

The Hydrogenation of Alkene Catalyzed by μ_3 -S/Se Bridging Heterometallic Cluster and Promoted by Oxygen Transfer Reagent

QING-SHAN LI, ER-RUN DING, SHU-LIN WU, YU-HUA ZHANG, and YUAN-QI YIN*

Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences,
Lanzhou, 730000, P. R. China

Received 3 March 1998

Accepted for publication 23 September 1999

The oxygen transfer reagent, $\text{Me}_3\text{NO} \cdot 2\text{H}_2\text{O}$ and PhIO, can distinctly promote the coordinative hydrogenation of hex-1-ene, methyl methacrylate, and styrene catalyzed by heterometallic carbonyl clusters, $(\mu_3\text{-S})\text{RuCo}_2(\text{CO})_9$ and $(\mu_3\text{-Se})\text{RuCo}_2(\text{CO})_9$. The tetrahedron structure of the metal cluster catalyst was confirmed by the single-crystal X-ray diffraction. The tetrahedral skeleton of the catalyst keeps intact in catalytic process. For hex-1-ene in methanol solution, $[\text{Hex-1-ene}]/[\text{Cat.}] = 200$, $[\text{Me}_3\text{NO} \cdot 2\text{H}_2\text{O}]/[\text{Cat.}] = 4$, $p = 5.0\text{--}6.0$ MPa, 60°C and 24 h are the best reaction conditions. A plausible mechanism of the promotion of the OTR is given.

Transition metal clusters attract a considerable attention recently [1–3]. One of the highlights of recent research is the application of metal clusters in catalysis [4–7].

However, there is little definitive evidence demonstrating conclusively that intact cluster skeleton serves as active homogeneous catalyst [2, 4]. Our research object is the application of a chiral skeletal cluster in an asymmetric reaction with an essential enantiomer excess of chiral product in the absence of any chiral organic auxiliary compounds [8, 9].

Due to the lability of conventional metal skeletal clusters, a facile fragmentation usually occurred under catalytic conditions. We advocate the use of transition metal clusters bound by stable, nonfluxional bridging ligands to inhibit the cluster fragmentation during catalytic process [8, 9]. We have solved this problem by synthesizing a series of chiral metal skeletal clusters containing μ_3 -S/Se bridging ligand [10–13]. A high stability of these metal skeletons during catalysis process has been confirmed [8]. Nevertheless, a subsequent question is the fairly low hydrogenation activities of these skeletal catalysts. Thus, the first problem is how to improve the skeletal activities of the catalyst in activation and transformation of hydrogen in catalysis. Here, we report on the hydrogenation of hex-1-ene, styrene, and methyl methacrylate catalyzed by a heterometallic cluster and promoted by oxygen transfer reagent (OTR), $\text{Me}_3\text{NO} \cdot 2\text{H}_2\text{O}$ and PhIO.

EXPERIMENTAL

All the solvents were dried by the previously reported method. $(\mu_3\text{-S})\text{RuCo}_2(\text{CO})_9$ [14], $(\mu_3\text{-Se})\text{RuCo}_2(\text{CO})_9$ [14], $\text{Me}_3\text{NO} \cdot 2\text{H}_2\text{O}$ [15] and PhIO [16] were prepared according to the literature. All the solvents and other reagents were of anal. grade.

IR spectra were recorded with a Nicolet FTIR 10DX spectrometer using KBr discs in the range $400\text{--}4000\text{ cm}^{-1}$. The organic products obtained in the catalytic reactions were analyzed with a Shanghai FID 1102-II gas chromatograph (Shanghai Apparatus Factory), equipped with a SE-52 capillary column ($0.3\text{ mm} \times 25\text{ m}$) [17]. The identification of hex-2-ene and hex-3-ene was carried out on an HP-5988A GC-MS spectrometer by comparison with their standard MS spectra.

Unless otherwise specified the hydrogenation was performed in sealed stainless steel vials (50 cm^3 volume), each containing 10 cm^3 of methanolic solution of a cluster and an alkene. The vial was flushed with hydrogen 3 times and was kept in thermostated oil for the chosen time on a magnetic stirrer. Details of the concentrations of clusters and substrates, and catalytic conditions are given in Table 1.

X-Ray Crystallography

The catalysts, $(\mu_3\text{-S/Se})\text{RuCo}_2(\text{CO})_9$, were measured by X-ray crystal diffraction to confirm their

*The author to whom the correspondence should be addressed.

Table 1. The Hydrogenation and Isomerization of Hex-1-ene Promoted by OTR^a

No.	[OTR]/[Cat.]	Mole ratio	Conv./%	Yield/%		
				Hexane	Hex-3-ene	Hex-2-ene
1	Me ₃ NO · 2H ₂ O/SRuCo ₂ (CO) ₉	0/1	1.0	1.0		
2	Me ₃ NO · 2H ₂ O/SRuCo ₂ (CO) ₉	1/1	2.4	2.4		
3	Me ₃ NO · 2H ₂ O/SRuCo ₂ (CO) ₉	2/1	17.8	8.0	5.9	3.9
4	Me ₃ NO · 2H ₂ O/SRuCo ₂ (CO) ₉	3/1	96.6	10.1	63.3	23.2
5	Me ₃ NO · 2H ₂ O/SRuCo ₂ (CO) ₉	4/1	56.2	20.7	20.8	14.7
6	Me ₃ NO · 2H ₂ O/SeRuCo ₂ (CO) ₉	0/1	—			
7	Me ₃ NO · 2H ₂ O/SeRuCo ₂ (CO) ₉	1/1	1.6	1.6		
8	Me ₃ NO · 2H ₂ O/SeRuCo ₂ (CO) ₉	2/1	12.1	4.1	4.8	3.2
9	Me ₃ NO · 2H ₂ O/SeRuCo ₂ (CO) ₉	3/1	18.5	7.2	6.9	4.4
10	Me ₃ NO · 2H ₂ O/SeRuCo ₂ (CO) ₉	4/1		Compare Table 3		
11	PhIO/SRuCo ₂ (CO) ₉	0/1	5.5	3.7	1.1	0.7
12	PhIO/SRuCo ₂ (CO) ₉	3/1	10.0	5.4	2.6	2.0
13	Me ₃ NO · 2H ₂ O/SRuCo ₂ (CO) ₉	3/1	61.7	9.0	31.6	21.1

a) Reaction conditions: methanol, 10 cm³; hex-1-ene, 4 mmol (0.5 cm³); catalyst (Cat.), 0.02 mmol. 1–10: pressure (*p*) = 4.0 MPa; temperature (*θ*) = 60 °C; time (*τ*) = 24 h; 11, 12: *p* = 5.0 MPa; *θ* = 60 °C; *τ* = 24 h; 13: *p* = 5.0 MPa; *θ* = 50 °C; *τ* = 12 h.

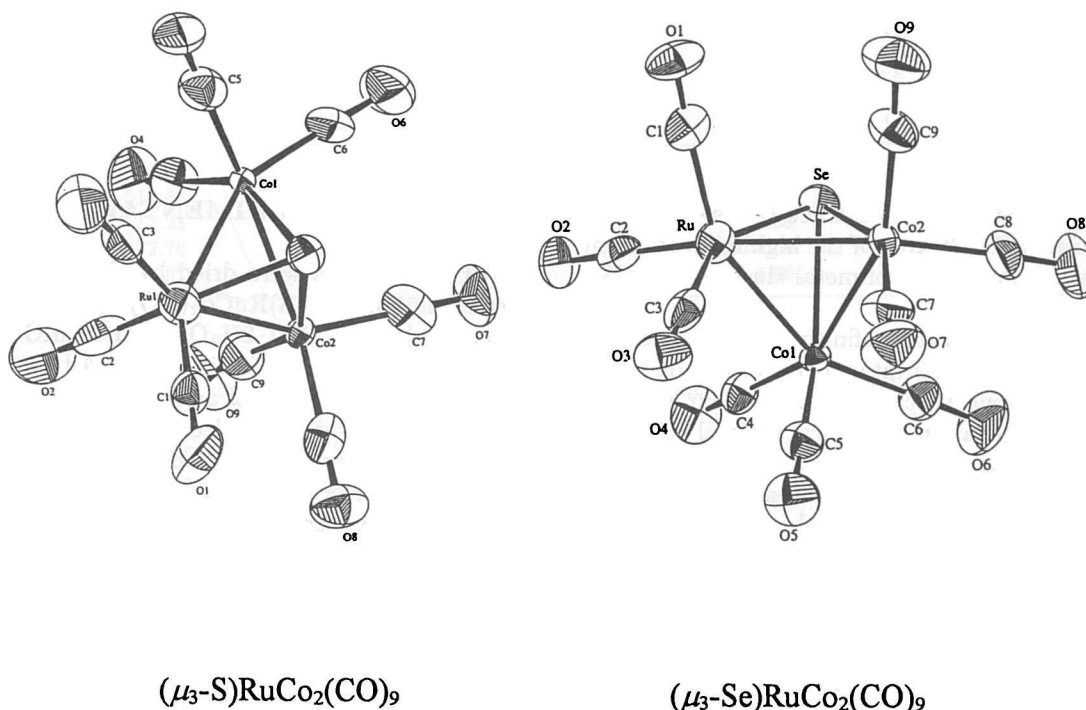


Fig. 1. The single-crystal structure of $(\mu_3\text{-S/Se})\text{RuCo}_2(\text{CO})_9$. Selected bond lengths (nm) and angles (°): in $(\mu_3\text{-S})\text{RuCo}_2(\text{CO})_9$, Ru(1)—Co(1) 0.2671(3), Ru(1)—Co(2) 0.2620(3), Ru(1)—S(1) 0.2240(5), Co(1)—Co(2) 0.2620(3), Co(1)—S(1) 0.2253(5), Co(2)—S(1) 0.2230(5); Co(1)—Ru(1)—Co(2) 59.35(7), Co(1)—Ru(1)—S(1) 53.8(1), Co(2)—Ru(1)—S(1) 53.9(1), Ru(1)—Co(1)—Co(2) 59.35(7), Ru(1)—Co(1)—S(1) 53.3(1), Co(1)—Co(2)—S(1) 54.7(1), Co(2)—Co(1)—S(1) 53.8, Ru(1)—Co(2)—S(1) 54.3; in $(\mu_3\text{-Se})\text{RuCo}_2(\text{CO})_9$, Ru—Se 0.2368(1), Ru—Co(1) 0.2594(1), Ru—Co(2) 0.2623(1), Se—Co(1) 0.2343(1), Se—Co(2) 0.2358(1), Co(1)—Co(2) 0.2597(1); Se—Ru—Co(1) 56.12(4), Se—Ru—Co(2) 56.10(4), Co(1)—Ru—Co(2) 59.70(3), Ru—Se—Co(1) 66.81(4), Ru—Se—Co(2) 67.43(4), Co(1)—Se—Co(2) 67.07(4), Ru—Co(1)—Co(2) 60.72(3), Se—Co(1)—Co(2) 56.75(4).

tetrahedral structures with a $\mu_3\text{-S/Se}$ bridging ligand.

The red prismatic crystals used for X-ray determination were obtained from their hexane solution at 0 °C. Preliminary examination and data collection were performed on a Rigaku AFC7R diffractometer with graphite monochromated Mo-*K* α radiation and a 12

kW rotating anode generator.

$(\mu_3\text{-S})\text{RuCo}_2(\text{CO})_9$: triclinic; lattice parameters, *a* = 1.3207(3) nm, *b* = 1.3505(3) nm, *c* = 0.9733(2) nm, α = 108.26(2)°, β = 97.16(2)°, γ = 109.37(2)°, *V* = 1.5036(6) nm³; space group, P1; *Z* = 2; *R* = 0.060; *R*_w = 0.080 (Fig. 1).

Table 2. The Promotion of OTR of the Hydrogenation of Other Alkenes

No.	Substrate	[OTR]/[Cat.]	Mole ratio	Conv./%	Yield/%
14	Methyl methacrylate	Me ₃ NO · 2H ₂ O/SRuCo ₂ (CO) ₉	0/1	20.3	—
15		Me ₃ NO · 2H ₂ O/SRuCo ₂ (CO) ₉	3/1	60.7	41.6
16		Me ₃ NO · 2H ₂ O/SeRuCo ₂ (CO) ₉	0/1	10.6	0.5
17		Me ₃ NO · 2H ₂ O/SeRuCo ₂ (CO) ₉	4/1	31.1	10.0
18	Styrene	Me ₃ NO · 2H ₂ O/SRuCo ₂ (CO) ₉	0/1	23.2	0.72
19		Me ₃ NO · 2H ₂ O/SRuCo ₂ (CO) ₉	3/1	58.4	18.8
20		Me ₃ NO · 2H ₂ O/SeRuCo ₂ (CO) ₉	0/1	32.0	2.2
21		Me ₃ NO · 2H ₂ O/SeRuCo ₂ (CO) ₉	3/1	65.4	25.6

Reaction conditions, 14—17: substrate methyl methacrylate, 9.4 mmol (1 cm³); methanol, 10 cm³; (μ_3 -S/Se)RuCo₂(CO)₉, 0.02 mmol; *p* = 6.0 MPa; θ = 60 °C; τ = 24 h; 18—21: substrate styrene, 8.7 mmol (1 cm³); methanol, 10 cm³; (μ_3 -S/Se)RuCo₂(CO)₉, 0.02 mmol; *p* = 6.0 MPa; θ = 50 °C (for 18 and 19); θ = 60 °C (for 20 and 21); τ = 24 h.

Table 3. The Effects of Hydrogen Pressure and Reaction Temperature on Hydrogenation and Isomerization of Hex-1-ene

No.	<i>p</i> /MPa	θ /°C	Conv./%	Yield/%		
				Hexane	Hex-3-ene	Hex-2-ene
22	3.0	60	66.2	6.5	35.1	24.6
5	4.0	60	56.2	20.7	20.8	14.7
23	5.0	60	52.3	26.6	15.3	10.4
24	6.0	60	98.4	27.0	58.3	13.1
25	6.0	70	95.9	16.4	55.8	23.7
26	4.0	40	5.3	4.5	—	0.8
27	4.0	50	18.6	7.2	6.9	4.5
10	4.0	60	64.5	9.2	32.2	23.1
28	6.0	50	18.9	8.4	7.1	3.4
29	7.0	70	83.0	15.0	44.7	23.3

Reaction conditions: methanol, 10 cm³; hex-1-ene, 4 mmol (0.5 cm³); catalyst (Cat.), 0.02 mmol; Me₃NO · 2H₂O, 0.08 mmol; [OTR]/[Cat.] = 4 (mole ratio); τ = 24 h. 22, 5, 23—25: Cat. SRuCo₂(CO)₉; 26, 27, 10, 28, 29: Cat. SeRuCo₂(CO)₉.

(μ_3 -Se)RuCo₂(CO)₉: triclinic; lattice parameters, *a* = 0.8893(2) nm, *b* = 1.1564(3) nm, *c* = 0.8048(2) nm, α = 100.29(2)°, β = 111.25(2)°, γ = 86.37(2)°, *V* = 0.7590(3) nm³; space group, P1; *Z* = 2; *R* = 0.053; *R_w* = 0.079.

The carbonyls are all terminal in (μ_3 -S/Se)RuCo₂(CO)₉.

RESULTS AND DISCUSSION

The Promotion of OTR to the Hydrogenation of Alkene

The catalysis shows a low catalytic activity in the hydrogenation and isomerization of hex-1-ene, but a distinct improvement is obtained when promoted by OTR, Me₃NO · 2H₂O or PhIO, in catalytic conditions (Table 1). However, the promotion of OTR is not so obvious until [Me₃NO · 2H₂O]/[(μ_3 -S/Se)RuCo₂(CO)₉] = 4 and [PhIO]/[(μ_3 -S)RuCo₂(CO)₉] = 3 (mole ratio), perhaps for the reason that the strong reduction conditions of high pressure hydrogen atmosphere make the oxidation of OTR lower (reactions 1—5 and 6—10). Comparing to that of Me₃NO · 2H₂O, the promotion of PhIO is somewhat

weaker, due to the existence of the following equilibrium in methanol solution (reactions 11—13).



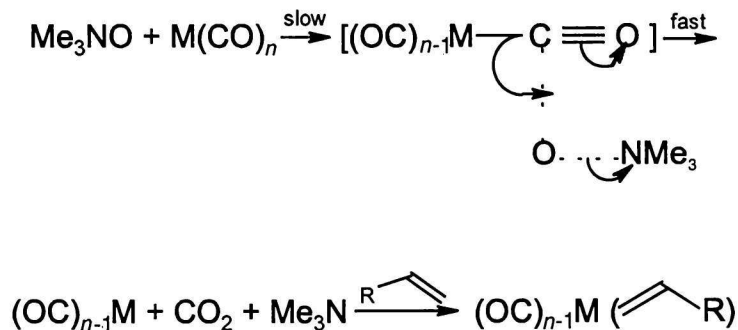
The promotion of OTR to the mixed-metal cluster also appeared in the catalytic hydrogenation of other alkenes, such as methyl methacrylate and styrene. The detailed results and catalytic conditions are listed in Table 2.

The Optimization of the Catalytic Conditions for the Hydrogenation and Isomerization of Hex-1-ene

The hydrogen pressure and reaction temperature have a great effect on the hydrogenation and isomerization of hex-1-ene. The increase of hydrogen pressure favours the hydrogenation, and the increase of temperature favours the isomerization of hex-1-ene (Table 3).

Mechanism of the Promotion of the OTR

The plausible mechanism of the promotion of the OTR can be elucidated as Scheme 1. The nucleophilic



Scheme 1

atom O of Me_3NO favours the attack mainly at a carbonyl carbon equivalent to a carbonyl converting to CO_2 released. Thus, the unsaturated intermediate can offer the substrate more opportunity to coordinate to the metal cluster [18, 19], which is the essential requirement in the hydrogenation of alkene. Therefore, the $(\text{OC})_{n-1}\text{M}$ can be believed to be an active intermediate complex.

IR Spectra of the Catalysts

The absorptions of carbonyl appeared at 2105 cm^{-1} , 2053 cm^{-1} , 1979 cm^{-1} and 2102 cm^{-1} , 2049 cm^{-1} , 1986 cm^{-1} in the respective $(\mu_3\text{-S})\text{RuCo}_2(\text{CO})_9$ and $(\mu_3\text{-Se})\text{RuCo}_2(\text{CO})_9$. The comparison of the IR spectra between the new species separated after reaction and the original cluster shows no obvious changes in carbonyl region, either in frequency or in intensity. The new absorptions appearing at 700.2 cm^{-1} , 758.1 cm^{-1} , 1599.1 cm^{-1} , and 3026.5 cm^{-1} in the IR spectra of the catalyst separated after reaction 8 (Table 2) suggest that the substrate styrene coordinated to the metal cluster, in other words, the skeleton of the cluster keeps intact in catalytic process.

REFERENCES

1. Qian, Y.-L. and Chan Albert, S. C., *Organometallic Chemistry and Catalysis*. Chemical Industry Press, Beijing, 1997.
2. Qian, Y.-L. and Liao, Shihtsien, *Advances in Homogeneous Catalysis*, p. 381. Chemical Industry Press, Beijing, 1989.
3. Richter, F. and Vahrenkamp, H., *Angew. Chem. Int. Ed. Engl.* 19, 65 (1980).
4. Pittman, C. U., Jr., Richmond, M. G., Absi-Halabi, M., Beurich, H., Richter, F., and Vahrenkamp, H., *Angew. Chem., Int. Ed. Engl.* 21, 786 (1982).
5. Mani, D. and Vahrenkamp, H., *J. Mol. Catal.* 29, 305 (1985).
6. Richmond, M. G., Absi-Halabi, M., and Pittman, C. U., Jr., *J. Mol. Catal.* 22, 367 (1984).
7. Mani, D., Schacht, H. T., Powell, A., and Vahrenkamp, H., *Organometallics* 9, 1360 (1987).
8. Li, Q. S., Ding, E. R., Liu, S. M., and Yin, Y. Q., *Chem. J. Chinese Univ. (Ch.)* 18, 1007 (1997).
9. Yin, Y. Q., Li, Q. S., Ding, E. R., and Zhao, Z. Y., *J. Mol. Catal. (Ch.)* 11 (6), 445 (1997).
10. Ding, E. R., Liu, S. M., Yin, Y. Q., and Sun, J., *Polyhedron* 16, 2387 (1997).
11. Ding, E. R., Liu, S. M., Zhao, Z. Y. Yin, Y. Q., and Sun, J., *Polyhedron* 16, 3273 (1997).
12. Wu, H. P., Yin, Y. Q., and Yang, Q. C., *Inorg. Chim. Acta* 245, 143 (1996).
13. Wu, H. P., Yin, Y. Q., Huang, X. Y., and Yu, K. B., *J. Organomet. Chem.* 498, 119 (1995).
14. Roland, E., Bernhardt, W., and Vahrenkamp, H., *Chem. Ber.* 119, 2566 (1986).
15. Dunstan, W. R. and Goulding, E., *J. Chem. Soc.* 75, 1005 (1899).
16. Saltzman, H. and Sharefkin, J. G., *Org. Synth.* 43, 60 (1963).
17. *The Handbook of Analytical Chemistry*, Part 4, Chromatographic Analysis, p. 318. Chemical Industry Press, Beijing, 1984.
18. Shi, Y. L., Gao, Y. C., and Shi, Q. Z., *Organometallics* 6, 1528 (1987).
19. Shen, J. K., Shi, Y. L., Shi, Q. Z., and Basolo, F., *J. Am. Chem. Soc.* 110, 2414 (1988).