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Ruthenium Catalyzed Hydrogenation of Aldehyde with Synthesis Gas

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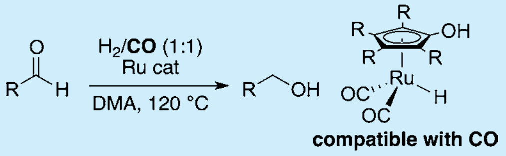
Supporting Information

ABSTRACT: The hydrogenation of aldehyde utilizing synthesis gas as a dihydrogen source was examined with various ruthenium catalysts, among which Ru−cyclopentadienone complexes (Shvo-type catalysts) exhibited higher activity than others. DFT calculations proved that the exchange of coordinated carbon monoxide by dihydrogen is relatively preferable in Shvo-type catalysts compared to others, which is a pre-equilibrium for the generation of the hydrogenation-active species.



Dihydrogen is a fundamental feedstock in industry and more than 500 billion m^3/year is consumed.[1a] Roughly 80% of the annual production of dihydrogen finds its use in chemical processes such as oil/coal refining and syntheses of ammonia, methanol, aldehyde, etc.[1b] Industrially, dihydrogen is most commonly prepared by steam reforming of petrochemicals to afford an admixture of dihydrogen and carbon monoxide, which is referred to as "synthesis gas",[1a] and successive purification steps require low temperature, high pressure, and/or chemical reaction processes.[1c] Since such separation steps are energy-consuming, direct use of synthesis gas as a dihydrogen source would be advantageous.

Efforts to utilize synthesis gas for hydrogenation can be seen in the tandem hydroformylation/hydrogenation of alkenes. Current industrial synthesis of *normal*-alcohol typically employ two sequential catalytic reactions: the hydroformylation of alkene to aldehyde by the reaction with synthesis gas[2] and the hydrogenation of the resulting aldehyde under pure dihydrogen.[3] A one-pot hydroformylation/hydrogenation process utilizing synthesis gas would be desirable where purification of dihydrogen from synthesis gas is omitted. Such a catalytic system has been well studied based on Co,[4a] Rh,[4b−h] Pd,[4i,j] and Ru[4k−m] centered catalysts. Previously, we demonstrated a dual catalyst system composed of Rh-based hydroformylation catalyst and Ru-based hydrogenation catalyst effective for the conversion[5] owing to the relatively high tolerance of Ru−cyclopentadienone complex (known as Shvo-type catalyst[6]) against poisoning by carbon monoxide compared to other Ru catalysts.

The unique feature of Shvo's catalyst (**1**) is described in Figure 1. Schematically, complex **1** is equivalent to **1′**, possessing a Ru metal center and a neighboring Lewis basic oxygen, which enable heterolytic cleavage of dihydrogen to give hydrogenation active Ru−H species. In this work, we present a comparative study of a series of Ru complexes with and without the neighboring Lewis base in hydrogenation of aldehyde with synthesis gas to reveal structural requirements for higher catalytic activity. Kinetic study and computational calculations based on density functional theory allowed us to propose that the higher catalytic activities observed with Shvo-type catalysts can be attributed to its relatively easy exchange of carbon monoxide by dihydrogen.

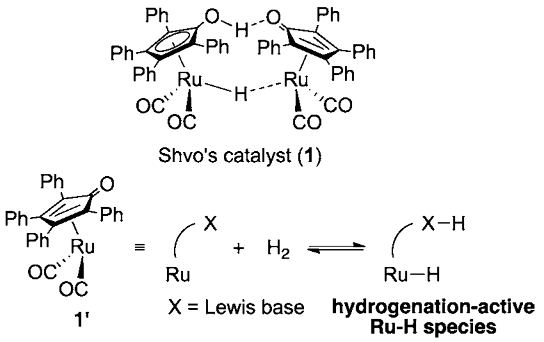


Figure 1. Schematic drawing of dihydrogen activation by Shvo's catalyst (**1**).

The catalytic activities of Ru-centered complexes are compared in Table 1. Unlike their original reports for hydrogenation under pure dihydrogen, the catalytic activity was lowered in all cases probably due to the catalyst poisoning by carbon monoxide.[7] Undecanal was treated with 2.5 mol % of catalyst under 2.0 MPa of synthesis gas (1 to 1 mixture of dihydrogen and carbon monoxide) in *N*,*N*-dimethylacetamide as a solvent at 120 °C, and the resulting average turnover frequencies (TOFs, h^{-1}) for undecanol are shown. Among the catalysts, Shvo's complex **1**[6a] (run 1) was significantly more active than other types of Ru catalysts with neighboring Lewis base; namely, nitrogen-based Shvo-type catalyst **2**[8] (run 2), Ru−phosphinoamine **3**[9] (run 3), and Ru−bis(phospinoamine) **4**[10] (run 4). The use of $Ru_3(CO)_{12}$ and $Ru(CO)H_2(PPh_3)_3$ catalysts without neighboring Lewis base also resulted in low

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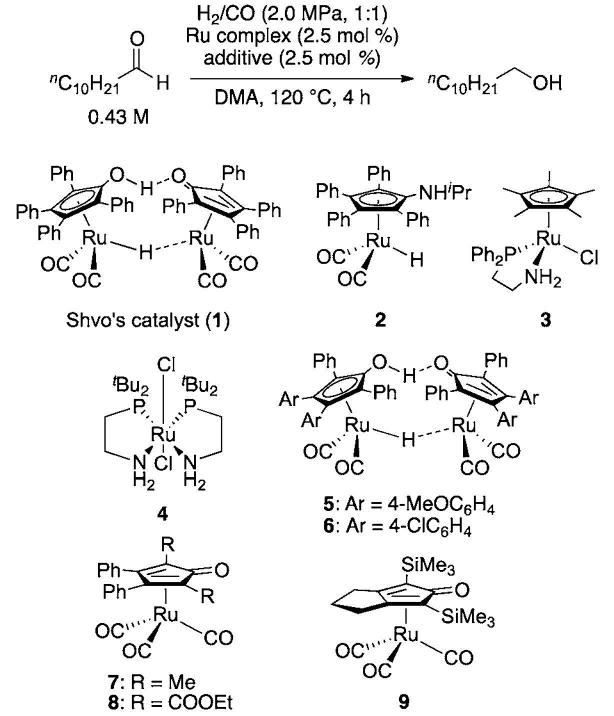
Table 1. Hydrogenation Activity of Various Ru Complexes[a]



run	cat.	conv (%)	yield (%)	TOF (h^{-1})
1	**1**	45	40	4.0
2	**2**	0	0	0
3	**3**[b]	21	<1	<0.1
4	**4**[b]	4	4	0.4
5	$Ru_3(CO)_{12}$[c]	<1	<1	<0.1
6	$Ru(CO)H_2(PPh_3)_3$[c]	5	4	0.1
7	**5**	49	42	4.2
8	**6**	41	31	3.1
9	**7**	37	32	3.2
10	**8**	20	10	1.0
11	**9**	8	2	0.2

[a] Conditions: undecanal 0.43 M, Ru complex 2.5 mol %, additive 2.5 mol %, H_2 1.0 MPa, CO 1.0 MPa, in *N,N*-dimethylacetamide, 120 °C, 4 h. Conversions of undecanal and yields of undecanol were determined by gas chromatography with dodecane as internal standard. [b] ^{t}BuOK was used as an additive. [c] 12 h.

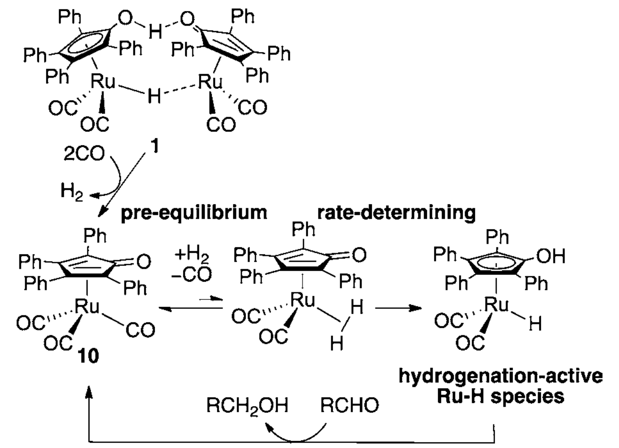
activities (runs 5 and 6). Derivatives of Shvo's complex were also examined. Introduction of substituents on the phenyl ring on cyclopentadienone[11a] made only minor differences (**5** and **6** in runs 7 and 8). On the other hand, more drastic changes of substituents on cyclopentadienone retarded the reaction. Neither methyl-,[11b] trimethylsilyl-,[5b] nor ethoxycarbonyl-substituted complex[5b] exhibited higher activity (**7**−**9** in runs 9−11), which could be interpreted that variation of electron density from **1** caused negative effect.[12]

The origin of distinct activities of Shvo-type catalysts compared to Ru−NH systems can be understood on the basis of mechanistic investigations (Scheme 1). In the previous work,[5b] complex **1** turned out to be rapidly converted to **10** under synthesis gas, and the rate-equation of hydrogenation of undecanal by **1** was determined as

$$d[\text{undecanal}]/dt = -k[H_2][Ru][CO]^{-1}[\text{undecanal}]^0$$

The generation of the hydrogenation-active Ru−H species requires the replacement of a carbon monoxide by a dihydrogen and sequential heterolytic cleavage of the hydrogen−hydrogen bond. After transfer of two hydrogen atoms to aldehyde, the resulting coordinatively unsaturated 16e complex is spontaneously coordinated by carbon monoxide to regenerate resting state **10**. Since the activation of a dihydrogen is the rate-determining step, the reaction rate is independent of undecanal concentration. In the case of **3** and **4**, coordinatively unsaturated 16e complexes after transfer of two hydrogen atoms are supposed to be trapped by carbon monoxide in ways similar to those for **1** to give resting states.[13] In order to explain the prominent activity of **1** compared to **3** and **4**, DFT calculations were performed for the generation of the active species from the resting states. For the calculation cost, *tert*-butyl groups on the phosphorus atoms of **4** were replaced by methyl groups. The whole picture is shown in Figure 2. It has been well studied that an alcohol molecule takes part in the metal−ligand concerted activation of dihydrogen, which was consistent with our computational study employing methanol as a model alcohol.[14] Namely, the lowest energy pathways start from proposed deactivated species stabilized by hydrogen bonding with methanol (**10-MeOH**, **11-MeOH**, or **12-MeOH**) followed by the exchange of carbon monoxide with dihydrogen to give **10-MeOH-H$_2$**, **11-MeOH-H$_2$**, or **12-MeOH-H$_2$**. Successive transition states of dihydrogen activation assisted by methanol (**10-TS**, **11-TS**, or **12-TS**) led to the hydrogenation active species **10-HH**, **11-HH**, or **12-HH**.[15] The result indicated that the exchange of carbon monoxide by dihydrogen is less endoergonic in the case of **10** compared to **11** and **12** (+23.5, +31.4, and +36.0 kcal/mol, respectively), whereas the activation energies for the dihydrogen-coordinated species to overcome the TSs are relatively low ($\Delta G^\ddagger$ = +3.8, +2.6 and −0.7 (no TS) kcal/mol respectively). Among the Shvo-type complexes derived from **1**, **2**, and **9**, the barrier for the carbon monoxide-dihydrogen exchange was similar to each other.[15] Therefore, the other steps should also contribute to the difference of the total turnover frequencies.

Scheme 1. Proposed Mechanism for the Hydrogenation of Aldehyde under H_2/CO



In summary, the catalytic hydrogenation of undecanal under synthesis gas with various Ru complexes was investigated. Remarkable activities of Shvo-type catalysts could be associated with relatively preferable exchange of carbon monoxide for dihydrogen, which is a pre-equilibrium for the rate-determining step. For the difference among Shvo-type catalysts, the dihydrogen-activation step should also contribute to the total

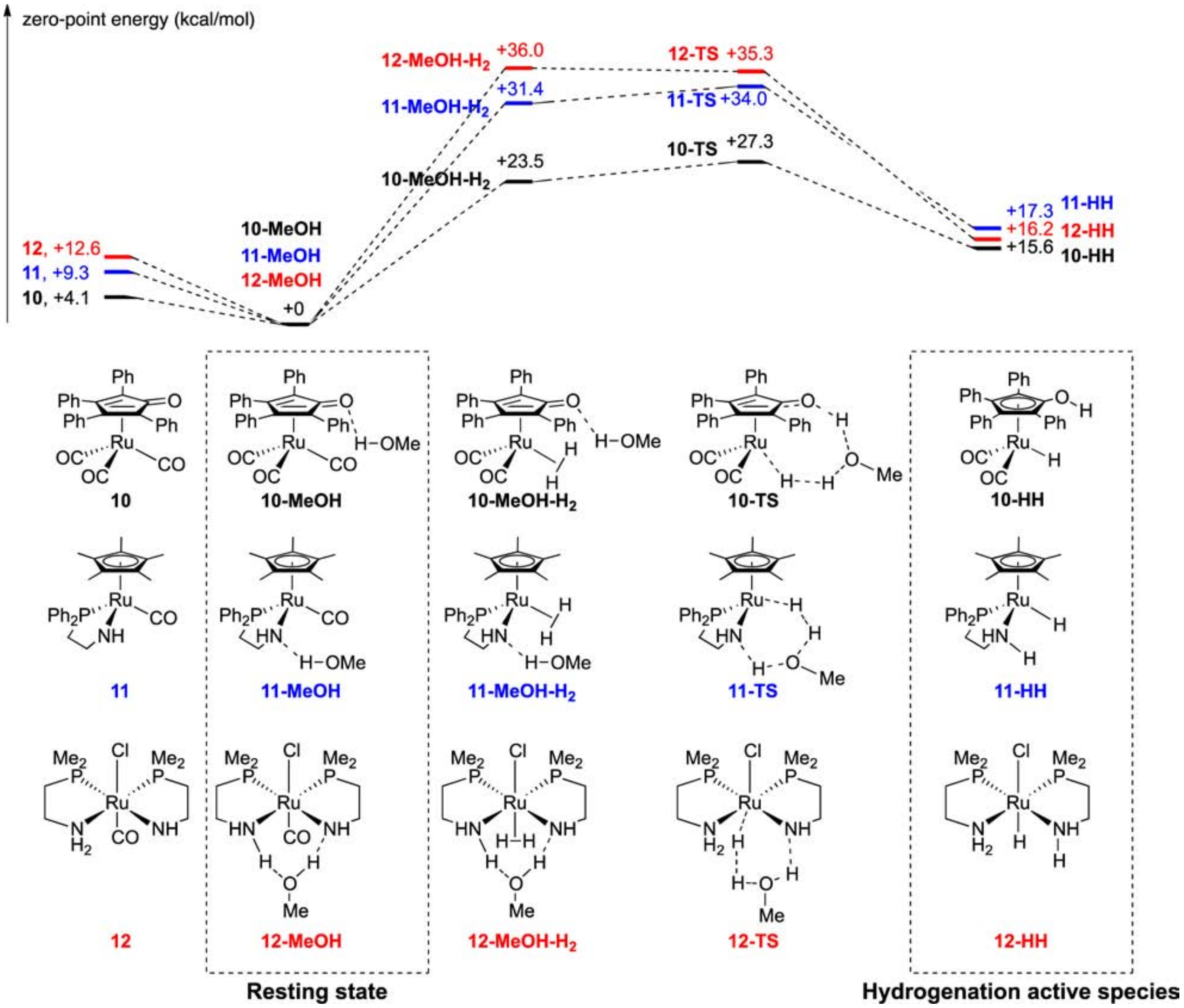


Figure 2. Energy level diagram for the generation of active species **10-HH**, **11-HH**, and **12-HH** from the deactivated species **10**, **11**, and **12** (B3LYP/6-31+G(d), LANL2DZ) with relative zero-point energies (kcal/mol).

reaction rate. Development of more carbon monoxide tolerant catalyst based on the present study is expected.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental and computational 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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■ DEDICATION

This paper is dedicated to Prof. Iwao Ojima on the occasion of his 70th birthday.

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(7) For example, the TOF at 60 °C by **1** under $H_2/CO = 1:1$ was estimated to be 4.9×10^{-3} h^{-1} from our results and in the absence of carbon monoxide reported as 3.2×10^{2} h^{-1} by Casey et al. (ref 6e), which corresponds to $\Delta G^{\ddagger} = +28.5$ kcal/mol and +21.2 kcal/mol, respectively.

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(12) The relative electron densities of Ru center of **7**, **8**, **9**, and **10** were estimated from IR bands for ligand C≡O stretch. The values were (complex: $\nu C{\equiv}O$ (cm^{-1})) = (**7**: 2066, 2011, 1989), (**8**: 2100, 2029, 2002), (**9**: 2070, 2006), (**10**: 2081, 2026, 2005), which represented the order of electron densities as **7** ≈ **9** > **10** > **8**.

(13) Examples of trap of coordinatively unsaturated 16e species by carbon monoxide are reported for Cp*Ru(PN) complex in: Wylie, W. N. O.; Lough, A. J.; Morris, R. H. *Organometallics* **2011**, *31*, 2137. For the results for $Ru(PN)_2$ complex, see: Wylie, W. N. O.; Lough, A. J. *Inorg. Chim. Acta* **1998**, *268*, 69.

(14) For previous experimental and/or computational studies, see ref 6d,g for Shvo's complex and ref 9 for the Cp*Ru(PN) complex. The RuP_2N_2 systemis discussed in: Hedberg, C.; Källström, K.; Arvidsson, P. I.; Brandt, P.; Andersson, P. G. *J. Am. Chem. Soc.* **2005**, *127*, 15083. A trace amount of water may have provided a proton at the beginning of the reaction. Similar acceleration by proton was reported in ref 6d.

(15) Reaction pathways free of methanol were also calculated to prove the higher energy barriers for the process with **10–12**. Full computational results for **2** and **9–12** are summarized in the Supporting Information.