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Synthesis of Enantiopure Ruthenium Tricarbonyl Complexes of a Bicyclic Cyclopentadienone Derivative

Min-soo Kim,[a] Jun Won Lee,[a] Jae Eun Lee,[a] and Jahyo Kang*[a]

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(–)-Menthone was converted stereoselectively into 3-menthylpropargyl alcohol **8** in several steps and subsequently converted into enantiopure cyclopentadienone ruthenium carbonyl complexes. In the malonate cases, ruthenacycle **15** was also formed during the cyclization reaction.

Introduction

Cyclopentadienones are useful synthetic intermediates[1] for polycyclic compounds[2] and polymers.[3] Additionally, transition-metal complexes containing chiral cyclopentadienyl ligands are widely used in asymmetric catalysis and olefin polymerization reactions.[4] In general, transition-metal-mediated alkyne–alkyne–CO couplings with metal carbonyl[5] compounds provides a direct and effective synthesis of cyclopentadienones, which are potentially useful owing to their occurrence in a diverse range of natural product molecules.[6] In this homocoupling reaction, two alkynes react with $Fe(CO)_5$ under a CO atmosphere to give the symmetrically substituted cyclopentadienone–$Fe(CO)_3$ complexes.[7]

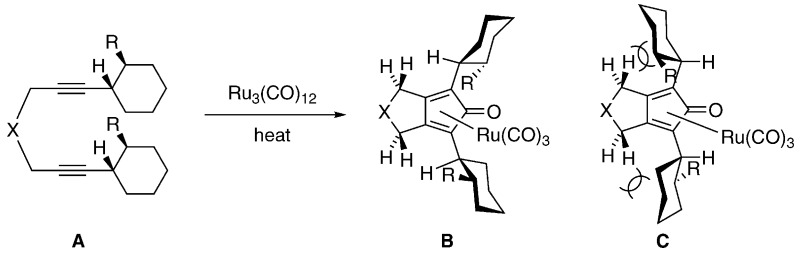
Herein is reported a general approach to cyclopentadienone–ruthenium carbonyl complexes of chiral cyclopentadienone derivatives, which may be useful in asymmetric synthesis, by cross-coupling of tethered diynes by $Ru_3(CO)_{12}$-promoted cyclocarbonylation (Scheme 1).[8]

Thus, the chiral cycloalkyl groups on the opposite side of the cyclopentadienone ligand would provide a C_2-symmetric environment around the ligand, which may be utilized in asymmetric synthesis. The underlying assumption is that both of the methine hydrogens on the side-chain ring point away from the carbonyl oxygen atom (as in **B**) because of the unfavorable interaction of the side-chain ring with the allylic hydrogens (as in **C**).

Incidentally, the cyclopentadienone–Ru complexes are also important intermediates for the Shvo complex, which is used as a catalyst in the racemization of optically active alcohols.[9]

Results and Discussion

(–)-Menthone was treated at –78 °C for 1 h with the lithio derivative of the *tert*-butyldimethylsilyl ether of propargyl alcohol in THF, which was generated by the reaction of the corresponding alkyne with *n*-butyllithium at –40 °C and subsequently at 0 °C (1 h). The product was purified by distillation (b.p. 142–144 °C/0.9–1.0 Torr) to give 90% yield of the diastereomeric mixture (≈2:1 preference for the axial alcohol) of the known epimeric alcohols **2**[10] (Scheme 2).



Scheme 1. The cyclopentadienone–Ru complex.

[a] Department of Chemistry, Sogang University, Mapo-gu, Seoul 121-742, Korea
Fax: +82-2-701-0967
E-mail: kangj@sogang.ac.kr

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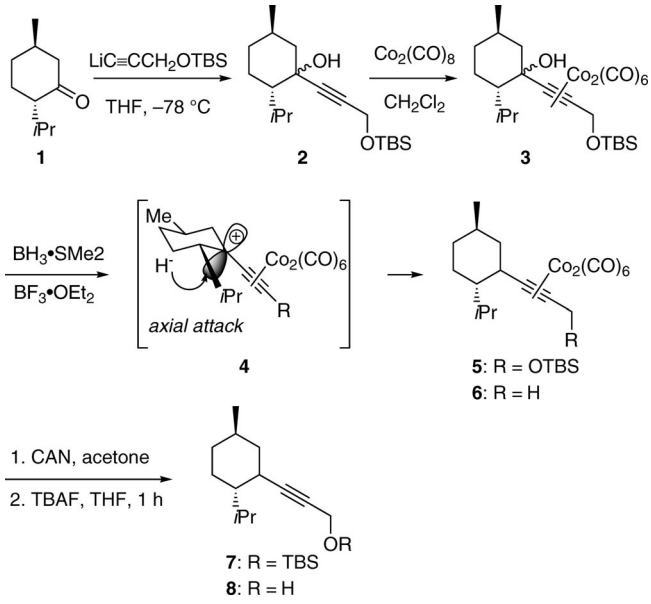
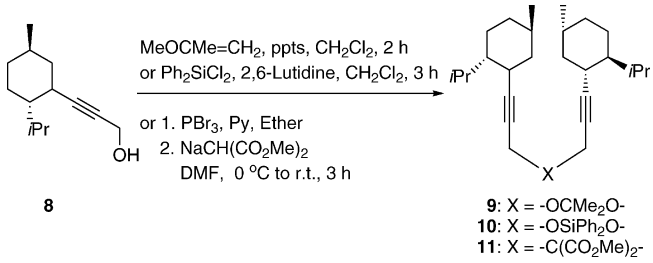


Scheme 2. Preparation of propargylic alcohol **8**.

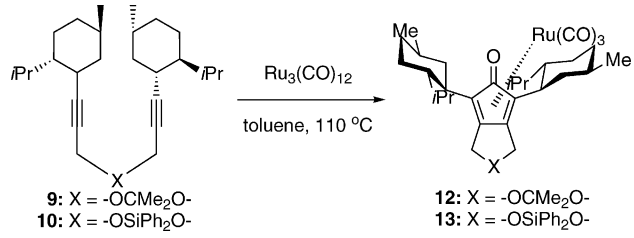
The tertiary hydroxy group of diastereomeric propargylic alcohol **2** was reduced stereoselectively to give the corresponding *trans* alcohol **8** in a series of three consecutive reactions. Thus, propargylic alcohol **2** was first treated with dicobalt octacarbonyl in CH_2Cl_2 at room temperature for 6 h to give the corresponding dicobalt hexacarbonyl complex of alkyne **3**. Subsequently, the more easily ionizable tertiary propargylic hydroxy group of monosilyl ether **3** was reduced by borane–dimethyl sulfide complex (hydride source) in the presence of boron trifluoride–diethyl ether (Lewis acid) at –78 °C. After aqueous workup and chromatography, the pure cobalt complex of propargylic ether **5** was isolated in 53% yield along with ca. 10% yield of completely reduced alkyne **6**. Evidently, the *trans* geometry resulted from the axial delivery of the hydride to incipient carbocation **4** (the stereochemistry of propargylic alcohol **5** was later confirmed by ^1H–^{13}C hetero COSY, ^1H–^1H homo COSY, and proton NOESY on the corresponding benzoate of alcohol **8**). Subsequent demetalation of cobalt complex **5** with ceric ammonium nitrate at 0 °C provided a mixture of silyl ether **7** (15% yield), and desilylated alcohol **8** (43% yield). Silyl ether **7** could be independently desilylated by tetrabutylammonium fluoride in THF at 0 °C to furnish pure propargylic alcohol **8** in 92% yield (Scheme 2). Gratifyingly, without purification of intermediates, the metalation with dicobalt octacarbonyl, reduction, and final demetalation of the cobalt residue (**2**→**5**) could be accomplished in 23% overall yield for the three steps.

With propargylic alcohol **8** in hands, various types of diyne compounds for the synthesis of the bicyclic ruthenium tricarbonyl complexes were prepared. Acetone ketal **9** was prepared by the reaction of 2-methoxypropene with propargylic alcohol **8** in the presence of pyridinium *p*-toluenesulfonate (ppts) in CH_2Cl_2 at 0 °C (87% yield). The corresponding bis(diphenylsilyl) ether **10** was prepared in 78% yield by the reaction of propargylic alcohol **8** with dichlorodiphenylsilane in CH_2Cl_2 in the presence of 2,6-lutidine[7b] (r.t., 8 h). Additionally, propargyl alcohol **8** was converted into the corresponding propargylic bromide in 76% yield by using phosphorus tribromide in pyridine, and it was then condensed with the sodio derivative of dimethyl malonate in DMF at 0 °C to give diyne compound **11** in 69% yield (Scheme 3).



Scheme 3. Preparation of diynes **9**–**11**.

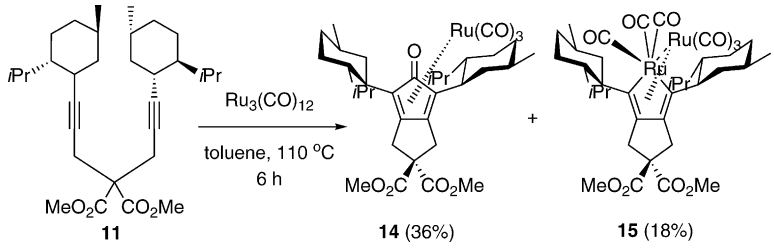
Finally, a mixture of diyne compound **9** or **10** and triruthenium dodecacarbonyl (0.5 mol/mol of the diyne, 50% excess) was heated to reflux in toluene for 5–10 h[11] to uneventfully provide cyclopentadienone–ruthenium tricarbonyl complex **12** or **13** as brown foams after purification by flash chromatography in ca. 30 and 24% yields, respectively (Scheme 4).



Scheme 4. Preparation of bicyclic cyclopentadienone–ruthenium tricarbonyl complexes **12** and **13**.

The reaction of dimethyl malonate **11** with $Ru_3(CO)_{12}$ provided two ruthenium-containing compounds: the usual cyclopentadienone adduct **14** [R_f = 0.33 (10% EtOAc/*n*-hexane); 36% yield after column chromatography and recrystallization] as colorless crystals and a slightly less-polar material [R_f = 0.41 (10% EtOAc/*n*-hexane)] as yellowish crystals, which exhibited almost the same NMR spectra but later was shown to be ruthenacylopentadiene[12] **15** (18% yield after column chromatography and recrystallization) by X-ray crystallography (Scheme 5). However, the more reactive tris(acetonitrile) complex $Ru_3(CO)_9(MeCN)_3$[13] did not give a significant increase in yield of cyclopentadienone adduct **14** (ca. 40% yield) or the formation of ruthenacycle **15**.

The structural features of bicyclic cyclopentadienone–ruthenium tricarbonyl complex **14** are quite informative. The cyclopentadienone carbonyl (C4–O4) approximately eclipses one of the terminally coordinated carbonyl ligands (C1–O1) on the ruthenium atom. This steric effect is reflected in the lengthening of the Ru–C1 bond [1.933(5) Å]. Thus, one may assume that the effect of this eclipsing would make the eclipsing carbonyl ligand on the ruthenium atom



Scheme 5. Preparation of bicyclic ruthenium tricarbonyl complexes **14** and **15**.

be more susceptible to dissociation, which is required step for the initiation of the catalytic cycle of the complex,[14] even though the fluxional behavior of this kind of complex in solution is expected.[15] As expected, both of the menthyl rings in bicyclic cyclopentadienone–ruthenium tricarbonyl complex **14** assume a chair conformation. The methine hydrogens on the connecting carbon atoms (C12 and C22) on each menthyl ring lie almost in the same plane as the diene unit (–21.2 and –160.0°), which was expected. More importantly, *both* of the two isopropyl groups on the menthyl rings are pushed away from the ruthenium metal center, despite the increased steric interaction of the menthyl ring with the allylic hydrogens (Scheme 1, **C**; Figure 1),[16] which was contrary to our initial expectation. It is also interesting that the overall structure of bicyclic diruthenium ruthenacycle complex **15** is similar to that of bicyclic cyclopentadienone–ruthenium tricarbonyl complex **14** except for the fact that the carbonyl group of complex **14** is replaced by one $Ru(CO)_3$ unit (Figure 2).[16]

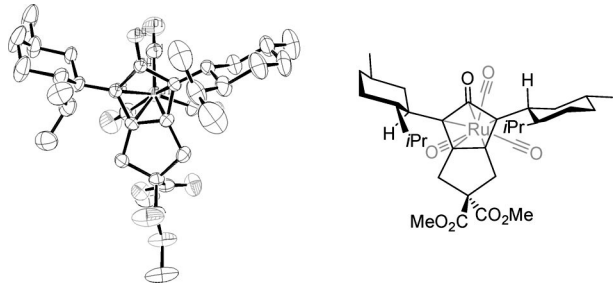


Figure 1. X-ray crystal structure of chiral bicyclic cyclopentadienone–ruthenium Complex **14**; hydrogen atoms have been omitted for clarity.

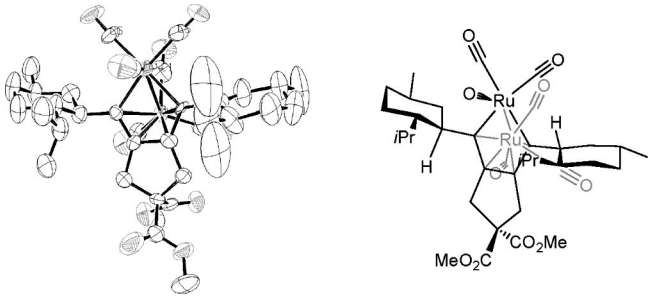


Figure 2. X-ray crystal structure of chiral bicyclic diruthenium ruthenacycle complex **15**; hydrogen atoms have been omitted for clarity.

Conclusions

We prepared various enantiopure bicyclic cyclopentadienone–ruthenium carbonyl complexes with menthyl side chains that reside on the opposite side of the cyclopentadienone ring. The complexes were derived stereoselectively from (–)-menthone in several steps.

Supporting Information (see footnote on the first page of this article): Experimental procedures.

Acknowledgments

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[1] Review: M. Ogliaruso, M. G. Romanelli, E. I. Becker, *Chem. Rev.* **1965**, *65*, 261–367.
[2] a) A. Gamba, R. Gandolfi, R. Oberti, N. Sardone, *Tetrahedron* **1993**, *49*, 6331–6348; b) T. Jikyo, M. Eto, K. Harano, *Tetrahedron* **1999**, *55*, 6051–6066; c) J. D. Rainier, J. E. Imbriglio, *Org. Lett.* **1999**, *1*, 2037–2039; d) A. J. Pearson, J. B. Kim, *Tetrahedron Lett.* **2003**, *44*, 8525–8527.
[3] U. Kumer, T. X. Meenan, *Macromolecules* **1995**, *28*, 124–130.
[4] a) A. H. Hoveyda, J. P. Morken, *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1262–1284; b) R. L. Halterman, *Chem. Rev.* **1992**, *92*, 965–994.
[5] Reviews on transition-metal-catalyzed cycloadditions: a) I. Ojima, M. Tzamarioudaki, Z. Li, R. J. Donovan, *Chem. Rev.* **1996**, *96*, 635–662; b) H.-W. Frühauf, *Chem. Rev.* **1997**, *97*, 523–596.
[6] a) G. Mehta, J. D. Umarye, *Org. Lett.* **2002**, *4*, 1063–1066; b) V. B. Birman, S. Danishefsky, *J. Am. Chem. Soc.* **2002**, *124*, 2080–2081; c) B. B. Snider, N. A. Hawryluk, *Org. Lett.* **2001**, *3*, 569–572.
[7] a) A. C. Filippou, T. Rosenauer, *Angew. Chem. Int. Ed.* **2002**, *41*, 2393–2396; b) A. J. Pearson, J. B. Kim, *Org. Lett.* **2002**, *4*, 2837–2840; c) A. J. Pearson, A. Perosa, *Organometallics* **1995**, *14*, 5178–5183; d) H.-J. Knölker, E. Baum, J. Heber, *Tetrahedron Lett.* **1995**, *36*, 7647–7650.
[8] a) Y. Yamamoto, Y. Miyabe, K. Itoh, *Eur. J. Inorg. Chem.* **2004**, 3651–3661; b) M. I. Bruce, J. R. Knight, *J. Organomet. Chem.* **1968**, *12*, 411–413.
[9] a) F. F. Huerta, A. B. E. Minidis, J.-E. Bäckvall, *Chem. Soc. Rev.* **2001**, *30*, 321–331; b) M.-J. Kim, Y. Ahn, J. Park, *Bull. Korean Chem. Soc.* **2005**, *26*, 515–522.
[10] C. Spino, C. Beaulieu, J. Lafrenière, *J. Org. Chem.* **2000**, *65*, 7091–7097.
[11] a) G. Cetini, O. Gambino, E. Sappa, M. Valle, *J. Organomet. Chem.* **1969**, *17*, 437–443; b) Y. Blum, Y. Shvo, *Isr. J. Chem.* **1984**, *24*, 144–148.

[12] a) G. Gervasio, D. Marabello, E. Sappa, A. Secco, *J. Organomet. Chem.* **2005**, *690*, 3730–3736; b) E. Sappa, *J. Organomet. Chem.* **1999**, *573*, 139–155.
[13] P. Grenouillet, C. de Bellefon, *J. Organomet. Chem.* **1996**, *513*, 155–162.
[14] a) Y. Blum, Y. Shvo, D. F. Chodosh, *Inorg. Chim. Acta* **1985**, *97*, L25–L26; b) B. Schneider, I. Goldberg, D. Reshef, Z. Stein, Y. Shvo, *J. Organomet. Chem.* **1999**, *588*, 92–98.
[15] L. Kruczynski, J. Takats, *Inorg. Chem.* **1976**, *15*, 3140–3147.
[16] CCDC-677374 (for **14**) and -677375 (for **15**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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