A New Ruthenium-catalyzed Reaction with Propargyl Alcohol: Cyclopropanation of Norbornene

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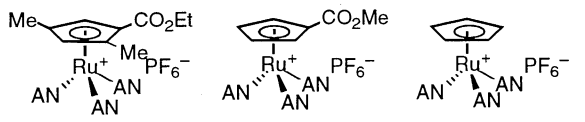
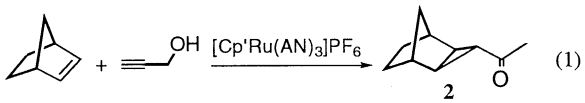
Cationic (η^5-cyclopentadienyl)tris(acetonitrile)ruthenium complexes catalyze a new reaction of propargyl alcohol with norbornene in methanol to give a cyclopropanation product, acetyltricyclooctane, in a quantitative yield.

Ruthenium-catalyzed condensation reactions between alkynes and alkenes are currently the subject of intense interest in terms of new methods for organic syntheses.[1, 2] Such development in the homogeneous catalysis is dependent on the progress in the chemistry of organoruthenium complexes; several new types of active ruthenium complexes[3] have been prepared over the last two decades. Recently we have also reported[4] the synthesis of novel (η^5-trisubstituted cyclopentadienyl)ruthenium complexes and examined the reactivity towards organic substrates having unsaturated bonds. In the course of our study, we have found a new type of ruthenium-catalyzed reaction between alkyne and alkene, and here wish to report the novel catalysis of cationic (cyclopentadienyl)tris(acetonitrile)ruthenium complexes towards a reaction between propargyl alcohol and norbornene which produces an unexpected product, acetyltricyclooctane **2**, in an excellent yield.



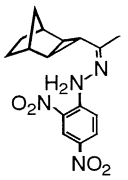
1a **1b** **1c**

(AN=acetonitrile)



(1)

In expectation of a [2+2] cycloaddition reaction,[2] we reacted 2-propyn-1-ol (5 mmol) with norbornene (5 mmol) in the presence of a catalytic amount (1 mol%) of cationic (trisubstituted cyclopentadienyl)tris(acetonitrile)ruthenium complex **1a** in methanol at room temperature, and isolated, after usual work-up, a colorless product, *exo*-3-acetyltricyclo[3.2.1.$0^{2,4}$]octane **2**,[5] unexpectedly. (eq. 1) The mass spectrum of compound **2** showed m/z 150 corresponding to the sum of the molecular weights of the starting substrates, 2-propyn-1-ol and norbornene but the IR and ^{13}C NMR spectra exhibited an absorption at 1683 cm^{-1} and a resonance at 208 ppm, respectively, due to a carbonyl group, indicating that a skeletal rearrangement of the starting materials must occur during the reaction. The structure of **2** including a stereochemistry was established by the ^{1}H and ^{13}C NMR spectroscopies with H-H and C-H cosy, and H-H noesy techniques. Although compound **2** has already been reported,[6] the reported physical and spectral data appeared to be significantly different from ours, then the molecular structure of **2** has been finally confirmed by an X-ray crystallographic analysis of its derivative, hydrazone **3** (orange crystals, mp. 142-143 °C), which was prepared by treatment of **2** with 2,4-dinitrophenylhydrazine.



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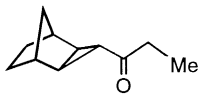

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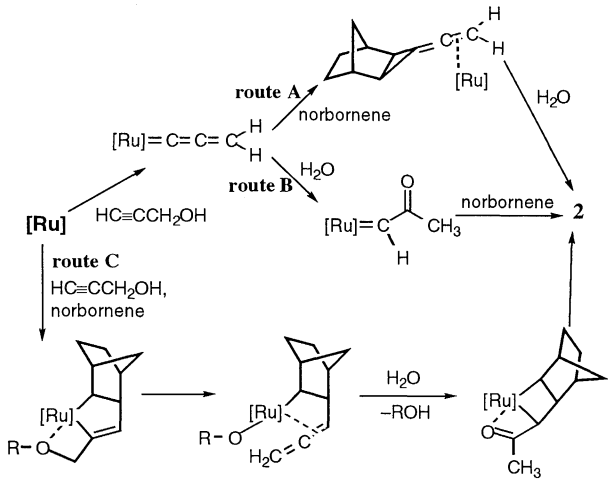
The ruthenium-catalyzed reaction of 2-propyn-1-ol with norbornene smoothly proceeds at room temperature in alcoholic solvents, and methanol is of the best choice as a solvent although almost no reaction occurs in solvents such as benzene, THF and dichloromethane (Table 1). Some cationic cyclopentadienyl-ruthenium complexes **1a-c** exhibit essentially the same catalytic activity toward the reaction, and among them, (trisubstituted cyclopentadienyl)ruthenium complex **1a** shows the highest activity resulting in the selective formation of **2** in a quantitative yield, while CpRuCl(cod) and $RuCl_2(PPh_3)_4$ are inactive under the same reaction conditions. 3-Butyn-2-ol similarly reacted with norbornene to afford product **4** in a moderate yield, while 2-methyl-3-butyn-2-ol did not react with norbornene and remained intact after the reaction for 3 h at room temperature. It is noteworthy that compound **2** was obtained as a sole product in 87% yield when methyl 2-propynyl ether was used instead of propargyl alcohol, suggesting the elimination of the hydroxy or the alkoxy group from the starting material during the reaction.[7] This result also means that the oxygen atom of the carbonyl group in compound **2** does not originate from that in the propargyl alcohol.

Table 1. Reactions of norbornene with propargyl alcohols[a]

Propargyl alcohol	Sovlent	Yield / % of **2**[b]
HC≡C-CH_2OH	methnol	99 (66)[c]
	ethanol	30
	benzene	3
	THF	3
	dichloromethane	0
HC≡C-CH(Me)OH	methanol	31[d]
HC≡C-CH_2OMe	methanol	87

[a] eaction conditions: norbornene, 5 mmol; propargyl alcohol, 5 mmol; catalyst **1a**, 1 mol%; solvent, 10 mL; 3 h; room temperature. [b] Determined by gas chromatography. [c] Isolated yield. [d] Product: **4**

Judging from the structure of the products, three possible



Scheme 1.

mechanisms for the reaction may be considered as shown in scheme 1. Routes A and B involve a ruthenium-allenylidene intermediate, which is well known to be formed from the reaction of propargyl alcohol with ruthenium complexes,[8] whereas route C passes through ruthenacyclopentene as a key intermediate. In order to obtain information on the mechanism, the cyclopropanation reaction with 2-propyn-1-ol was carried out employing MeOD and D_2O as the solvent. The reaction gave compound **6** which bears only one deuterium atom at the acetyl group.[5] Methyl 2-propynyl ether also reacted with norbornene to give **6**, implying that the cyclopropanation proceeds via neither routes A nor B because these routes predict the formation of a *dideuterated* derivative of **2**. In route C, formation of a ruthenacylopentene complex from the reaction of norbornene with propargyl alcohol (the first step) may be understood by the study of Trost on the ruthenium-catalyzed C-C bond formation from allylic alcohol and alkyne giving γ,δ-unsaturated ketones.[1] In addition the attack of a hydroxy nucleophile at the β-carbon of π-allene ligands (the third step) is known for iron complexes.[9] Then rout C involving a ruthenacycle and π-allene species as key-intermediates is tentatively proposed.

Catalytic activities of transition metal complexes including ruthenium complexes towards cyclopropanation reactions of olefins have been well documented so far,[10] however diazo compounds are generally used as a carben source in the reactions. Although the cyclopropanation of norbornene with an oxa-π-allylpalladium species has been reported,[6, 11] the reaction described here is the first example of cyclopropanation using propargyl alcohol as a methylene source.[12] Studies on the scope and mechanism of the reaction are now in progress.

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References and Notes

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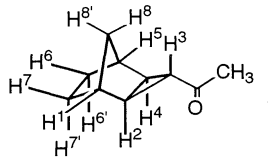
5 Selected data. **2**, mp 43.0 - 44.0 °C; Anal. Calcd. for $C_{10}H_{14}O$: C 79.96, H 9.39. Found: C 80.03, H 9.20. ^1H NMR (400 MHz $CDCl_3$) δ = 2.35 (s, 2H, H^1 and H^5), 2.19 (s, 3H, $COCH_3$), 1.89 (t, 1H, J = 2.4 Hz, H^3), 1.58-1.44 (m, 2H, H^6 and H^7), 1.38 (d, 2H, J = 2.2 Hz, H^2 and H^4), 1.33-1.27 (m, 2H, $H^{6'}$ and $H^{7'}$), 0.95 (dt, 1H, J = 10.7, 2.0 Hz, H^8), 0.71 (d, 1H, J = 10.7 Hz, $H^{8'}$); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 208.50, 36.04, 30.83, 28.83, 28.81, 28.64, 25.08; Mass (EI, 70 eV) m/z = 150.



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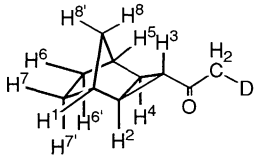

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6, ^1H NMR (400 MHz $CDCl_3$) δ = 2.35 (s, 2H, H^1 and H^5), 2.19 (t, 2H, J = 1.6 Hz, $COCH_2D$), 1.89 (t, 1H, J = 2.4 Hz, H^3), 1.58-1.44 (m, 2H, H^6 and H^7), 1.38 (d, 2H, J = 2.2 Hz, H^2 and H^4), 1.33-1.27 (m, 2H, $H^{6'}$ and $H^{7'}$), 0.95 (dt, 1H, J = 10.7, 2.0 Hz, H^8), 0.71 (d, 1H, J = 10.7 Hz, $H^{8'}$); Mass (EI, 70 eV) m/z = 151.

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