml of hexane. The organic solution was washed with water (3 × 100 ml) and brine (3 × 100 ml), and finally dried over magnesium sulfate. The dark green organic layer was evaporated by a rotary evaporator, and the residue was treated by flash chromatography on a silica gel. Elution with hexane/ethyl acetate (50:1) afforded the allylidencyclopropane **3** as the major product.

2.3. Reaction of (OC)₅CrC(OMe)Me (**1a**) with vinylidencyclopropane **2a** to give allylidencyclopropane **3a** and ketone **8**

The crude mixture from the reaction of **1a** (0.12 g, 0.50 mmol) with **2a** (0.10 g, 0.67 mmol) was flash-chromatographed on silica gel, followed by short path distillation to give **3a** (0.061 g, 0.29 mmol, 52%) and **8** (11 mg, 0.06 mmol, 11%).

Compound **3a**: ¹H NMR (400 MHz, CDCl₃) δ: 1.15 (s, 3H); 1.17 (s, 3H); 1.18 (s, 3H); 1.19 (s, 3H); 1.38 (d, *J* = 6.4 Hz, 3H); 1.89 (s, 3H); 3.21 (s, 3H); 4.16 (q, *J* = 6.4 Hz, 1H); 4.94 (s, 1H); 5.31 (s, 1H) ppm. ¹³C NMR (100.4 MHz, CDCl₃) δ: 19.5; 20.9; 21.1; 21.2; 21.7; 21.8; 21.9; 23.2; 56.0; 79.9; 112.1; 129.0; 140.4; 145.7 ppm. IR (CH₂Cl₂) (cm⁻¹): 3092; 2926; 1609; 1455; 1372; 1253; 1205; 1157; 1056; 963; 922. MS (EI) *m/z* of major fragments: 208 (M⁺, 1%); 177 (83); 161 (100); 121 (50); 83 (50). High-resolution MS for C₁₄H₂₄O: Calc.: 208.1827. Found: 208.1832.

Compound **8**: ¹H NMR (400 MHz, CDCl₃) δ: 1.04 (d, *J* = 6.8 Hz, 6H); 1.22 (s, 6H); 1.26 (s, 6H); 2.27 (s, 3H); 2.98 (septet, *J* = 6.8 Hz, 1H) ppm. ¹³C NMR (100.4 MHz, CDCl₃) δ: 19.9; 20.7; 21.7; 22.2; 28.0; 28.7; 136.9; 156.9; 199.7 ppm. IR (CH₂Cl₂) (cm⁻¹): 2991; 2984; 2957; 2870; 1658; 1460; 1423; 1375; 1358; 1257; 1099; 1047; 906; 893. MS (EI) *m/z* of major fragments: 194 (M⁺, 100%); 179 (100); 165 (40); 151 (48); 137 (76); 121 (55); 109 (58); 95 (60); 81 (40).

2.4. Reaction of (OC)₅CrC(OMe)Me (**1a**) with vinylidencyclopropane **2b** to give allylidencyclopropane **3b**

The crude mixture from the reaction of **1a** (0.12 g, 0.50 mmol) with **2b** (0.25 g, 1.0 mmol) was flash-chromatographed on silica gel, followed by short path distillation to give **3b** (0.14 g, 0.46 mmol, 91%). ¹H NMR (400 MHz, CDCl₃) δ: 1.43 (d, *J* = 6.8 Hz, 3H); 1.91 (s,

3H); 3.23 (AB, q, 2H); 3.24 (s, 3H); 4.37 (q, *J* = 6.8 Hz, 1H); 4.41 (s, 1H); 5.43 (s, 1H); 7.14–7.31 (m, 10H) ppm. ¹³C NMR (100.4 MHz, CDCl₃) δ: 14.6; 20.3; 56.0; 56.8; 58.6; 73.4; 106.7; 125.7; 125.8; 127.8; 128.2; 128.4; 130.0; 132.4; 136.3; 142.1; 148.7; 158.6 ppm. IR (CH₂Cl₂) (cm⁻¹): 3056; 3032; 2972; 2932; 1687; 1600; 1492; 1445; 1276; 1089; 908; 718. MS (EI) *m/z* of major fragments: 304 (M⁺, 8%); 225 (10); 77 (10); 28 (100). High-resolution MS for C₂₂H₂₄O: Calc.: 304.1827. Found: 304.1832.

2.5. Reaction of (OC)₅CrC(OMe)Me (**1a**) with vinylidencyclopropane **2c** to give allylidencyclopropane **3c**

The crude mixture from the reaction of **1a** (0.12 g, 0.50 mmol) with **2c** (0.16 g, 1.0 mmol) was flash-chromatographed on silica gel, followed by short path distillation to give **3c** (0.082 g, 0.38 mmol, 75%). ¹H NMR (400 MHz, CDCl₃) δ: 0.90 (m, 2H); 1.03 (m, 2H); 1.26 (m, 2H); 1.37 (d, *J* = 6.8 Hz, 3H); 1.42 (m, 2H); 1.73 (m, 4H); 1.92 (s, 3H); 3.19 (s, 3H); 4.29 (q, *J* = 6.8 Hz, 1H); 4.94 (s, 1H); 5.20 (s, 1H) ppm. ¹³C NMR (100.4 MHz, CDCl₃) δ: 15.1; 20.6; 23.3; 24.4; 25.1; 26.2; 34.9; 35.0; 55.5; 79.2; 111.5; 128.9; 135.4; 141.1 ppm. IR (CH₂Cl₂) (cm⁻¹): 3051; 2984; 2930; 2854; 1446; 1265; 1147; 1095. MS (EI) *m/z* of major fragments: 220 (M⁺, 8%); 205 (16); 291 (66); 113 (75); 59 (100). High-resolution MS for C₁₅H₂₄O: Calc.: 220.1827. Found: 220.1836.

2.6. Reaction of (OC)₅CrC(OMe)Ph (**1b**) with vinylidencyclopropane **2a** to give allylidencyclopropane **3d**

The crude mixture from the reaction of **1b** (0.17 g, 0.54 mmol) with **2a** (0.16 g, 1.07 mmol) was flash-chromatographed on silica gel, followed by short path distillation to give **3d** (0.12 g, 0.43 mmol, 81%). ¹H NMR (400 MHz, CDCl₃) δ: 1.09 (s, 3H); 1.13 (s, 3H); 1.18 (s, 3H); 1.19 (s, 3H); 1.79 (s, 3H); 3.32 (s, 3H); 4.77 (s, 1H); 4.96 (s, 1H); 5.02 (s, 1H); 7.19–7.29 (m, 5H) ppm. ¹³C NMR (100.4 MHz, CDCl₃) δ: 19.7; 20.8; 21.1; 21.9; 22.5; 23.0; 30.8; 56.5; 85.1; 114.1; 125.8; 126.5; 127.3; 127.8; 142.2; 148.7 ppm. IR (CH₂Cl₂) (cm⁻¹): 3030; 2938; 2872; 1610; 1492; 1450; 1373; 1188; 1096; 982; 962. MS (EI) *m/z* of major fragments: 270 (M⁺, 2%); 255 (4); 237 (68); 222 (32); 121 (32); 91 (39); 77 (32); 73 (100). High-resolution MS for C₁₉H₂₆O: Calc.: 270.1984. Found: 270.1993.

2.7. Reaction of (OC)₅CrC(OMe)Ph (**1b**) with vinylidencyclopropane **2b** to give allylidencyclopropane **3e**

The crude mixture from the reaction of **1b** (0.16 g, 0.50 mmol) with **2b** (0.25 g, 1.0 mmol) was flash-chromatographed on silica gel, followed by short path distillation to give **3e** (0.16 g, 0.43 mmol, 86%). ¹H NMR (400 MHz, CDCl₃) δ: 1.70 (s, 3H); 1.82 (d, *J* = 9.8 Hz, 1H); 1.90 (d, *J* = 9.8 Hz, 1H); 3.41 (s, 3H); 4.93 (s, 1H); 5.03 (s, 1H); 5.27 (s, 1H); 7.18–7.39 (m, 15H) ppm. ¹³C

NMR (100.4 MHz, CDCl_3) δ : 22.9; 23.1; 33.5; 56.9; 85.2; 115.3; 125.8; 126.1; 126.2; 126.5; 127.1; 127.8; 128.0; 128.1; 128.2; 130.9; 133.4; 141.4; 141.6; 143.8 ppm. IR (CH_2Cl_2) (cm^{-1}): 3034; 2978; 2930; 1602; 1493; 1446; 1278; 1252; 1189; 1092; 1014; 973. MS (EI) m/z of major fragments: 366 (M^+ , 1%); 334 (2); 285 (4); 121 (5); 105 (4); 42 (57); 38 (100). High-resolution MS for $\text{C}_{27}\text{H}_{26}\text{O}$: Calc.: 366.1983. Found: 366.1960.

2.8. Reaction of $(\text{OC})_5\text{CrC}(\text{OMe})\text{Ph}$ (**1b**) with vinylidenecyclopropane **2c** to give allylidencyclopropane **3f**

The crude mixture from the reaction of **1b** (0.16 g, 0.5 mmol) with **2c** (0.16 g, 1.0 mmol) was flash-chromatographed on silica gel, followed by short path distillation to give **3f** (0.12 g, 0.43 mmol, 86%). ^1H NMR (400 MHz, CDCl_3) δ : 0.83 (d, $J = 8.8$ Hz, 1H); 0.92 (d, $J = 8.8$ Hz, 1H); 1.13 (m, 2H); 1.31 (m, 2H); 1.47 (m, 2H); 1.77 (m, 4H); 1.91 (s, 3H); 3.40 (s, 3H); 4.89 (s, 1H); 5.08 (s, 1H); 5.25 (s, 1H); 7.21–7.35 (m, 5H) ppm. ^{13}C NMR (100.4 MHz, CDCl_3) δ : 15.6; 23.1; 25.0; 25.7; 26.1; 35.0; 56.5; 85.1; 113.2; 126.1; 127.9; 138.8; 140.2; 142.0 ppm. IR (CH_2Cl_2) (cm^{-1}): 3036; 2928; 2852; 1612; 1492; 1446; 1279; 1090; 962; 921. MS (EI) m/z of major fragments: 282 (M^+ , 3%); 250 (8); 121 (15); 43 (32); 28 (100). High-resolution MS for $\text{C}_{20}\text{H}_{26}\text{O}$: Calc.: 282.1983. Found: 282.1978.

2.9. Reaction of $(\text{OC})_5\text{CrC}(\text{OMe})\text{C}_6\text{H}_4\text{OMe-o}$ (**1c**) with vinylidenecyclopropane **2a** to give allylidencyclopropanes **3g** and diene **9**

The crude mixture from the reaction of **1c** (0.086 g, 0.25 mmol) with **2a** (0.075 g, 0.5 mmol) was flash-chromatographed on silica gel, followed by short path distillation to give **3g** (0.045 g, 0.15 mmol, 60%) and **9** (0.009 g, 0.03 mmol, 12%).

Compound **3g**: ^1H NMR (400 MHz, CDCl_3) δ : 0.81 (s, 3H); 1.07 (s, 3H); 1.18 (s, 3H); 1.19 (s, 3H); 1.93 (s, 3H); 3.36 (s, 3H); 3.81 (s, 3H); 4.87 (s, 1H); 4.97 (s, 1H); 5.42 (s, 1H); 6.86 (d, $J = 8.3$ Hz, 1H); 6.94 (t, $J = 8.3$ Hz, 1H); 7.23 (t, $J = 7.8$ Hz, 1H); 7.38 (d, $J = 7.8$ Hz, 1H) ppm. ^{13}C NMR (100.4 MHz, CDCl_3) δ : 20.5; 20.8; 20.9; 21.5; 21.7; 21.8; 23.1; 55.2; 57.3; 78.2; 110.2; 111.5; 120.2; 127.9; 128.1; 128.4; 129.7; 142.9; 145.6; 157.4 ppm. IR (CH_2Cl_2) (cm^{-1}): 3076; 3038; 2984; 2930; 1629; 1598; 1488; 1460; 1440; 1422; 1371; 1279; 1243; 1160; 1107; 1049; 1029; 977; 931. MS (EI) m/z of major fragments: 300 (M^+ , 11%); 269 (100); 254 (64); 73 (90). High-resolution MS for $\text{C}_{20}\text{H}_{28}\text{O}_2$: Calc.: 300.2089. Found: 300.2092.

Compound **9**: ^1H NMR (400 MHz, CDCl_3) δ : 0.97 (s, 6H); 1.08 (s, 1H); 1.17 (s, 6H); 1.65 (s, 3H); 3.27 (s, 3H); 3.79 (s, 3H); 4.34 (s, 1H); 4.46 (s, 1H); 6.85 (d, $J = 7.8$ Hz, 1H); 6.90 (t, $J = 7.3$ Hz, 1H); 7.08 (dd, $J = 7.3, 2.0$ Hz, 1H); 7.26 (m, 1H) ppm. ^{13}C NMR

(100.4 MHz, CDCl_3) δ : 18.0; 22.3; 22.4; 23.2; 33.0; 54.9; 55.0; 110.0; 112.3; 119.7; 121.0; 124.9; 128.9; 131.4; 144.1; 149.7; 157.7 ppm. IR (CH_2Cl_2) (cm^{-1}): 3053; 2941; 1726; 1599; 1464; 1257; 1249; 1118; 850. MS (EI) m/z of major fragments: 300 (M^+ , 7%); 243 (10); 135 (100); 97 (28). High-resolution MS for $\text{C}_{20}\text{H}_{28}\text{O}_2$: Calc.: 300.2089. Found: 300.2091.

2.10. Reaction of $(\text{OC})_5\text{CrC}(\text{OMe})\text{C}_6\text{H}_4\text{OMe-o}$ (**1c**) with vinylidenecyclopropane **2c** to give allylidencyclopropanes **3h** and diene **10**

The crude mixture from the reaction of **1c** (0.10 g, 0.31 mmol) with **2c** (0.10 g, 0.62 mmol) was flash-chromatographed on silica gel, followed by short path distillation to give **3h** (0.055 g, 0.17 mmol, 56%) and **10** (0.037 g, 0.12 mmol, 37%).

Compound **3h**: ^1H NMR (400 MHz, CDCl_3) δ : 0.54 (d, $J = 9.3$ Hz, 1H); 0.79 (d, $J = 9.3$ Hz, 1H); 0.94–1.70 (m, 10H); 1.93 (s, 3H); 3.36 (s, 3H); 4.78 (s, 3H); 4.90 (s, 1H); 5.07 (s, 1H); 5.53 (s, 1H); 6.83 (d, $J = 8.3$ Hz, 1H); 6.92 (t, $J = 7.3$ Hz, 1H); 7.22 (t, $J = 7.8$ Hz, 1H); 7.38 (d, $J = 7.3$ Hz, 1H) ppm. ^{13}C NMR (100.4 MHz, CDCl_3) δ : 16.2; 23.1; 23.5; 25.1; 26.2; 34.9; 35.0; 55.4; 57.0; 78.3; 110.3; 111.2; 120.2; 127.3; 127.8; 128.1; 129.7; 136.8; 142.3; 157.2 ppm. IR (CH_2Cl_2) (cm^{-1}): 3078; 2930; 1658; 1601; 1489; 1462; 1444; 1243; 1185; 1080; 1030. MS (EI) m/z of major fragments: 312 (M^+ , 15%); 290 (48); 285 (15); 239 (20); 191 (65); 150 (100); 135 (37). High-resolution MS for $\text{C}_{21}\text{H}_{28}\text{O}_2$: Calc.: 312.2089. Found: 312.2091.

Compound **10**: ^1H NMR (400 MHz, CDCl_3) δ : 0.29 (t, $J = 4.4$ Hz, 1H); 0.59 (dd, $J = 8.3, 4.4$ Hz, 1H); 1.24 (m, 2H); 1.42–1.49 (m, 7H); 1.66 (s, 3H); 1.67 (m, 2H); 3.31 (s, 3H); 3.80 (s, 3H); 4.31 (s, 1H); 4.52 (s, 1H); 6.83 (d, $J = 8.3$ Hz, 1H); 6.88 (t, $J = 8.3$ Hz, 1H); 7.10 (d, $J = 7.8$ Hz, 1H); 7.26 (d, $J = 7.8$ Hz, 1H) ppm. ^{13}C NMR (100.4 MHz, CDCl_3) δ : 18.3; 22.8; 23.4; 24.9; 25.5; 26.2; 26.6; 30.7; 37.8; 55.2; 55.5; 110.2; 114.2; 119.8; 122.8; 125.3; 128.3; 129.1; 131.8; 144.5; 157.9 ppm. IR (CH_2Cl_2) (cm^{-1}): 3078; 2928; 2850; 1636; 1597; 1518; 1488; 1461; 1447; 1250; 1120; 1096; 1029; 960. MS (EI) m/z of major fragments: 312 (M^+ , 13%); 281 (13); 228 (100); 182 (13); 135 (21). High-resolution MS for $\text{C}_{21}\text{H}_{28}\text{O}_2$: Calc.: 312.2089. Found: 312.2097.

2.11. Reaction of $(\text{OC})_5\text{CrC}(\text{OMe})\text{Ph}$ (**1b**) with vinylidenecyclopropane **2d** to give allylidencyclopropane **3i**

The crude mixture from the reaction of **1b** (0.16 g, 0.5 mmol) with **2d** (0.17 g, 1.0 mmol) was flash-chromatographed on silica gel, followed by short path distillation to give **3i** (0.068 g, 0.24 mmol, 47%) as a mixture of two diastereomers in a ratio of 2:1. The diastereomeric ratio value of two isomers was determined directly on the crude product by integration of the

appropriate, characteristic ^1H NMR signals. ^1H NMR (400 MHz, CDCl_3) δ : 1.02 (dd, $J = 9.8, 9.3$ Hz, 1H); 1.22 (dd, $J = 9.8, 4.9$ Hz, 1H); 1.83 (s, 3H); 2.77 (dd, $J = 9.3, 4.9$ Hz, 1H); 3.54 (s, 3H); 4.91 (s, 1H); 5.19 (s, 1H); 5.35 (s, 1H); 7.07–7.46 (m, 10H) ppm. IR (CH_2Cl_2) (cm^{-1}): 3030; 2934; 1604; 1493; 1449; 1376; 1093; 1030; 921. MS (EI) m/z of major fragments: 290 (M^+ , 20%); 275 (3); 259 (47); 199 (40); 124 (80); 121 (100); 91 (85). High-resolution MS for $\text{C}_{21}\text{H}_{22}\text{O}$: Calc.: 290.1670. Found: 290.1647.

2.12. Reaction of $(\text{OC})_5\text{MoC}(\text{OMe})\text{Bu}$ (11) with vinylidenecyclopropane 2a to give allylidene cyclopropane 3j

The crude mixture from the reaction of 11 (0.10 g, 0.30 mmol) with 2a (0.10 g, 0.62 mmol) was flash-chromatographed on silica gel, followed by short path distillation to give 3j (0.03 g, 0.12 mmol, 40%). ^1H NMR (400 MHz, CDCl_3) δ : 0.87 (t, $J = 7.3$ Hz, 3H); 1.15 (s, 3H); 1.17 (s, 6H); 1.19 (s, 3H); 1.27–1.32 (m, 4H); 1.66 (m, 1H); 1.75 (m, 1H); 1.88 (s, 3H); 3.21 (s, 3H); 3.90 (t, $J = 7.0$ Hz, 1H); 4.92 (s, 1H); 5.31 (s, 1H) ppm. ^{13}C NMR (100.4 MHz, CDCl_3) δ : 14.0; 19.4; 21.0; 21.4; 21.7; 22.0; 22.7; 23.4; 29.0; 34.7; 56.0; 85.1; 112.4; 128.0; 140.7; 146.5 ppm. IR (CH_2Cl_2) (cm^{-1}): 3070; 2993; 2934; 2866; 1601; 1458; 1373; 1275; 1257; 1093; 912. MS (EI) m/z of major fragments: 250 (M^+ , 2%); 235 (16); 219 (100); 175 (40); 161 (53).

Acknowledgments

We thank the National Science Council (82-0208-M-003-006) of the Republic of China for financial support.

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