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Practical Selective Hydrogenation of α-Fluorinated Esters with Bifunctional Pincer-Type Ruthenium(II) Catalysts Leading to Fluorinated Alcohols or Fluoral Hemiacetals

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Supporting Information

ABSTRACT: Selective hydrogenation of fluorinated esters with pincer-type bifunctional catalysts RuHCl(CO)(dpa) **1a**, *trans*-$RuH_2(CO)$(dpa) **1b**, and *trans*-$RuCl_2(CO)$(dpa) **1c** under mild conditions proceeds rapidly to give the corresponding fluorinated alcohols or hemiacetals in good to excellent yields. Under the optimized conditions, the hydrogenation of chiral (*R*)-2-fluoropropionate proceeds smoothly to give the corresponding chiral alcohol without any serious decrease of the ee value.

An incorporation of fluorine atoms into organic molecules is of particular interest because of their unique biological, pharmaceuticals, and optoelectronic properties.[1,2] To access this important class of compounds, hydrogenation of fluorinated esters is one of the most straightforward and clean processes in organic synthesis. However, contrary to ketones, a limited progress in the hydrogenation of carboxylic esters despite of its tremendous potential for synthetic organic chemistry has been made during the last few decades.[3] The reduction of carboxylic acid derivatives still relies mostly on the stoichiometric use of metal hydrides. Since discovery in 2006 of the hydrogenation of esters with Milstein's pincer-type Ru catalysts,[4] a rapid advance of particularly ester hydrogenation has been achieved by utilization of bifunctional catalysts based on the metal−ligand cooperation.[5] Newly developed bifunctional catalysts can efficiently hydrogenate both activated and/or nonactivated esters. However, most catalyst systems still need relatively forced reaction conditions for the smooth reaction except for a limited number of catalyst systems.[6] Herein we disclose practical and selective hydrogenation of α-fluorinated esters with commercially available pincer-type bifunctional complex, RuHCl(CO)(dpa)[5e] **1a** (dpa = bis-(2-diphenylphosphinoethyl)amine) under mild conditions and its application to synthesis of fluorinated alcohols and fluoral hemiacetal intermediates from fluorinated esters. The present hydrogenation is a practical and environmentally benign access to fluorinated alcohols or hemiacetals, which are key compounds in synthetic organic chemistry.[1,2,7]

Our early works on the hydrogenation of esters and lactones with Cp*RuCl(L-N)[3,5c,d] (L-N: $(C_6H_5)_2P(CH_2)_2NH_2$, P-N), 2-$C_5H_4NCH_2NH_2$, N-N) as precatalysts clearly showed that fluorinated esters can be rapidly hydrogenated albeit under relatively forced conditions. These results prompted us to quest for practical catalyst systems for the hydrogenation of fluorinated esters to valuable fluorinated alcohols. We found that bifunctional catalyst RuHCl(CO)(dpa) **1a** efficiently effects hydrogenation of methyl difluoroacetate **2a** with S/C = 5000 in methanol containing sodium methoxide under 10 atm of H_2 at 40 °C giving fluorinated alcohols in almost quantitative yields as listed in Table 1. The reaction of methyl trifluoroacetate **2b** also gave satisfactory result. Notably, nonfluorinated methyl acetate and methyl trifluoropropionate bearing fluorine atoms at the β-position were hydrogenated inefficiently. Hence, the introduction of the fluorine atom at α-position of esters caused a marked increase in the rate of the reaction. Methanol is the solvent of choice for the present hydrogenation. THF and toluene gave unsatisfactory results. The catalyst **1a** is active enough at lower temperatures 5−30 °C to hydrogenate **2a**, **2b** giving the corresponding alcohols in reasonably good yields. The catalyst *trans*-$RuH_2(CO)$(dpa) **1b**, which is derived from **1a** (vide infra), exhibits similar catalytic activity within experimental accuracy. The complex *trans*-$RuCl_2(CO)$(dpa) **1c** also worked well albeit under longer reaction times. A substoichiometric amount of the base, $NaOCH_3$, is crucial for smooth reaction, although the role of the base is still unclear.[5d] After optimization of reaction conditions, a large-scale hydrogenation of **2a** with catalysts **1a** under an S/C = 20 000 at 40 °C proceeded completely for 23 h. After direct distillation, pure 2,2-difluoroethanol was obtained in 77% isolated yield.

Scheme 1. Selective Hydrogenation of Fluorinated Esters with Ruthenium Catalysts 1

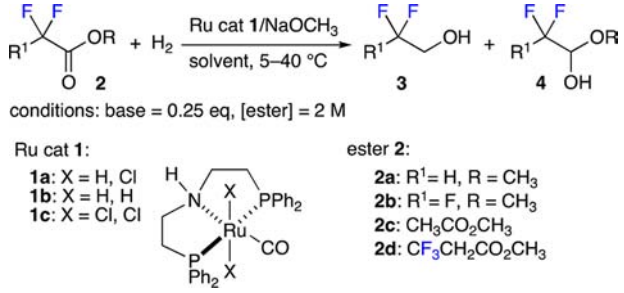

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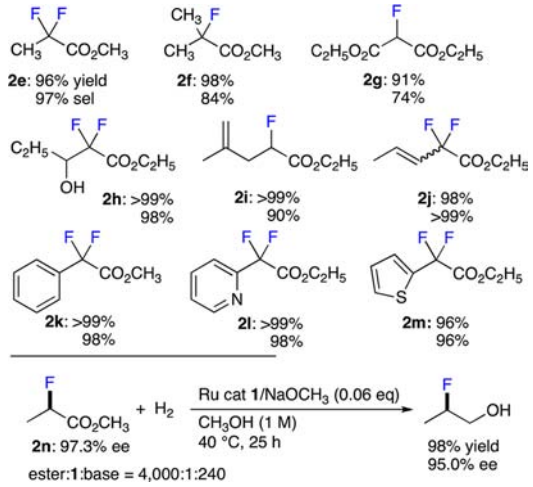
Table 1. Hydrogenation of Fluorinated Esters Catalyzed by RuHCl(CO)(dpa) or *trans*-$RuX_2(CO)(dpa)$ (X = H, Cl)[a]

run	cat	ester	S/C	solvent	time, h	temp, °C	H_2, atm	3 yield, %[b]
1	**1a**	**2a**	5000	CH_3OH	6	40	10	>99
2	**1a**	**2b**	2000	CH_3OH	24	40	25	98
3	**1a**	**2c**	5000	CH_3OH	18	40	10	17
4	**1a**	**2d**	2000	CH_3OH	22	40	30	5
5	**1a**	**2a**	5000	THF	19	40	10	39
6	**1a**	**2a**	5000	toluene	22	40	10	31
7	**1a**	**2a**	5000	CH_3OH	6	30	10	87
8	**1a**	**2a**	5000	CH_3OH	6	15	10	58
9	**1a**	**2a**	5000	CH_3OH	6	5	10	24
10	**1a**	**2a**	10 000	CH_3OH	8	40	10	>99
11	**1b**	**2a**	5000	CH_3OH	6	40	10	>99
12	**1c**	**2a**	5000	CH_3OH	21	40	10	65
13	**1c**	**2a**	1000	CH_3OH	23	40	10	>99

[a]Standard reaction conditions: substrate (40 mmol), ester:base = 1:0.25, solvent (20 mL). [b]Determined by GC or ^{19}F NMR.

Various α-fluorinated esters were smoothly hydrogenated to the corresponding fluorinated alcohols in methanol containing the catalyst **1a** and the base under mild conditions described in Chart 1. Aliphatic and aromatic difluoro esters were reducible

Chart 1. Scope of Substrates Including Chiral Ester



with good to excellent conversion and selectivity. In the case of aliphatic monofluoro esters, the reaction proceeded smoothly in high yields but less selectivity probably because of formation of the epoxide generated by cyclization from fluorinated primary alcohols.

Other functionalized groups in the esters, such as olefinic (**2i**, **2j**), α-pyridyl (**2l**), α-thienyl (**2m**) groups, are intact during the reaction. The carbonyl selective hydrogenation is applicable to synthesis of α-fluorinated unsaturated alcohols. For example, ethyl 2,2-difluoropentenoate (**2j**) was reduced to unsaturated alcohol with 99.6% selectivity (Chart 1), in which the *E*/*Z* ratio (94/6) of the substrate was invariable during the reaction. Noticeably, the hydrogenation of chiral (*R*)-2-fluoropropionate (**2n**) proceeded smoothly to give the corresponding alcohol in almost quantitative yield albeit with a low ee due to the basic conditions. To avoid long exposure of chiral esters to the strong base, the slow addition of **2n** during 14 h under otherwise identical condition was tried. It provided the corresponding chiral monofluorinated alcohol without any serious decrease of the ee value after 25 h reaction.

Thanks to excellent reactivity of the catalysts under mild conditions, fluorinated esters, including $CF_2HCO_2CH_3$ **2a**, $CF_3CO_2CH_3$ **2b**, $CClF_2CO_2CH_3$ **2o**, and $C_2F_5CO_2CH_3$ **2q**, were selectively hydrogenated with **1a** or **1b** in the reaction with S/C = 5000 to hemiacetal intermediates, which are among the most important synthons for organic synthesis.[7] As shown in Table 2, the outcome of the reaction was delicately influenced by the reaction conditions. In fact, a decrease of the reaction temperature to 15 °C in the hydrogenation of **2a** caused a drastic change in the product ratio of **3**/**4**, giving preferentially the corresponding hemiacetals **4** although in moderate yield. When hydrogen pressure was decreased under <10 atm at 40 °C, the hemiacetals **4b**, **4o**, and **4q** were obtainable preferentially. These results suggest that the highly fluorinated hemiacetal is stable enough to resist further conversion to alcohols under the reaction conditions. On the other hand, the reaction of bromodifluoroacetate **2p** provided unsatisfactory results in terms of the reactivity probably due to the steric effect of bromine atom. Notably, a decrease of the amount the base caused a preferential formation of hemiacetal (runs 4,9), although the precise role of the base is unclear. After optimization of hydrogenation conditions, a preparative scale reaction of methyl trifluoroacetate **2b**, 128 g with S/C = 20 000 using the catalyst **1a** gave fluoral hemiacetal **4b** in 89% yield and with 96% selectivity. After simple distillation 87 g of **4b** was obtained in 67% isolated yield.

The catalyst precursor, RuHCl(CO)(dpa) **1a**, was found to be readily converted to the real catalyst, *trans*-RuH_2dpa(CO) **1b** (δ ^1H −5.84 ppm, m, 2H, overlapped; $^1H\{^{31}P\}$ −5.81 ppm, brs, 1H; −5.86 ppm, brs, 1H; δ $^{31}P\{^1H\}$ 66.9 ppm, s) by treatment of **1a** with 1 equiv of *tert*-BuOK at −80 °C in THF-d_8 and following 10 min stirring at room temperature under the dihydrogen atmosphere. The resulting *trans*-$RuH_2(CO)(dpa)$ **1b** has an almost identical catalytic performance to RuHCl(CO)(dpa) **1a** in the ester hydrogenation as shown in Tables 1 and 2. Noticeably, contrary to the complex **1a**, the complex **1b** readily reacted with methanol to evolve vigorously H_2 gas. Similarly, the complex **1b** readily reacted with hemiacetal **4b** with H_2 release albeit less vigorously. Recently, methanol dehydrogenation to hydrogen gas[8a] or transformation of ethanol to ethyl acetate[8b,c] in the presence of complex **1a**/base was reported. These experimental data suggest existence of the dihydrogen complex on the reaction coordinate between **1b** with methanol or **4b**.

To gain the insights into the mechanism of selective hydrogenation of fluorinated esters to hemiacetals, theoretical studies on the hydrogenation of methyl trifluoroacetate as a model system were performed. The hydrogenation of $CF_3C(O)OCH_3$ into $CF_3CH(OH)OCH_3$ is exergonic ($\Delta G°_{298K}$ = −3.4 kcal·mol^{-1}) in continuum methanol reaction field under ωB97X-D/6-311++G**/SMD(CH_3OH) level of theory, whereas further dissociation of the hemiacetal into fluoral and CH_3OH is endergonic by 2.4 kcal·mol^{-1}. The α-fluorinated hemiacetals are known to be stabilized by strong electron-withdrawing groups giving stable compounds.[9] On the other hand, the hydrogenation of fluoral into CF_3CH_2OH is thermodynamically favorable, $\Delta G°_{298K}$ = −24.6 kcal·mol^{-1}, thus the present optimized conditions for the catalytic formation of the hemiacetal are a pure kinetic phenomenon. This is further supported by the experimental results: the molar ratio of $CF_3CH(OH)OCH_3/CF_3CH_2OH$ diminishes upon increasing the temperature or hydrogen pressure.

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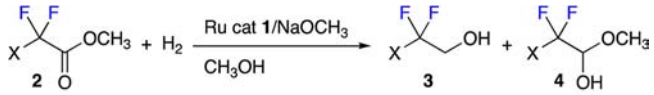
Table 2. Hydrogenation of Fluorinated Esters Catalyzed by RuHCl(CO)(dpa) or *trans*-RuX$_2$(CO)(dpa) (X = H, Cl)[a]



run	cat	ester	S/C	time, h	temp, °C	H_2, atm	yield, %[b]	3	4
1	**1a**	**2a**	5000	6	40	10	>99	100	0
2	**1a**	**2a**	5000	6	15	10	58	8	92
3	**1a**	**2b**	2000	6	40	20	99	85	15
4[c]	**1a**	**2b**	5000	6	40	10	92	9	91
5	**1a**	**2o**	2000	22	40	20	>99	100	0
6	**1a**	**2o**	2000	22	40	10	83	11	89
7	**1a**	**2p**	3000	22	40	30	<10	–	–
8	**1a**	**2q**	2000	22	40	10	58	100	0
9[c]	**1a**	**2q**	5000	22	40	5	84	20	80
10[c]	**1b**	**2b**	5000	8	40	10	89	8	92
11	**1c**	**2b**	3000	21	40	10	84	4	96

[a]Standard reaction conditions: substrate (40 mmol), ester:base = 1:0.25, CH_3OH solvent (20 mL). [b]Determined by GC or ^{19}F NMR. [c]Ester:base 1:0.1

We propose the mechanism of fluoral methyl hemiacetal formation as shown in Figure 1. Continuum methanol reaction

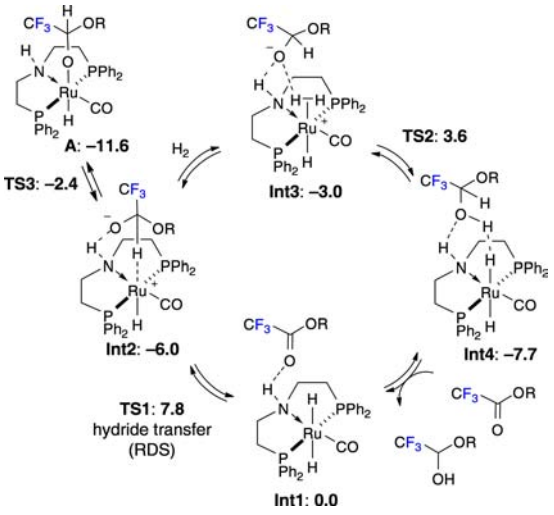
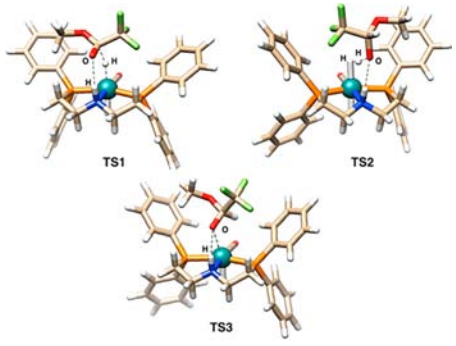


Figure 1. A possible catalytic cycle for the formation of trifluoroacetaldehyde methyl hemiacetal. All the free energies (ΔG°_{298K}, kcal·mol^{-1}) are calibrated relative to **Int1** ($R = CH_3$).

field DFT[10] analysis of unambridged molecules under ωB97X-D[11]/6-311++G**(C,H,N,O,F)/SDD(Ru) level of theory with the SMD[12] (solvation model based on density) reveals a very facile outer-sphere hydride transfer ($\Delta G^{\neq}_{298K}$ = 7.6 kcal·mol^{-1}) from the *trans*-RuH$_2$dpa(CO) **1b** to $CF_3C(O)OCH_3$ through H-bonded complex **Int1** via **TS1** (i611 cm^{-1}) via a two-step process to afford the inner-sphere ion pair[13] intermediate **Int2**. The intermediate **Int2** is stabilized via two hydrogen bonds, the strong ionic NH···$^-$OCH(OCH$_3$)(CF$_3$) and very weak "non-classical" Ru···(H)C bonds.[14] The presence of the later is suggested by the structural analysis: Slightly elongated C−H bond of the anion that is directed toward Ru atom with the $d_{C\text{-}H}$ of 1.1136 Å, $d_{Ru\cdots(H)C}$ 3.41 Å (cf. 3.73 Å, the sum of the van der Waals of radii of Ru and carbon),[15] angle Ru···H−C 127°.

The intermediate **Int2** is a branching point of the reaction. The N−H proton transfer from the Ru cation to the hemiacetal anion could afford directly the hemiacetal **4b** and the putative 16e Ru



amido complex. No stationary point was found when a constrained potential energy surface (PES) scan was performed along N−H or H···$^-$O coordinate along the vector N−H···O$^-$ in **Int2**. This is due to a very high basicity of the putative amido complex. The O$^-$ anion reorientation via **TS3** (i95 cm^{-1}) affords hemiacetaloxo complex A ($\Delta G^{\neq}_{298K}$ = 3.6 kcal·mol^{-1}). Because of the intrinsic nature of the hemiacetal anion, **Int2** is also intermediate to afford further fluoral and CH_3OH. The possibility for neutralizing the produced anion, $^-$OCH(OCH$_3$)(CF$_3$) by the media, rather than by N−H proton transfer from the Ru cationic complex, was also probed via mixed continuum/discrete solvation model containing up to 4 explicit methanol molecules. All the attempts to transfer the proton from methanol via different constrained PES scans were unsuccessful; all these scans resulted in the O$^-$ anion coordination to afford the hemiacetaloxo complex **A**. These results suggest that the anion is unlikely to be neutralized by the media, this is further supported by the very basic reaction conditions. The located stationary point of **A** is 5.6 kcal·mol^{-1} (ΔG°_{298K}) below **Int2**. Hence this complex could be a possible candidate for the resting state "off catalytic cycle". Among two outlined proton sources available in the media, there is a third possibility under hydrogenation condition, namely dihydrogen complex **Int3** obtained from **Int2** via the H_2 coordination. The located stationary point for **Int3** is only 3.0 kcal·mol^{-1} (ΔG°_{298K}) higher than **Int2**. The $d_{H\text{-}H}$ of 0.82 Å for the coordinated hydrogen places **Int3** into the category of the "true H_2 complexes".[16] The acidity of such η^2-H_2 compounds sometimes is as strong as that of sulphuric or triflic acid.[16] Indeed deprotonation of dihydrogen in **Int3** via **TS2** (i935 cm^{-1})

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leading to the dihydrogen-bonded intermediate **Int4** is very facile ($\Delta G^{\neq}_{298K}$ = 6.6 kcal·mol^{-1}). The dihydrogen bonding in the obtained DHB-adduct **Int4** precedes the proton transfer (reverse reaction) to afford the cationic dihydrogen complex **Int3** being a hydrogen-bonded ion pair. Such processes are well-documented in the literature.[17] The intermediate **Int1** is further regenerated by the reaction of **Int4** with the ester and product **4b** release into solution. Thus the rate-determining transition state[18] of the catalytic cycle is the outer-sphere hydride transfer (**TS1**) and not H_2 cleavage.[19]

In conclusion, selective hydrogenation of fluorinated esters **2** with highly efficient bifunctional RuHCl(CO)(dpa) **1a** or *trans*-RuH_2(CO)(dpa) **1b** catalysts proceeded rapidly under mild conditions to give the corresponding fluorinated alcohols in almost quantitative yields. Under the optimized conditions, the hemiacetals intermediates are obtainable from the reaction of α-fluorinated esters in good to excellent yields. DFT analysis of the selective hydrogenation of **2b** suggests that the hydride transfer from the dihydride complex **1b** to the ester occurs in the outer-sphere to produces a contact ion pair intermediate **Int2**. The latter further coordinates the molecular hydrogen and affords the final hemiacetal via intramolecular deprotonation, a step during which H-H bond is cleaved.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental procedure and analysis details. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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