Journal of Catalysis **205,** 294–298 (2002)
doi:10.1006/jcat.2001.3429, available online at http://www.idealibrary.com on IDEAL®

Extremely Active Catalysts for the Hydrogenation of Terminal Alkenes

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Received June 5, 2001; revised October 1, 2001; accepted October 1, 2001; published online January 3, 2002

Titanocene complexes combined with nanometer-size sodium hydride are extremely active and selective catalysts for the hydrogenation of terminal alkenes under normal pressure. The initial turnover frequencies ($TOF_{initial}$) may reach 100–300 s^{-1} in the hydrogenation of 1-hexene. The highest catalytic efficiency turnover (TO) reaches 1.5×10^5 in 2 h for the hydrogenation of styrene. These catalytic systems exhibit specific selectivity toward alkene substrates. Only terminal alkenes can be hydrogenated. No isomerization of carbon–carbon double bonds occurs during hydrogenation. A suitable substituent on the cyclopentadienyl ring of titanocene and the use of nanometric sodium hydride are key factors in the high efficiency of these catalytic systems.

Key Words: **catalytic hydrogenation; nanometric sodium hydride; substituted titanocene complexes; alkenes.**

INTRODUCTION

A bicomponent catalyst composed of a titanocene complex and a reducing agent for the hydrogenation of unsaturated hydrocarbons has attracted much attention (1–17). Among the reducing agents employed, lithium alkyls, aluminum alkyls, Grignard reagent, lithium aluminum hydride and its derivatives, as well as alkali metals have been widely studied (18–23). In previous papers we have reported the use of alkali metal hydride in a very active form as a cocatalyst for titanocenes to form active catalysts for the hydrogenation of unsaturated hydrocarbons (14, 17). These catalysts display high activity; however, the catalyst stability is still not satisfactory. If the breakdown in catalytic activity could be postponed, the catalyst efficiency would be significantly improved. In this paper the effect of titanocenes with substituents of varying bulkiness on the cyclopentadienyl ring is reported. A nanometer-size sodium hydride is used as a co-catalyst. The reaction conditions have been optimized to achieve very high catalyst activity and efficiency.

EXPERIMENTAL

All the substituted titanocenes used in the experiments were prepared in the laboratory. Methods for synthesizing these substituted titanocenes have been published elsewhere (23–26). All reactions and operations were carried out under dry argon using the Schlenk technique. Argon and hydrogen were dried and deoxygenated by a type 5A molecular sieve column and an activated Cu column at 220°C. Tetrahydrofuran (THF), toluene, 1-hexene, 2-hexene, 1-octene, 2-octene, phenylacetylene, and styrene were dried over a type 5A molecular sieve, then refluxed, and finally distilled from sodium benzophenone under argon immediately before use. High-purity hydrogen (>99.995%) was used for the catalytic experiments. $TiCl_4$ was distilled before use. Sodium and naphthalene were commercial products and used as purchased.

The nanometric sodium hydride (27) was prepared by adding metallic sodium (100 matom, cut into 10 pieces) and naphthalene (5 mmol) to an already evacuated dry reaction vessel, which was then filled with argon. This was evacuated at 10^{-2} Torr for 30 min to remove the volatile impurities from the sodium metal surface and filled with argon again. THF (40 ml) and $TiCl_4$ (2 mmol) were then added under argon. The argon was evacuated, and hydrogen was passed into the reaction vessel. The uptake of hydrogen was measured with a constant-pressure gas burette. The reaction was maintained at 40°C in an oil bath, and the reaction mixture was stirred magnetically. The prepared hydride slurry was centrifuged, and the solids were washed three times with THF and then evacuated to dryness at 80°C. The specific surface area of NaH is 90 m^2/g, as calculated from BET measurements. A transmission electron micrograph shows that the average primary particle size of NaH is 23 nm. The commercial sodium hydride (Serva Feinbiochemica) was washed three times with THF and then evacuated to dryness at 80°C.

The hydrogenation of 1-hexene was carried out in a 50-ml three-necked, jacketed flask closed with a self-sealing silicon rubber septum and connected to the vacuum, argon, hydrogen lines, and to a constant-pressure gas burette. The

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0021-9517/02 $35.00

temperature of the water circulating through the jacket was maintained by a thermostat. Agitation was provided by a magnetic stirrer. The reaction flask was alternately evacuated and flushed with argon three times, and the hydride was added. After alternate evacuation and flushing with hydrogen three times further, 10 ml of toluene, 2 ml of 1-hexene, and the catalyst were injected through the silicon rubber septum, and hydrogen uptakes were immediately followed using a constant-pressure gas burette. The reaction mixture was analyzed by GC in the hydrogenation.

TABLE 1

Effect of Titanocene Concentration on Catalytic Activity and Efficiency in the Hydrogenation of 1-Hexene Catalyzed by 4/NaH[a]

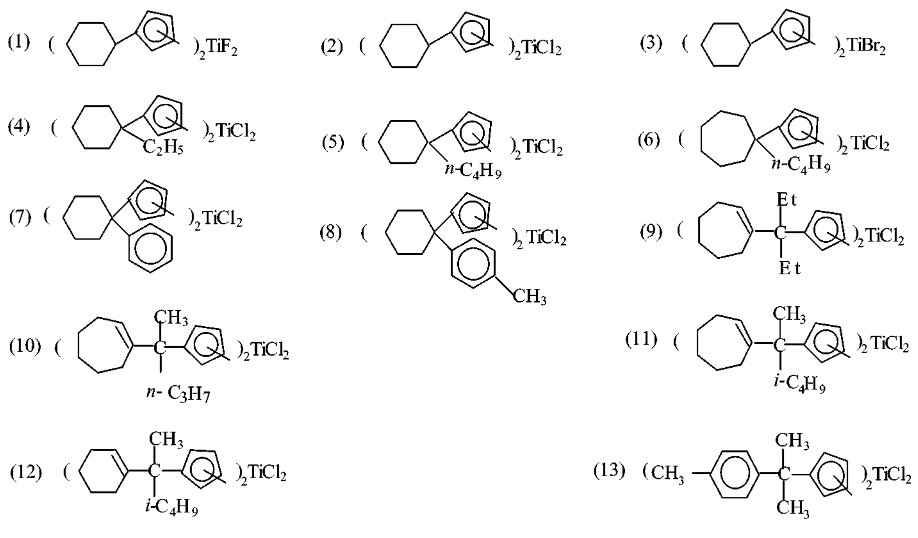
Titanocene concentration (μmol/L)	$\mathrm{TOF}_{\mathrm{initial}}$ (s^{-1})	TO	$\mathrm{TO/TOF}_{\mathrm{initial}}$
67	81	17,000	210
33	139	30,700	221
17	209	43,200	207
6.7	298	33,000	111

[a] Reaction conditions: 20°C, 1 atm H_2, 2 h, rate of agitation 1100 r/min, 10 ml toluene, 2 ml 1-hexene, 12 mg NaH.

RESULTS AND DISCUSSION

The common disadvantage of bicomponent hydrogenation catalysts composed of titanocenes and alkali metal hydride is their poor stability. Although they usually exhibit very high initial catalytic activities, the catalytic efficiencies are not high enough in comparison to the high initial catalytic activities. To increase the catalytic efficiency, the stability of the active species must be increased. For these titanium catalysts, it is generally believed that the breakdown in catalytic activity is due to the dimerization of titanium species in a low valent state (3, 4). The use of titanocene with a bulky substituent might hinder the dimerization of active species. In this paper, we use ring-substituted titanocenes with varying substituent bulkiness in combination with nanoparticles of sodium hydride for the hydrogenation of unsaturated hydrocarbons. Scheme 1 shows the titanocenes with substituted groups of varying bulkiness on the cyclopentadienyl ring that were investigated in the experiments.

For extremely active catalysts, the choice of reaction parameters is very important to avoid the influence of diffusion or even diffusion control on the rate of reaction. In the hydrogenation reaction in the gas–liquid phase this diffusion includes the solution of hydrogen gas through the gas–liquid interphase and the diffusion of dissolved hydrogen and substrate in the solvent. To ensure that the reaction is free from the diffusion problem, the rate of agitation is important to provide a sufficiently large gas–liquid interphase. For an extremely active catalyst, the use of a high rate of agitation alone sometimes cannot solve the diffusion problem entirely. In this case, an extremely small amount of catalyst should be employed. The results listed in Table 1 show the influence of titanocene concentration on catalytic activity and efficiency in the hydrogenation of 1-hexene. When the titanocene concentration is decreased, both initial catalytic activity ($\mathrm{TOF}_{\mathrm{initial}}$, average value in the first 30 s) and catalytic efficiency (TO in 2 h) are increased significantly. When the titanocene concentration is decreased to 0.67 μmol/L, although the $\mathrm{TOF}_{\mathrm{initial}}$ is still higher, the catalytic efficiency becomes lower. This lower catalytic efficiency might be due to the cumulative impurities from hydrogen gas, especially with the presence of a trace amount of moisture which cannot be entirely excluded. In our previous reports (14, 17), the catalytic activity and efficiency



SCHEME 1

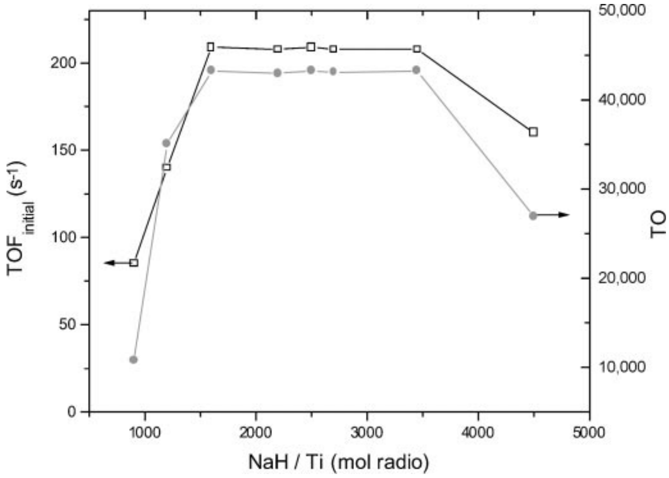


FIG. 1. Effect of NaH/Ti ratio on catalytic activity and efficiency in the hydrogenation of 1-hexene catalyzed by 4/NaH.

were lower, mainly because the catalyst concentration was not low enough to ensure the exclusion of the effect of diffusion. The ratio of NaH to titanocene also plays a role in catalytic behavior. Catalytic activity and efficiency attain their maximum at NaH/Ti ratios between 1600 and 3460. However, TOF$_{initial}$ and TO drop at still higher ratios (Fig. 1). The rate of agitation of the reaction mixture also affects the reaction performance. Fig. 2 shows the variation of TOF$_{initial}$ and TO with the rate of agitation. After the rate of agitation is increased to 850 rpm in the experimental reactor, a further increase in the stirring rate no longer changes the catalytic performance, which indicates the elimination of the influence of diffusion. In the following tables and figures, all experiments were carried out at an agitation rate of 1100 rpm and with a titanocene concentration of 17 μmol/L.

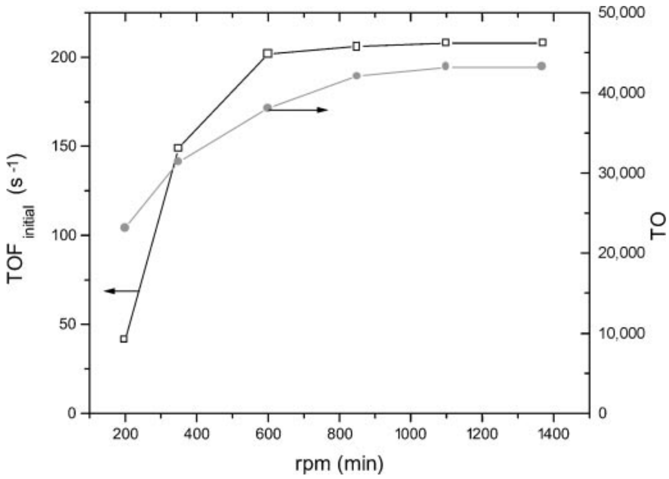


FIG. 2. Effect of the rate of agitation on the catalytic activity and efficiency in the hydrogenation of 1-hexene catalyzed by 4/NaH.

TABLE 2

Hydrogenation of 1-Hexene Catalyzed by Various Titanocenes Using NaH as Co-catalyst[a]

Entry	Catalyst	TOF$_{initial}$ (s^{-1})	TO	TO/TOF$_{initial}$
1	Cp_2TiCl_2/NaH	313	25,300	81
2	Cp_2TiF_2/NaH	306	25,000	82
3	1/NaH	231	32,200	139
4	2/NaH	238	32,700	137
5	3/NaH	228	31,700	139
6	4/NaH	209	43,200	207
7	5/NaH	179	27,600	154
8	6/NaH	116	31,400	271
9	7/NaH	19	28,100	1480
10	8/NaH	21	23,800	1130
11	9/NaH	15	20,900	1390
12	10/NaH	29	40,800	1410
13	11/NaH	32	13,900	434
14	12/NaH	43	36,000	837
15	13/NaH	22	16,000	727

[a] Reaction conditions: 20°C, 1 atm H_2, 2 h, rate of agitation 1100 r/min, 10 ml toluene, 2 ml 1-hexene, titanium complexes 0.2 μmol (equivalent to a titanium concentration of 17 μmol/L), 12 mg NaH, 1-hexene : NaH : titanocene = 80,000 : 2500 : 1.

Among the titanocenes we have studied, Cp_2TiCl_2 gives the highest initial catalytic activity and fairly good catalytic efficiency (Table 2). In most cases, titanocenes with substituted groups on the cyclopentadienyl ring exhibit lower initial catalytic activities but better catalytic efficiencies (see entries 3–14 in Table 2). Titanocene catalysts with a bulkier substituents have a tendency to exhibit a lower initial catalytic activity and higher catalytic efficiency. The catalytic efficiency is dependent on the catalytic activity and stability. If we take the ratio TO/TOF$_{initial}$ as a criterion for the stability of the catalyst, the data listed in Table 2 clearly show that a bulkier substituent has a tendency to give better catalyst stability. The replacement of chlorine atoms by fluorine or bromine in titanocenes does not change their catalytic behavior (compare entries 1–5 in Table 2). Since the halogen atom should be removed from the titanocene by the reducing agent (NaH), they were being mixed

TABLE 3

Effect of Reaction Temperature on Catalytic Activity and Efficiency in the Hydrogenation of 1-Hexene Catalyzed by 4/NaH[a]

Temperature (°C)	TOF$_{initial}$	TO	TO/TOF$_{initial}$
–20	121	38,900	321
0	163	40,100	246
20	209	43,200	207
40	220	45,700	208
60	236	48,800	206

[a] Reaction conditions are the same as those in Table 2 except for the temperature.

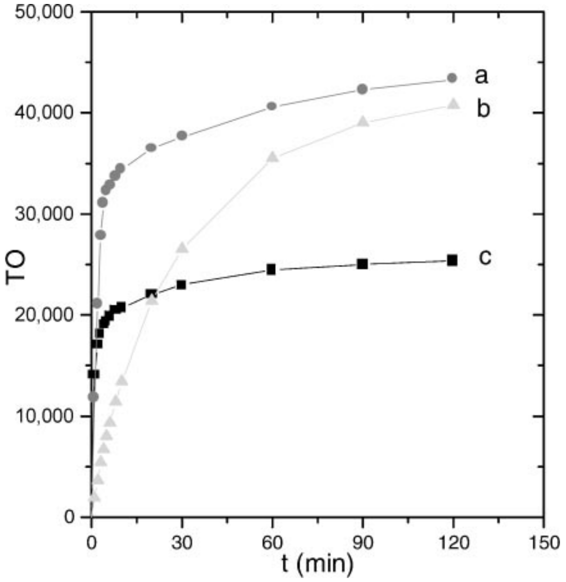


FIG. 3. Kinetic curves of 1-hexene hydrogenation catalyzed by various titanocene complexes using nanometric NaH as co-catalyst. a, 4/NaH; b, 10/NaH; c, Cp_2TiCl_2/NaH. Reaction conditions are the same as those in Table 2.

together, the resulting catalytic active species would be the same.

The kinetic curves shown in Fig. 3 show the stability of the catalysts with substituents of varying bulkiness. The Cp_2TiCl_2 system loses its catalytic activity rapidly, while the substituted titanocenes give better stability. Catalyst 4/NaH exhibits high $TOF_{initial}$ (209 s^{-1}) and TO (43,200 in 2 h) with a fairly good stability, whereas the initial TOF of catalyst 10/NaH with a bulky substituent is only 29 s^{-1}; however, this catalyst gives a rather high TO (40,800 in 2 h) and a high TO/$TOF_{initial}$ ratio (Table 2).

The activities of these catalytic systems exhibit very low temperature dependence. In the case of catalyst 4/NaH, when the reaction temperature is raised from −20 to 60°C, the initial TOFs are increased only from 121 to 236 s^{-1}, whereas the increase in turnover at 2 h is even smaller, only 25%. These results indicate that the activation energy of hydrogenation over this catalytic system is rather low, and the catalyst stability is somewhat higher at low temperatures. An Arrhenius plot of $TOF_{initial}$ vs $1/T$ between 253 and 293 K shows that the apparent activation energy is around 8.5 $kJ \cdot mol^{-1}$.

The use of nanometric sodium hydride is the key factor in the high catalytic activity of these catalyst systems. When commercial sodium hydride is used instead of nanometric sodium hydride, we use a large amount of sodium hydride. The catalyst exhibits no activity at a total NaH surface area larger than that of the nanometric catalysts (Table 4).

TABLE 4

Comparison of Nanometric and Commercial Sodium Hydride as Co-catalyst in the Hydrogenation of 1-Octene Catalyzed by Cp_2TiCl_2/NaH[a]

Catalyst	Sodium hydride (g)	Specific surface area (m^2/g)	Total surface area (m^2)	$TOF_{initial}$ (s^{-1})	TO
Cp_2TiCl_2/NaH (nanometric)	0.012	90	1.1	113	17,000
Cp_2TiCl_2/NaH (commercial)	0.074	1.4	0.1	0	0
Cp_2TiCl_2/NaH (commercial)	1.040	1.4	1.5	0	0

[a] Reaction conditions are the same as those in Table 2 except for the amount of NaH.

Styrene can be hydrogenated to ethylbenzene at an initial reaction rate similar to that of 1-hexene, but the catalyst is more stable, as shown by the extremely high turnover with styrene as a substrate. The turnover can be as high as 152,000 in 2 h with 12/NaH as a catalyst (Table 5). The TO/$TOF_{initial}$ ratios are higher than those with 1-hexene as a substrate. In this case the catalyst stability can be seen from the kinetic curves shown in Fig. 4.

The titanocene/NaH catalyst systems are highly selective. No isomerization of the alkenes or other side reactions during hydrogenation have been found by the GC analysis of the reaction products. These catalysts display rather peculiar specific selectivity toward olefin substrates. Only terminal alkenes can be hydrogenated. Internal alkenes and cyclic alkenes such as 2-hexene, 2-octene, cyclohexene, and cyclopantadiene cannot be hydrogenated. When a mixture of 1-octene and 2-octene was used as a substrate, the rate of hydrogenation of 1-octene was not affected by the presence of 2-octene. Alkynes cannot be hydrogenated by these catalyst systems, probably due to the strong coordination of the carbon–carbon triple bond on the titanium active species. The hydrogenation of 1-octene or styrene can be stopped by adding only a drop of phenylacetylene into the reaction mixture, which indicates that alkyne is a catalyst poison for the hydrogenation of terminal alkenes over these catalyst systems.

TABLE 5

Hydrogenation of Styrene Catalyzed by Various Substituted Titanocenes Using NaH as a Co-catalyst[a]

Catalyst	$TOF_{initial}$	TO	TO/$TOF_{initial}$	Conversion (%)
9/NaH	13	43,400	3300	24.9
10/NaH	31	118,000	3800	67.8
11/NaH	30	147,000	4900	84.5
12/NaH	37	152,000	4100	87.3
13/NaH	27	48,000	1800	27.6

[a] Other reaction conditions are the same as those in Table 2 except for 4 ml styrene. Styrene : NaH : $(RCp)_2TiCl_2$ = 174,000 : 2500 : 1 (mole ratio).

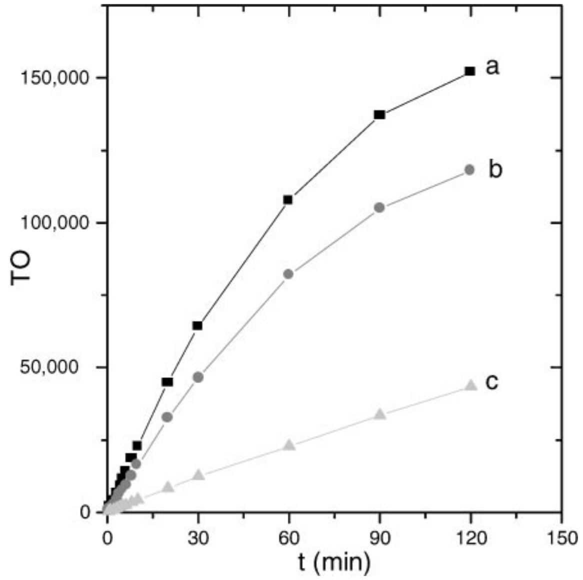


FIG. 4. Kinetic curves of styrene hydrogenation catalyzed by various titanocenes using nanometric NaH as co-catalyst a, 12/NaH; b, 10/NaH; c, 13/NaH. Reaction conditions are the same as those in Table 5.

The active species of these catalyst systems are believed to be heterogeneous in nature. These catalysts are composed of titanocenes (soluble in THF) and nano-NaH (insoluble in THF). We mixed the two catalyst components in THF and stirred for 15 min. The solution was then centrifuged. The upper liquid layer and the lower solid part were separated and subjected to hydrogenation separately using 1-octene as a substrate. The upper layer gave almost no catalytic activity, while the solid part was the active catalyst, which meant that the reduced titanium species were supported on the surface of insoluble nanometric sodium hydride. The sodium hydride acts as both a reducing agent and a catalyst carrier.

CONCLUSION

In this paper, extremely active catalysts for the hydrogenation of terminal olefins have been presented. These catalysts are composed of titanocenes and nanometric sodium hydride. The latter acts as both a reducing agent and a catalyst carrier. The use of nanometric sodium hydride with a large specific surface area as a co-catalyst is the key factor in the high activity of the titanium catalyst, while a suitable bulky substituent on the cyclopentadienyl ring of titanocene is the main factor in the stability of this catalyst. These catalysts are rather specific toward substrates. Only terminal alkenes can be hydrogenated, and the hydrogenation proceeds with 100% selectivity.

ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (No. 50071025) and the Educational Council of Liaoning Province (No. 20042095).

REFERENCES

1. Sloan, M. F., Matlack, A. S., and Breslow, D. S., *J. Am. Chem. Soc.* **85**, 4014 (1963).
2. Tajima, Y., and Kunioka, E., *J. Org. Chem.* **33**, 1689 (1968).
3. Bonds, W. D., Jr., Brubaker, C. H., Jr., Chandrasekaran, E. S., Gibbons, C., Grubbs, R. H., and Kroll, L. C., *J. Am. Chem. Soc.* **97**, 2128 (1975).
4. Bochmann, M., *in* "Comprehensive Organometallic Chemistry II" (E. W. Abel, F. G. A. Stone, and G. Wilkinson, Eds.), p. 221. Elsevier, Oxford, 1995 (and refs. therein).
5. Dozzi, G., Cucinella, S., and Mazzei, A., *J. Organomet. Chem.* **164**, 1 (1979).
6. Samuel, E., *J. Organomet. Chem.* **198**, C65 (1980).
7. Smith, J. A., and Brintzinger, H. H., *J. Organomet. Chem.* **218**, 159 (1981).
8. Pez, G. P., and Armor, J. N., *in* "Advances in Organometallic Chemistry" (F. G. A. Stone and R. West, Eds.), Vol. 19, p. 1. Academic Press, New York, 1981.
9. Demerseman, B., Coupanec, P. L., and Dixneuf, P. H., *J. Organomet. Chem.* **287**, C35 (1985).
10. Harrod, J. F., and Yun, S. S., *Organometallics* **6**, 1381 (1987).
11. Qian, Y. L., Li, G. S., and Huang, Y. Z., *J. Mol. Catal.* **54**, L19 (1989).
12. Capka, M., and Reissova, A., *Collect. Czech. Chem. Commun.* **54**, 1760 (1989).
13. Scott, F., Raubenheimer, H. G., and Pretorius, G., *J. Organomet. Chem.* **384**, C17 (1990).
14. Zhang, Y. P., Liao, S. J., Xu, Y., and Chen, S. S., *J. Organomet. Chem.* **382**, 69 (1990).
15. Chamberlain, L. R., and Gibler, C. J., U.S. Patent 5,173,537 (1992).
16. Sun, Q., Liao, S. J., Xu, Y., Zhang, Y. P., Yang, R. W., Sun, R. A., and Chen, S. S., *Chem. J. Chinese Univ.* **17**, 1441 (1996).
17. Fan, Y. H., Liao, S. J., Xu, Y., Qian, Y. L., and Huang, J. L., *Chem. J. Chin. Univ.* **18**, 1683 (1997).
18. Grubbs, R. H., Gibbons, C., Kroll, L. C., Bonds, W. D., Jr., and Brubaker, C. H., Jr., *J. Am. Chem. Soc.* **95**, 2373 (1973).
19. Jackson, R., Ruddlesden, J., Thompson, D. J., and Whelan, R., *J. Organomet. Chem.* **125**, 57 (1977).
20. Skupinski, W., Cieslowska, I., and Malinowski, S., *J Organomet. Chem.* **182**, C33 (1979).
21. Verdet, L., and Stille, K. J., *Organometallics* **1**, 380 (1982).
22. Booth, B. L., Ofunne, G. C., Stacey, C., and Tait, P. J. T., *J. Organomet. Chem.* **315**, 143 (1986).
23. Huang, Q.-C., Qian, Y.-L., Tang ,Y.-Q., and Chen, S.-S., *J. Organomet. Chem.* **340**, 179 (1988).
24. Li, G. H., Qian, Y. L., Huang, Y. Z., and Chen, S. S., *J. Mol. Catal.* **72**, L15 (1992).
25. Chen, S. S., and Yao, W. Q., *Chin. J. Inorg. Chem.* **7**, 267 (1991).
26. Qian, Y. L., Zhuang, J. M., Xu, M. Z., Xu, W. H., He, Y. X., and Li, B. H., *Chin. J. Inorg. Chem.* **4**, 90 (1986).
27. Zhang, Y. P., Liao, S. J., and Xu, Y., *J. Mol. Catal.* **84**, 211 (1993).