A Direct Synthesis of Alkenyl Alkylidene Bicyclo[3.1.0]hexane Derivatives via Ruthenium(II)-Catalysed Bicyclisation of Allenynes

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Dedicated to the late Professor Yoshihiko Ito for his outstanding contribution to catalysis and synthesis

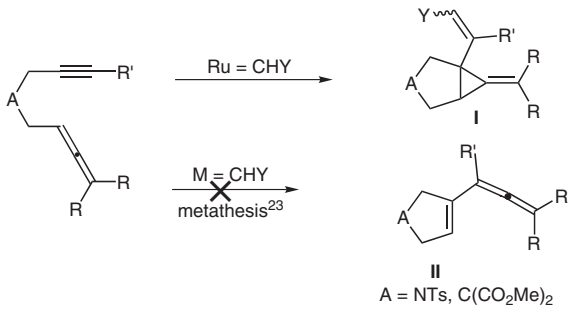
Abstract: The reaction of allenynes with $N_2CHSiMe_3$ in the presence of RuCl(cod)Cp* catalyst at room temperature constitutes a selective, general route to alkylidenebicyclo[3.1.0]hexanes having an adjacent *Z*-CH=CHSiMe$_3$ group. The reaction shows that the RuCl(Cp*) moiety favours reductive elimination of a metallacyclobutane intermediate and not the enyne metathesis process.

Keywords: allenynes, C–C coupling cyclisation, homogeneous catalysis, ruthenium

Methylenecyclopropanes play a key role in the construction of 5-membered cycles, via initial metal-catalysed opening of the cyclopropane moiety, thus offering a three-carbon component for cycloaddition with unsaturated molecules.[1,2] Initial works have shown that palladium(0)- and nickel(0)-catalysed activation of methylenecyclopropanes leads to the formation of alkylidenecyclopentanes[3,4] or 5-membered heterocycles.[5,6] Methylenecyclopropanes are now offering applications for hydrocarbonation,[7,8] cobalt-catalysed carbonylation[9] and hydroamination.[10,11] There is a renaissance of alkylidenecyclopropanes in synthesis via their skeleton rearrangements to build small cycles,[12] the formation of alkylidene cyclopentanones via nickel(0)-catalysed cycloaddition with alkenyl metal carbenes,[13] and especially their rearrangement into cyclobutenes catalysed by palladium(II)[14] or $PtCl_2$.[15]

The above recent applications motivate the search for easy functional methylenecyclopropane syntheses. Simple methylenecyclopropanes can be prepared by two main routes.[1] The first one involves the cyclopropane ring formation by carbene addition to unsaturated compounds such as allenes and olefins,[16] or by elimination reactions.[17] The second route involves the synthesis of methylenecyclopropanes from cyclopropane substrates, with subsequent formation of a double bond,[18] including double bond shift reactions[19] and Wittig olefination.[20]

Recently, the selective transformation of enynes into alkenylbicyclo[3.1.0]hexane derivatives has been promoted by ruthenium(II) catalyst on reaction with diazoalkanes.[21,22] We then reasoned that such a reaction could offer an entry to bicyclic alkylidenecyclopropanes **I** by activation of allenynes on the condition that the possible enyne metathesis product (**II**) formation[23] could be inhibited (Scheme 1). However, the catalytic transformation of allenynes raises questions about the regioselectivity of initial interaction of allene C=C bond with a carbene Ru=C bond that can not be predicted. The reaction of allenes with electrophilic alkenes promoted by RuCl(cod)Cp complex has shown that the internal double bond is involved in the oxidative coupling,[24] whereas RuCl(cod)Cp*, with sterically hindered allenylboronates, promoted the [2+2] cycloaddition of only the terminal allene C=CH$_2$ bond.[25]



Scheme 1

Herein we report that the RuCl(cod)Cp* catalyst precursor in the presence of $N_2CHSiMe_3$ does not promote the coupling with terminal allene bond, but the regioselective transformation of allenynes into the new alkylidenebicyclo[3.1.0]hexane derivatives of type **I** containing an adjacent *Z*-alkenyl group. From the synthetic point of view, the products **I** are of high interest due to the reactivity of the cyclopropane ring which is expected to be enhanced by simultaneous substitution with alkylidene and alkenyl groups.

The reaction of allenyne **1a** with $N_2CHSiMe_3$ (1.1 equiv) in Et_2O with RuCl(cod)Cp* (8 mol%) for one hour at room temperature led to 85% conversion of **1a** and to the formation of **2a**, isolated in 52% yield (Table 1). The allenynes **1b–d**, bearing a nitrogen linkage with $N_2CHSiMe_3$ (1.1 equiv, 2 M in Et_2O), reacted with RuCl(cod)Cp* (8 mol%) in Et_2O at room temperature and led to products **2b–d**, isolated after purification by silica gel chromatography (Table 1).[26]

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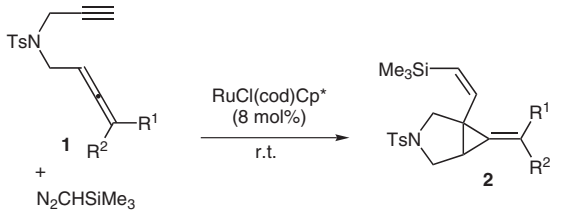
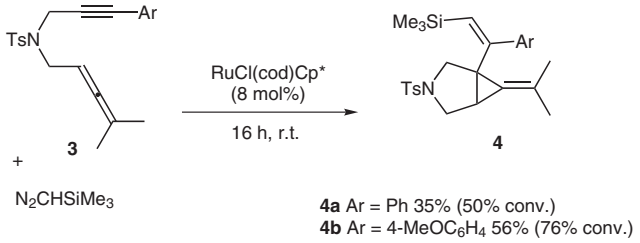
Table 1



Entry	R^1	R^2	Time (h)	Conv. (%)	Yield (%)
a	Me	Me	1	85	52
b	Me	Et	19	100	71
c	*i*-Pr	*i*-Pr	10	100	85
d	-$(CH_2)_5$-		6	95	40

Whereas **1a** reached 85% conversion after one hour, the conversion of **1b** and **1c** containing bulkier R^1 and R^2 groups was complete only after 19 hours and 10 hours and the corresponding products **2b** (two isomers, 55:45) and **2c** were obtained in 71% and 85% isolated yields, respectively. However, **1d** reached 95% conversion after six hours, though **2d** was isolated in only 40% yield.[26] For all derivatives **2a**–**d** the *Z*-configuration of the alkenyl group was observed. Thus, this reaction shows high regioselectivity of the interaction of the allene internal C=C bond with the catalyst.

The allenynes **3** containing the dimethylallene function and an aryl group at the alkyne C(1) [**3a** (Ar = Ph), **3b** (Ar = *p*-$MeOC_6H_4$)] reacted as previously for 16 hours at room temperature.[26] The alkenyl alkylidene bicyclo[3.1.0]hexane derivatives were formed in modest conversion and yield for **4a** (35%) (Scheme 2). At room temperature **3b** gave a convenient conversion (76%) and isolated yield (56%) of **4b**.

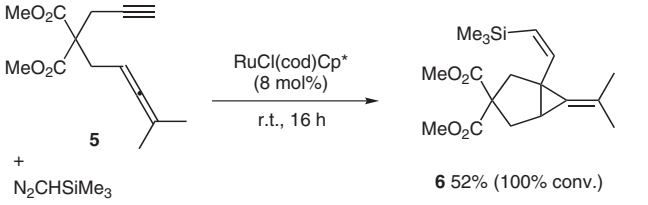


Scheme 2

Under similar conditions the allenyne **5** with a carbon bridge between the allene and yne functions led to compound **6** in 52% yield (Scheme 3).[26]

On the basis of the above results, a catalytic cycle can be proposed (Scheme 4).

(a) The generation of the [Cp*(Cl)Ru=$CHSiMe_3$] moiety and its [2+2] cycloaddition with the alkyne bond is expected to afford the intermediate **A**. Simple models show that steric interactions allow this [2+2] addition to take place only with *anti* position of the Cp* and $SiMe_3$ groups.

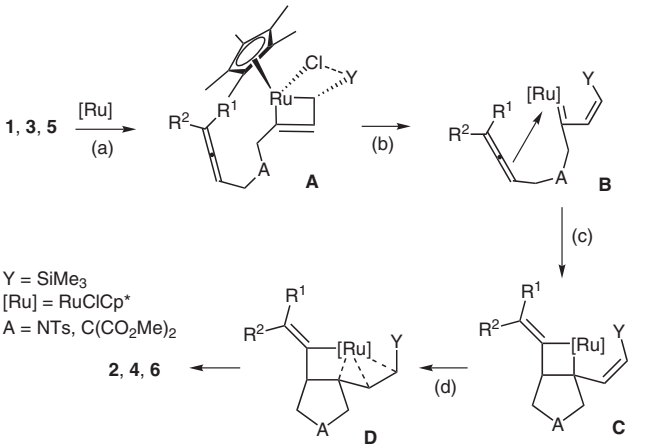


Scheme 3

(b) The opening of the ruthenacyclobutene **A** can then afford intermediate **B**. The **A** → **B** transformation leads to the *Z* configuration of the alkenyl group. This stereoselectivity may result from intramolecular Cl–$SiMe_3$ bond interaction in the intermediate **A**.

(c) The trapping of the allene internal C=C bond by the Ru=C bond and [2+2] addition is expected to lead to the metallacyclobutane **C**.

(d) The last step leads to the cyclopropane formation thus affording the alkylidene bicyclo[3.1.0]hexane derivative. Indeed, DFT calculations show that the [Ru(Cl)(Cp*)] unit, inside a metallacyclobutane moiety, with an adjacent vinyl group, favours reductive elimination rather than a metathesis process (retro-[2+2] addition),[22] by the initial coordination of the vinyl group leading to the alkyl allyl ruthenium intermediate of type **D**.



Scheme 4

The above results show a novel access to alkylidenebicyclo[3.1.0]hexanes with a neighbouring *Z*-alkenyl group. It appears to be the most direct route to bicyclic compounds containing a reactive alkylidenecyclopropane unit. The formed molecules offer potential for catalytic access to 5- to 8-membered cycles enhanced by the simultaneous presence of a vinyl cyclopropyl unit.[27] The described reaction also demonstrates that the Cp*(Cl)Ru moiety, inside a metallacyclobutane intermediate, resulting from Ru=C and C=C bond addition, favours reductive elimination and inhibits retro-[2+2] addition such as an alkene metathesis process. This phenomenon deserves to be explored and is expected to give a new life to ruthenium carbenes in catalysis.

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(26) Low isolated product yields were obtained only when the reaction was performed with a small substrate quantity (0.1 mmol) due to inefficient extraction techniques for small quantities; for example, for **1c** 40% and 85% isolated yields were obtained from 0.1 mmol and 0.3 mmol, respectively.
Typical Procedure for the Catalytic Reaction: In a Schlenk tube under an inert atmosphere, to a solution of the allenyne in degassed Et_2O (1.5 mL) was added the (trimethylsilyl)diazomethane solution (2.0 M; 1.1 equiv) in Et_2O. Next, the precatalyst RuCl(cod)Cp* (8 mol%) was introduced. The mixture was stirred at r.t. Reaction completion was monitored using TLC or ^{1}H NMR techniques. The products were obtained after purification by silica gel chromatography with an Et_2O–pentane eluting mixture.
Data for compounds 2a–d, 4a,b, and 6:
Compound **2a**: ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 0.12 (s, 9 H, $SiMe_3$), 1.68 (s, 3 H, Me), 1.69 (s, 3 H, Me), 1.95 (m, 1 H, CH), 2.45 (s, 3 H, Me), 3.26 (dd, *J* = 4.1, 9.4 Hz, 1 H, NCH_2), 3.27 (d, *J* = 9.0 Hz, 1 H, NCH_2), 3.64 (d, *J* = 9.4 Hz, 1 H, NCH_2), 3.80 (d, *J* = 9.1 Hz, 1 H, NCH_2), 5.49 (d, *J* = 15.6 Hz, 1 H, =CHSiMe$_3$), 6.02 (d, *J* = 15.6 Hz, 1 H, CH=), 7.32 (d, *J* = 7.8 Hz, 2 H, Ph), 7.67 (d, *J* = 8.2 Hz, 2 H, Ph). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 145.1, 143.3, 133.7, 129.5, 129.4, 127.6, 127.5, 122.3, 53.1, 50.0, 35.9, 29.9, 22.2, 21.6, 21.5, 0.8. HRMS: *m*/*z* calcd for $C_{20}H_{29}NO_2SiS$: 375.1688; found: 375.1684.
Compound **2b** (two isomers, 55:45): Major isomer: ^{1}H NMR (300.08 MHz, $CDCl_3$): δ = 0.11 (s, 9 H, $SiMe_3$), 0.97 (t, *J* = 7.7 Hz, 3 H, Me), 1.70 (s, 3 H, Me), 1.91 (m, 1 H, CH), 1.99 (m, 2 H, CH_2), 2.45 (s, 3 H, Me), 3.24 (m, 1 H, NCH_2), 3.28 (d, *J* = 9.0 Hz, 1 H, NCH_2), 3.65 (d, *J* = 9.2 Hz, 1 H, NCH_2), 3.75 (d, *J* = 9.0 Hz, 1 H, NCH_2), 5.47 (d, *J* = 15.6 Hz, 1 H, =CHSiMe$_3$), 6.01 (d, *J* = 15.6 Hz, 1 H, CH=), 7.32 (d, *J* = 7.9 Hz, 2 H, Ph), 7.68 (d, *J* = 8.2 Hz, 2 H, Ph). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 145.4, 143.3, 133.8, 133.0, 129.5, 129.2, 127.6, 121.2, 53.1, 50.5, 36.3, 30.5, 29.2, 21.5, 20.1, 12.0, 0.8. Minor isomer: ^{1}H NMR (300.08 MHz, $CDCl_3$): δ = 0.13 (s, 9 H, $SiMe_3$), 1.02 (t, *J* = 7.4 Hz, 3 H, Me), 1.62 (s, 3 H, Me), 1.99 (m, 2 H, CH_2), 2.01 (m, 1 H, CH), 2.45 (s, 3 H, Me), 3.24 (m, 1 H, NCH_2), 3.28 (d, *J* = 9.0 Hz, 1 H, NCH_2), 3.63 (d, *J* = 9.1 Hz, 1 H, NCH_2), 3.81 (d, *J* = 8.9 Hz, 1 H, NCH_2), 5.49 (d, *J* = 15.6 Hz, 1 H, =CHSiMe$_3$), 6.00 (d, *J* = 15.5 Hz, 1 H, CH=), 7.32 (d, *J* = 7.9 Hz, 2 H, Ph), 7.68 (d, *J* = 8.2 Hz, 2 H, Ph). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 145.8, 143.3, 133.2, 133.0, 129.5, 128.9, 127.6, 121.5, 53.4, 50.0, 36.3, 29.4, 28.7, 21.5, 20.5, 12.4, 0.8. HRMS: *m*/*z* calcd for $C_{21}H_{31}NO_2SiS$: 389.1845; found: 389.1854.
Compound **2c**: ^{1}H NMR (200.13 MHz, $CDCl_3$): δ = 0.11 (s, 9 H, $SiMe_3$), 1.06 (m, 12 H, Me), 1.94 (m, 1 H, CH), 2.38 (m,

2 H, CH), 2.44 (s, 3 H, Me), 3.19 (dd, *J* = 4.1, 8.8 Hz, 1 H, NCH_2), 3.25 (d, *J* = 8.3 Hz, 1 H, NCH_2), 3.64 (d, *J* = 8.8 Hz, 1 H, NCH_2), 3.72 (d, *J* = 8.5 Hz, 1 H, NCH_2), 5.45 (d, *J* = 15.7 Hz, 1 H, =CH$SiMe_3$), 5.94 (d, *J* = 15.7 Hz, 1 H, CH=), 7.32 (d, *J* = 7.7 Hz, 2 H, Ph), 7.70 (d, *J* = 8.1 Hz, 2 H, Ph). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 148.3, 146.9, 143.4, 133.7, 129.5, 127.7, 127.6, 119.0, 53.1, 50.5, 33.8, 33.6, 32.9, 28.5, 22.9, 22.6, 22.5, 22.2, 21.5, 1.0. HRMS: *m*/*z* calcd for $C_{24}H_{37}NO_2SiS$: 431.2314; found: 431.2304.

Compound **2d**: ^{1}H NMR (300.08 MHz, $CDCl_3$): δ = 0.12 (s, 9 H, $SiMe_3$), 1.50 (m, 6 H, CH_2), 1.98 (m, 1 H, CH), 2.07 (m, 4 H, CH_2), 2.45 (s, 3 H, Me), 3.23 (dd, *J* = 4.1, 13.2 Hz, 1 H, NCH_2), 3.26 (d, *J* = 8.6 Hz, 1 H, NCH_2), 3.61 (d, *J* = 9.2 Hz, 1 H, NCH_2), 3.76 (d, *J* = 8.8 Hz, 1 H, NCH_2), 5.48 (d, *J* = 15.6 Hz, 1 H, =CH$SiMe_3$), 6.04 (d, *J* = 15.5 Hz, 1 H, CH=), 7.33 (d, *J* = 7.9 Hz, 2 H, Ph), 7.68 (d, *J* = 8.2 Hz, 2 H, Ph). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 145.5, 143.3, 135.3, 133.8, 129.6, 129.1, 127.6, 119.1, 53.2, 50.1, 47.5, 35.4, 33.2, 32.8, 29.3, 27.7, 26.4, 21.5, 0.8. HRMS: *m*/*z* calcd for $C_{23}H_{33}NO_2SiS$: 415.2001; found: 415.1994.

Compound **4a**: ^{1}H NMR (200.13 MHz, $CDCl_3$): δ = 0.13 (s, 9 H, $SiMe_3$), 1.20 (s, 3 H, Me), 1.53 (s, 3 H, Me), 1.94 (m, 1 H, CH), 2.44 (s, 3 H, Me), 3.46 (dd, *J* = 4.1, 9.7 Hz, 1 H, NCH_2), 3.48 (d, *J* = 9.2 Hz, 1 H, NCH_2), 3.60 (d, *J* = 9.6 Hz, 1 H, NCH_2), 4.06 (d, *J* = 9.2 Hz, 1 H, NCH_2), 5.60 (s, 1 H, =CH$SiMe_3$), 7.07 (m, 2 H, Ph), 7.31 (m, 5 H, Ph + Ts), 7.78 (d, *J* = 8.2 Hz, 2 H, Ts). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 155.2, 146.6, 143.2, 134.3, 132.5, 129.5, 127.8, 127.4, 126.8, 126.7, 120.3, 55.4, 50.3, 38.4, 28.0, 22.7, 21.5, 20.9, 0.8. HRMS: *m*/*z* calcd for $C_{26}H_{33}NO_2SiS$: 451.2001; found: 451.2008.

Compound **4b**: ^{1}H NMR (200.13 MHz, $CDCl_3$): δ = 0.13 (s, 9 H, $SiMe_3$), 1.24 (s, 3 H, Me), 1.54 (s, 3 H, Me), 1.95 (m, 1 H, CH), 2.44 (s, 3 H, Me), 3.44 (dd, *J* = 4.1, 9.5 Hz, 1 H, NCH_2), 3.46 (d, *J* = 9.5 Hz, 1 H, NCH_2), 3.60 (d, *J* = 9.1 Hz, 1 H, NCH_2), 3.79 (s, 3 H, OMe), 4.04 (d, *J* = 9.1 Hz, 1 H, NCH_2), 5.61 (s, 1 H, =CH$SiMe_3$), 6.70 (m, 3 H, *p*-C_6H_4OMe), 7.29 (m, 3 H, *p*-C_6H_4OMe + Ph), 7.67 (d, *J* = 8.2 Hz, 2 H, Ph). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 158.2, 154.2, 147.2, 142.7, 142.4, 131.5, 128.7, 126.6, 118.5, 54.6, 54.4, 49.5, 37.4, 27.2, 20.7, 20.2, 19.5, 0.0. HRMS: *m*/*z* calcd for $C_{27}H_{35}NO_3SiS$: 481.2107; found: 481.2101.

Compound **6**: ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 0.20 (s, 9 H, $SiMe_3$), 1.67 (s, 3 H, Me), 1.71 (s, 3 H, Me), 1.89 (m, 1 H, CH), 2.35 (dd, *J* = 4.6, 12.6 Hz, 1 H, NCH_2), 2.50 (d, *J* = 12.3 Hz, 1 H, NCH_2), 2.81 (d, *J* = 12.6 Hz, 1 H, NCH_2), 3.03 (d, *J* = 12.3 Hz, 1 H, NCH_2), 3.64 (s, 3 H, OMe), 3.70 (s, 3 H, OMe), 5.44 (d, *J* = 15.5 Hz, 1 H, =CH$SiMe_3$), 6.11 (d, *J* = 15.5 Hz, 1 H, CH=). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 172.0, 171.2, 148.4, 128.1, 127.1, 125.0, 59.4, 52.9, 52.6, 39.7, 36.1, 35.9, 29.8, 22.2, 21.5, 1.20. HRMS: *m*/*z* calcd for $C_{18}H_{28}O_4Si$: 336.1757; found: 336.1750.

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