DOI: 10.1002/adsc.200505401

[CpRu(IV)(π-C_3H_5)(2-quinolinecarboxylato)]PF_6 Complex: A Robust Catalyst for the Cleavage and Formation of Allyl Ethers

Shinji Tanaka, Hajime Saburi, Masato Kitamura*

Research Center for Materials Science and the Department of Chemistry, Nagoya University, Chikusa, Nagoya 464-8602, Japan
Fax: (+81)-52-789-2261, e-mail: kitamura@os.rcms.nagoya-u.ac.jp

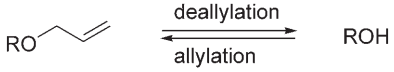
Received: October 11, 2005; Accepted: December 15, 2005

Supporting Information for this article is available on the WWW under http://asc.wiley-vch.de/home/ or from the author.

Abstract: A facile and efficient method for the quantitative synthesis of [CpRu(IV)(π-C_3H_5)(2-quinolinecarboxylato)]PF_6 from [CpRu(CH_3CN)$_3$]PF_6, 2-quinolinecarboxylic acid, and 2-propen-1-ol has been established. The cationic Ru(IV) complex is air- and moisture-stable, and can be stored in a vial for at least six months. This complex realizes a simple and easy operation for both the deallylation of allyl ethers in methanol and the dehydrative allylation of alcohols. Furthermore, with removal of the volatile allyl methyl ether co-product from the reaction system, the robust catalyst can attain a turnover of 10000 cycles of allyl ether cleavage.

Keywords: allylation; deallylation; homogeneous catalysis; protecting groups; 2-quinolinecarboxylic acid; ruthenium

Allyl ethers **1**, which are structurally simple and stable in both acidic and basic conditions, have a high potential for affording the best protection of hydroxy groups.[1] Their removal, however, requires a two-step process, which is typically Rh- or Ir-catalyzed isomerization, followed by acidic or oxidative cleavage of the intermediary alkenyl ethers, to yield the corresponding alcohols **2**.[2] The single-step deprotection of allyl ethers can also be attained by using an Ni, Pd, or Os complex, but in the presence of excess acid, base, reducing agent, or oxidizing agent.[3] These indispensable prerequisites often decrease the practicality of the complexes in terms of chemoselectivity, reactivity, operational simplicity, and product isolation, among others. The disadvantages have been recently overcome to a great extent by the development of a new catalyst system consisting of [CpRu(CH_3CN)$_3$]PF_6 (**3**) and 2-quinolinecarboxylic acid (**4**).[4,5] This catalyst functions as a highly reactive cleaver of allyl ether in alcoholic solvents under very mild and additive-free conditions. Furthermore, by using non-alcoholic solvents or no solvent, the highly efficient catalytic dehydrative allylation of alcohols with 2-propen-1-ol can be achieved.[6,7] A novel CpRu(II) catalyst would certainly increase the utility of allyl ethers in protecting group chemistry but, from a practical viewpoint, the instability of Ru(II) catalysts is a drawback.[8] Herein we report on a solution to this problem to update the original method.[4,6]



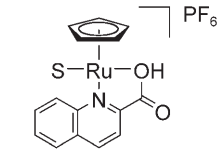
1 **2**

a: R = $C_6H_5CH_2CH_2$
b: R = 2-indanyl
c: R = $C_6H_5CH_2(CH_3)_2C$
d: R = C_6H_5

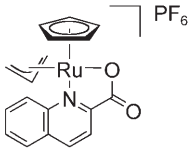
The CpRu(II)-**4**-catalyzed reactions are thought to proceed *via* an intermediate catalyst–substrate complex, which is generated *via* olefin-mediated coordination of 2-propan-1-ol onto a CpRu(II)/2-quinolinecarboxylic acid species **5**. Here, a hydrogen bond is formed between the COOH moiety of the catalyst part and the OH group of 2-propen-1-ol, and the σ-donative sp^2-N atom of the quinoline moiety and the monoanionic η^5-Cp ligand strongly coordinate to the Ru ion.[4,6] These simultaneous events synergistically enhance the electrophilicity of C(3) and the nucleophilicity of Ru,[9] thereby accelerating the generation of the cationic CpRu(IV)(π-C_3H_5) carboxylate species **6**.[10] The π-allyl complex **6** was successfully isolated as a single crystal, and its molecular structure was determined by X-ray diffraction analysis.[6] We have established the reliable, practical, and quantitative preparation of **6** by taking advantage of the higher stability of Ru(IV). The robustness as

well as the catalytic reactivity in the title reactions have also been investigated.

When $[CpRu(CH_3CN)_3]PF_6$ and 2-quinolinecarboxylic acid were mixed in a 1.0:1.0 ratio in acetone at room temperature, ligand exchange between CH_3CN and **4** occurred immediately to form the CpRu(II)-**4** complex **5**. This complex was then treated with an acetone solution containing a 1.0 mol amount of 2-propen-1-ol at room temperature for 15 min. Concentration of the solution to about a tenth of the total volume, followed by filtration, afforded the Ru(IV)-π-allyl complex **6** as a pale yellow solid in a quantitative yield (see Experimental Section). This procedure is operationally simple because the only co-product is water, and its reproducibility is high in a range of 1–10 g. Thus prepared, the π-allyl complex **6** could be stored in a standard vial at room temperature for at least six months without any decomposition.



5



6

Complex **6** exhibited the same reactivity and chemoselectivity as the original CpRu(II)-**4** combined system, not only in the removal of the allyl group from allyl ethers but also in the formation of allyl ethers from alcohols and 2-propen-1-ol. Representative results are shown in Table 1. 2-Phenylethyl allyl ether (**1a**) was smoothly deallylated in methanol at 30 °C with the concentrations of [**1a**] = 500 mM and [**6**] = 1 mM to give, after 3 h, 2-phenylethanol (**2a**) in a quantitative yield (entry 1). A complex that had been kept in air for over six months showed identical reactivity (entry 2). When the reaction was carried out with occasional removal of the methanol solvent and the co-product, allyl methyl ether, followed by addition of the removed amount of methanol, the turnover number (TON) approached 10000. Even when a 0.1 mmol amount of **6** was used, all of the substrate **1a** was quantitatively converted to **2a** after 35 h (entry 3). The turnover frequency (TOF) was calculated to be 500 h^{-1}. The allyl groups of secondary and tertiary alkanols, as well as those of an aromatic alcohol such as **1b**, **1c**, or **1d**, were also quantitatively removed (entries 4–6). In a similar way, **2a** was allylated with a 1.0 mol amount of 2-propen-1-ol either without solvent or in dichloromethane to give **1a** in >90% yield (entries 7 and 8).[9]

In conclusion, the cationic CpRu(IV)(π-C_3H_5)-2-quinolinecarboxylato complex **6** has been shown to be a robust and highly active catalyst for the cleavage and formation of allyl ethers. The complex can be quantitatively prepared *via* an easy and simple one-pot synthesis and can be kept for a long time without protection from air and moisture with no loss of catalytic activity. In comparison to the original Ru(II)-based method,[4,6] the advantages afforded by the new complex **6** should further enhance the practical value of allyl ethers for hydroxy protection in organic synthesis.

Experimental Section

Catalyst Preparation

Acetone was distilled over 4 Å molecular sieves under argon into a Schlenk tube, and used after being degassed by three freeze–thaw cycles. $[CpRu(CH_3CN)_3]PF_6$[12] and 2-quinolinecarboxylic acid were purchased from Strem and Aldrich, respectively, and used without purification. $[CpRu(CH_3CN)_3]PF_6$ (3.28 g, 7.56 mmol) was placed in a dry and argon-filled 500-mL Schlenk tube containing a Teflon-coated magnetic stir-

Table 1. Catalytic deallylation of allyl ethers and allylation of alcohols by [CpRu(IV)(π-C_3H_5)(2-quinolinecarboxylato)]PF_6 (**6**).

Entry	Substrate (mM)	Product	Solvent	S/C	Temp [°C]	Time [h]	Yield [%][a]
1	**1a** (500)	**2a**	CH_3OH	500	30	3	>99
2[b]	**1a** (500)	**2a**	CH_3OH	500	30	3	>99
3[c]	**1a** (2000)	**2a**	CH_3OH	10000	30	35	>99
4	**1b** (500)	**2b**	CH_3OH	500	30	3	99
5	**1c** (500)	**2c**	CH_3OH	500	30	3	>99
6	**1d** (100)	**2d**	CH_3OH	100	30	3	>99
7	**2a** (–)	**1a**	–	2000	70	6	92
8	**2a** (500)	**1a**	CH_2Cl_2	500	reflux	3	93

[a] The yield was determined by GC analysis with a DB-WAX column.[11]
[b] The catalyst was used after being stored in air for over six months.
[c] The reaction was carried out with occasional removal of volatiles under reduced pressure followed by addition of methanol to keep the initial concentration.

ring bar. The whole system was evacuated and filled with argon gas, and then acetone (150 mL) was introduced, resulting in a pale yellow solution. To this, a solution of 2-quinolinecarboxylic acid (1.30 g, 7.56 mmol) in acetone (50 mL), prepared in a similar way, was introduced through a cannula with a slightly positive argon pressure. After stirring for 30 min at 27 °C, a solution of 2-propen-1-ol (520 μL, 7.56 mmol) in acetone (25 mL) was introduced to the resulting dark reddish solution through a cannula, and the mixture was stirred for 15 min at 27 °C. During this period, the color faded to yellow. The whole mixture was concentrated to ca. 30 mL, leading to precipitation of a pale yellow solid. The supernatant was removed through a cannula, one end of which was capped by filter paper. The pale yellow solid remaining in the Schlenk was washed three times with cold acetone (total 20 mL, 0 °C) in the same way. Drying at 0.005 mmHg for 12 h gave the [CpRu(IV)(π-C_3H_5)(2-quinolinecarboxylato)]PF_6 complex; yield: 3.93 g (7.50 mmol), 99%); anal. calcd. for $C_{18}H_{16}F_6NO_2PRu$: C 41.23, H 3.08, N 2.67; found: C 41.48, H 2.95, N 2.73. The ^{1}H- and ^{13}C-NMR, HR-mass, and IR spectra were consistent with those reported in the previous paper.[6]

The complex (100 mg) was kept in a screw-capped vial at 27 °C for six months. The catalytic activity of the stored complex in the deallylation of 1a was identical to that of freshly prepared **6** (Table 1, entries 1 and 2).

Deallylation

[CpRu(π-C_3H_5)(2-quinolinecarboxylato)]PF_6 (**6**; 1.9 mg, 3.7 μmol) was placed in a 20-mL Schlenk tube under an argon stream. To this was added a mixture of allyl 2-phenylethyl ether (**1a**; 0.300 g, 1.85 mmol) and methanol (3.4 mL) which was degassed three times by the freeze-thaw method via a cannula. The yellow solution was stirred for 3 h at 30 °C. GC analysis determined the yield of 2-phenylethanol (**2a**) to be >99%.[11] The reaction mixture was concentrated under reduced pressure to give a crude product, which was separated by chromatography on silica gel (AP 300, 15 g; eluent, 7:3 hexane–ethyl acetate) to give pure **2a**; yield: 0.225 g (99%). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 2.88 (t, 2H, J = 6.42 Hz, $C_6H_5CH_2$), 3.87 (t, 2H, J = 6.42 Hz, CH_2CH_2OH), 7.23–7.34 (m, 5H, aromatic).

Allylation

No solvent system: 2-Phenylethan-1-ol (**2a**; 0.782 g, 6.40 mmol) and 2-propen-1-ol (0.372 g, 6.40 mmol) were placed in a 20-mL Schlenk tube equipped with a Young's tap, and the whole mixture was degassed three times by the freeze-thaw method. [CpRu(π-C_3H_5)(2-quinolinecarboxylato)]PF_6 (1.7 mg, 3.2 μmol) was placed in another 20-mL Schlenk tube equipped with a Young's tap under an argon stream. To this was added the **2a** and 2-propen-1-ol mixture through a cannula under an argon stream. The yellow homogeneous mixture was stirred at 70 °C for 6 h. GC analysis determined the yield of allyl 2-phenylethyl ether (**1a**) to be 92%.[11]

CH_2Cl_2 system: 2-Phenylethan-1-ol (**2a**; 0.268 g, 2.19 mmol), 2-propen-1-ol (0.127 g, 2.19 mmol), and dichloromethane (4.0 mL) were placed in a 20-mL Schlenk tube equipped with a Young's tap, and the whole mixture was degassed three times by the freeze-thaw method. [CpRu(π-C_3H_5)(2-quinolinecarboxylato)]PF_6 (**6**; 2.3 mg, 4.4 μmol) was placed in another 20-mL Schlenk tube equipped with a Young's tap under an argon stream. To this was added the **2a** and 2-propen-1-ol solution through a cannula under an argon stream. The yellow homogeneous solution was stirred for 3 h in a 70 °C oil bath. GC analysis determined the yield of allyl 2-phenylethyl ether (**1a**) to be 93%.[11]

Acknowledgements

This work was aided by a Grant-in-Aid for Scientific Research (No. 14078212) from the Ministry of Education, Science, Sports and Culture, Japan. We are grateful to Messrs. T. Noda, K. Oyama, and Y. Maeda for their technical support in reaction vessel production and spectral measurements.

References and Notes

[1] F. Guibé, *Tetrahedron* **1997**, *53*, 13509–13556; T. W. Greene, P. G. M. Wuts, *Protective Groups in Organic Synthesis*, 3rd edn., John Wiley & Sons, New York, **1999**.

[2] Rh: E. J. Corey, J. W. Suggs, *J. Org. Chem*. **1973**, *38*, 3224; Ir: J. J. Oltvoort, C. A. A. van Boeckel, J. H. de Koning, J. H. van Boom, *Synthesis* **1981**, 305–308; for a recent paper, see: C. Cadot, P. I. Dalko, J. Cossy, *Tetrahedron Lett*. **2002**, *43*, 1839–1841, and references cited therein.

[3] Ni: a) T. Taniguchi, K. Ogasawara, *Angew. Chem. Int. Ed.* **1998**, *37*, 1136–1137; Pd: b) H. Murakami, T. Minami, F. Ozawa, *J. Org. Chem*. **2004**, *69*, 4482–4486; c) H. Tsukamoto, Y. Kondo, *Synlett* **2003**, 1061–1063; d) D. R. Vutukuri, P. Bharathi, Z. Yu, K. Rajasekaran, M.-H. Tran, S. Thayumanavan, *J. Org. Chem.* **2003**, *68*, 1146–1149; e) S. Chandrasekhar, C. R. Reddy, R. J. Rao, *Tetrahedron* **2001**, *57*, 3435–3438; f) M. Honda, H. Morita, I. Nagakura, *J. Org. Chem.* **1997**, *62*, 8932–8936; g) R. Beugelmans, S. Bourdet, A. Bigot, J. Zhu, *Tetrahedron Lett.* **1994**, *35*, 4349–4350; Os: h) P. I. Kitov, D. R. Bundle, *Org. Lett*. **2001**, *3*, 2835–2838.

[4] S. Tanaka, H. Saburi, Y. Ishibashi, M. Kitamura, *Org. Lett*. **2004**, *6*, 1873–1875.

[5] For allyl ester cleavage using **3** and triphenylphosphine, see: M. Kitamura, S. Tanaka, M. Yoshimura, *J. Org. Chem*. **2002**, *67*, 4975–4977.

[6] H. Saburi, S. Tanaka, M. Kitamura, *Angew. Chem. Int. Ed*. **2005**, *44*, 1730–1732.

[7] Other example of activation of allyl alcohol by use of Pd complex, see: F. Ozawa, T. Ishiyama, S. Yamamoto, S. Kawagishi, H. Murakami, M. Yoshifuji, *Organometallics* **2004**, *23*, 1698–1707; see also ref.[3b]

[8] The Ru(II) complex consisting of [CpRu(II)(CH_3CN)$_3$]-PF_6 and 2-quinolinecarboxylic acid decomposes under aerobic conditions, leading to deactivation of the catalyst.

[9] For the original papers on the donor-acceptor bifunctional catalyst, see: R. Noyori, M. Kitamura, *Angew. Chem. Int. Ed. Engl*. **1991**, *30*, 49–69; M. Kitamura, S. Suga, K. Kawai, R. Noyori, *J. Am. Chem. Soc*. **1986**, *108*, 6071–6072.

[10] E. Rüba, W. Simanko, K. Mauthner, K. M. Soldouzi, C. Slugovc, K. Mereiter, R. Schmid, K. Kirchner, *Organometallics* **1999**, *18*, 3843–3850; T. Kondo, H. Ono, N. Satake, T. Mitsudo, Y. Watanabe, *Organometallics* **1995**, *14*, 1945–1953; H. Nagashima, K. Mukai, Y. Shiota, K. Yamaguchi, K. Ara, T. Fukahori, H. Suzuki, M. Akita, Y. Moro-oka, K. Itoh, *Organometallics* **1990**, *9*, 799–807.
[11] For details, see Supporting Information.
[12] E. P. Kündig, F. R. Monnier, *Adv. Synth. Catal.* **2004**, *346*, 901–904.

