Journal of Catalysis **210,** 192–197 (2002)
doi:10.1006/jcat.2002.3664

Highly Stable Chiral and Achiral Nitrogen–Base Adducts of Methyltrioxorhenium(VII) as Catalysts in the Epoxidation of Alkenes

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Received February 8, 2002; revised April 29, 2002; accepted May 1, 2002

Nitrogen-based adducts derived from methyltrioxorhenium(VII) and mono- and polihalogenated pyridines are excellent stable catalysts for the selective epoxidation of 1-hexene. On the other hand, moderate stereoinduction values can be achieved when determined prochiral olefins are epoxidized with chiral rhenium(VII) complexes formed with the amines (*S*)-2-aminomethylpyrrolidine, (*R*)-(+)-phenyl ethylamine, and L-prolinamide as catalysts.

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Key Words: **MTO; epoxidations; chirality; enantioselectivity.**

INTRODUCTION

The catalytic epoxidation of olefins is a subject of growing interest in the production of chemicals and fine chemicals. This is specially true in the field of asymmetric synthesis because one or two neighboring chiral centers can be created with a high degree of enantioselectivity by means of powerful catalytic methods. Among them, chiral manganese salen complexes, chiral ketone catalysts, and functionalized iminium salt systems have been found to be highly efficient enantioselective catalysts (1–3).

Similarly, zeolites and mesoporous molecular sieves containing isolated framework Ti atoms have shown capabilities as epoxidation catalysts using H_2O_2 and organic peroxides as oxidants (4–9). Recently, an impressive amount of work has been carried out on the catalytic properties of methyltrioxorhenium(VII) (MTO) and more specifically on its possibilities as a selective epoxidation catalyst using H_2O_2 as oxidant (10–16). Although it is generally found that this catalyst is quite efficient for producing epoxides, it also catalyzes the transformation of the epoxide into 1,2-diols, which sometimes undergo cleavage and rearrangement reactions. Such secondary reactions can be suppressed by replacing hydrogen peroxide with the urea/hydrogen peroxide adduct (UHP) as primary oxidant, which enables epoxidation to be carried out in nonaqueous media whereby the epoxide ring opening is largely avoided (17).

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A second alternative is based on the tendency of organorhenium(VII) oxides to increase their coordination numbers to form Lewis acid–base adducts (18, 19). In this way, complexes formed with certain nitrogen bases have been found to be excellent catalysts in epoxidations when an excess of amine is present (20–22). It is certainly of interest to prepare stable complexes that can avoid the use of excess of amines in the reaction media. Hence in the present work a series of MTO adducts with mono- and bidentate nitrogen bases were prepared showing the possibility of forming stable complexes, which is especially likely when using halogenated pyridines.

Finally, we show that by preparing adducts using chiral ligand bases it is possible to obtain moderate chirality with Re(VII)-derived complexes for the epoxidation of prochiral olefins.

EXPERIMENTALS AND METHODS

Preparation of Rhenium(VII) Complexes

In a typical procedure 0.5 mmol of amine was added to a stirred solution of 0.5 mmol of MTO in 10 ml of either diethyl ether or toluene at temperatures ranging from −40 to 0°C. A few minutes after, a yellow precipitate was formed. The solids were filtered off, washed with *n*-pentane, and dried.

Characterization Data of (Pyridine)methyl(trioxo) rhenium(VII) Complex

^{1}H NMR ($CDCl_3$): 1.99 (3H, s), 7.32 (2H, m), 7.73 (1H, dd) 8.37 (2H, dd). IR (KBr): 1600 (m), 1450 (m), 1220 (m), 1060 (m), 980 (s), 959 (s), 710 (m), 630 (m). Anal. Calcd for $C_6H_8NO_3Re$: C, 21.95; H, 2.46; N, 4.29. Found: C, 22.02; H, 2.33; N, 4.25.

Characterization Data of (3-Cyanopyridine)methyl (trioxo)rhenium(VII) Complex

^{1}H NMR ($CDCl_3$): 2.59 (3H, s), 7.46 (1H, dd), 7.9 (1H, dd), 8.85 (1H, dd), 8.91 (1H, s). IR (KBr): 2231 (m),

0021-9517/02 $35.00
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1595 (m), 1450 (m), 1416 (m), 921 (s), 955 (s). Anal. Calcd for $C_7H_7N_2O_3Re$: C, 23.79; H, 1.99; N, 7.96. Found: C, 23.88; H, 1.92; N, 7.83.

Characterization Data of (4-Phenylpyridine)methyl (trioxo)rhenium(VII)

^{1}H NMR ($CDCl_3$): 1.59 (3H, s), 7.2-7.6 (7H, m), 8.5 (2H, dd). IR(KBr): 1608 (m), 1413 (m), 1065 (m), 927 (s), 910 (m), 840 (m), 768 (m). Anal. Calcd for $C_{12}H_{12}NO_3Re$: C, 35.63; H, 2.99; N, 3.48. Found: C, 35.27; H, 2.99; N, 3.33.

Characterization Data of (4,4′-Diphenyl-2,2′-bipyridine) methyl(trioxo)rhenium(VII) Complex

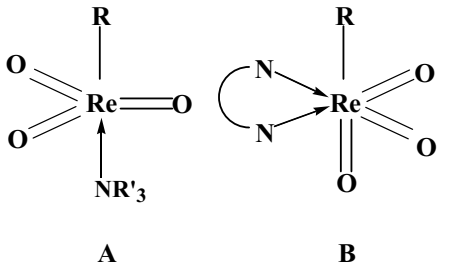
^{1}H NMR ($CDCl_3$): 1.54 (3H, s), 7.52 (6H, m), 7.62 (2H, m), 7.8 (4H, m), 8.65 (2H, s), 8.8 (4H, m). IR(KBr): 1605 (s), 1410 (m), 936 (s), 910 (s), 831 (s), 757 (s). Anal. Calcd for $C_{23}H_{19}N_2O_3Re$: C, 49.53; H, 3.43; N, 5.04. Found: C, 49.55; H, 3.44; N, 4.96.

Catalytic Experiments

The catalytic reactions were carried out under continuous stirring in a glass flask immersed in a refrigerated bath with temperature control. In a typical experiment, 0.05 mmol of the catalyst (and 0.05 mmol of the corresponding amine, in the case of *in situ* generated complex), 10 g of solvent, and a given amount (2 mmol) of diluted hydrogen peroxide (sol, 35 wt% in water) were mixed in the flask under agitation until the reaction temperature was reached. At this time, 8 mmol of the substrate was added (time zero). Small aliquots were taken at selected reactions times, quenching the reaction in each sample by addition of MnO_2 in catalytic amounts. The products were separated and analyzed by gas chromatography in a capillary column (5% methylphenylsilicone, 25-m length) using a FID detector. When chiral complexes (0.2 mmol of catalyst) were used as catalysts, the products were analyzed by gas chromatography in a chiral capillary column (Beta-Dex 120, 30-m length) to calculate the corresponding enantiomeric or diasteromeric excess. Identification of the different compounds was done by GC–MS using available reference standards. Finally, unreacted hydrogen peroxide was measured by standard iodometric titration.

RESULTS AND DISCUSSION

Based on the strong Lewis acidic character of organorhenium(VII) trioxides, a complete set of derivatives of MTO was prepared by adduct formation with nitrogen bases as electron donors (18, 19). In principle, two different types of nitrogen bases were chosen to form these complexes, namely mono- and bidentate amines, which presumably would lead to trigonal bipyramidal complexes and bidentate bases afforded to adducts with distorted octahedral geometries, as based on literature references (Scheme 1).



SCHEME 1

As expected, the newly formed complexes exhibited a common behavior when they were characterized by ^{1}H NMR (23). Thus, initially the chemical shift of the methyl group of MTO in deuterated chloroform was observed at 2.65 ppm, but after addition of the amine, the methyl signal was high-field shifted in all cases. It has been reported that the magnitude of these shifting is directly related to the electron donor character or pK_b of the base; i.e., the higher the electron density given to the Re(VII) center by the donor ligand, the larger the high-field shift of the ^{1}H NMR signal in the Re–CH_3 group. Indeed, electron-rich pyridine derivatives induced the strongest up-field shift of the methyl signal (23). In contrast, less information could be obtained from IR spectroscopy, since a direct correlation between the Re=O vibration band shifts and the pK_b values of the bases could not be established.

It is necessary to point out that the resulting adducts were stable yellow powders that could be easily crystallized from different solvents. In those cases where the complexes could not be isolated, we found it very useful to generate the complexes *in situ* before adding the reactants.

Hence, 1-hexene was used as a model reactant, and its epoxidation was carried out at −5°C in a biphasic system formed by the organic solvent, in which only the rhenium complex and the olefin were soluble with the H_2O_2(35%) in aqueous solution. It must be emphasized that in our reaction conditions, epoxidation of 1-hexene hardly took place with other classical oxidants, like iodosobenzene, *tert*-butyl hydroperoxide, and bleach.

Then, when 1-hexene was allowed to react in the presence of MTO, the 1,2-epoxide was formed, which further reacted to give the corresponding diol, thus decreasing epoxide selectivity (Table 1). As could be expected, the incorporation of nitrogen bases was found to improve the chemoselectivity of the reaction by largely suppressing the undesired epoxide ring-opening reaction (Table 1) (20–22, 24). On the other hand, it is necessary to emphasize that despite that fact the amines can be readily oxidized to the corresponding N-oxides, this reaction was of minor importance under our reaction conditions since in general all studied catalysts were efficient, selective, and stable during the experiments (25, 26).

TABLE 1

MTO–Amine-Catalyzed Oxidation of 1-Hexene with Hydrogen Peroxide as Oxygen Source

Amine	Conversion (mol %)[a]		Selectivity (mol %)			
	1-Hexene[c]	H_2O_2[d]	H_2O_2[e]	Epoxide	Diol	T.O.N.[b]
—	74	98	57	65	25	29
Pyridine	64	71	91	99	1	26
3-Cyanopyridine	29			87	7	12
4-Phenylpyridine	59			100	0	24
2,2′-Bipyridine	78			99	1	32
2,9-Dimethyl-1,10-phenantroline[f]	78			100	0	32
4,4′-Diphenyl-2,2′-bypiridine	59			100	0	24
2-Fluoropyridine[f]	98	100	97	100	0	39
3-Fluoropyridine[f]	53			98	2	21
2,6-Difluoropyridine[f]	83	76	75	100	0	33
3,6-Difluoropyridine[f]	68			96	4	27
2,3,5,6-Tetrafluoropyridine[f]	73	99	75	98	2	29
2,3,4,5,6-Pentafluoropyridine[f]	75	99	76	100	0	30
2-Chloropyridine[f]	91	99	92	85	12	36
2,3-Dichloropyridine[f]	93			89	10	37
2,3,5-Trichloropyridine[f]	91	90	85	99	1	36

[a] Reaction conditions: 8 mmol of substrate, 2 mmol of H_2O_2, 0.05 mmol of catalyst, 10 ml of dichloromethane, $T^a = -5°C$, time = 7 h.

[b] Calculated as moles of product obtained/mole of catalyst.

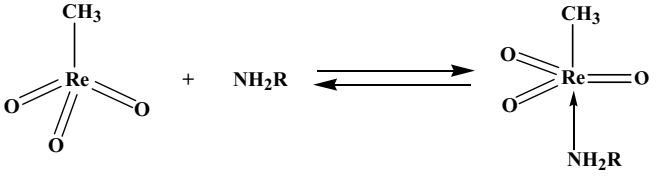
[c] Calculated as percentage of the maximum amount of 1-hexene that can be converted.

[d] Calculated as percentage of the initial amount of oxidant.

[e] Moles of oxidized products/mole of $H_2O_2 \times 100$.

[f] MTO–amine adduct prepared *in situ* in the catalysis solution.

From the obtained results, it can be said that under these experimental conditions electron-rich pyridines, either mono- or bidentate, gave important yields of 1,2-epoxide with excellent selectivities and very reasonable turnovers (Table 1). In contrast, the incorporation of electron-withdrawing groups in the meta position (3-cyanopyridine) slowed the activity and selectivity toward the obtaining of the epoxide with respect to unsubstituted pyridine (Table 1). These results have been explained in the literature by considering the fact that the coordination of the amine to rhenium is labile and in certain conditions the base dissociation can readily occur (Scheme 2) (19). Indeed, with weak electron donors the dissociation equilibrium of adduct complexes $RReO_3 \cdot L$ (L = amine) can led to creation of an open coordination site at the metal center. Then, only small concentrations of OH^- can coordinate to MTO (19). This resulting complex is known to decompose readily with formation of methane and perrhenate, explaining the pronounced water sensitivity of these complexes in solution (27). This fact implies that the incorporation of strong bases that can compete with the OH^- in the coordination with MTO is crucial to avoid such a reaction and to produce a good catalyst (19).



SCHEME 2

It is interesting that we found that mono- and polifluorinated pyridines coordinated to rhenium behaved as excellent catalyst for the epoxidation of 1-hexene. This occurred even when the halogen group was present in the meta position, as for the 3-fluoropyridine, which gave conversion and selectivity values very similar to those obtained with the unsubstituted pyridine (Table 1). On the other hand, the introduction of one chlorine atom in position two of the pyridine ring was detrimental to the epoxidation selectivity, but conversion improved when increasing the chlorine content of the pyridine ligand. It can therefore be said that halogenation afforded highly stable and reactive catalysts with regard to other pyridine adducts. This effect of halogen substitution is intriguing, since the resulting amine-MTO adducts could not be isolated, and *in situ* ^{1}H NMR data of these complexes revealed that the amines were weakly coordinated to the rhenium center. This fact could be deduced by the appearance of a unique singlet signal (attributable to the methyl group of the newly formed adduct) close to the initial methyl shifting of free MTO. The possibility that this methyl group would correspond to uncomplexed MTO was discarded since the hypothetically formed adduct exhibited much better activity and selectivity toward epoxidations than the original MTO. It is curious

that the high-field shifting of the methyl group upon coordination to halogenated pyridines is similar to that measured for the cyanopyridine adduct (see Experimentals and Methods); nevertheless the catalytic perfomance of the halogenated complexes is superior to that observed for the cyanopyridine adduct. Why do both types of amines, which show similar coordination to MTO, behave catalytically so differently? For halogenated complexes it is possible that a combination of electronic and steric effects of substituents could account for the high stability of the adducts under our reaction conditions. Effectively, despite the evident weak coordination (from NMR data) it is reasonable to suppose that introduction of the small and nonpolarizable fluorine or chlorine atoms into the aromatic amine would result in more hydrophobic adducts, which should be less sensitive to water and therefore would slow down the decomposition of MTO.

For comparison, several experiments were conducted additionally in trifluoroethanol and nitromethane as solvents, with the former giving significant improvements in the reaction rates and yields even for terminal alkenes (10, 20). In fact, the results collected in Table 2 show that the epoxidation of 1-hexene gave much better results when the experiments were conducted in trifluoroethanol. However, the high polarity of trifluoroethanol makes difficult the solubilization of less polar alkenes (stilbenes and C_{12} or higher alkenes), for which the epoxidation reaction becomes rather problematic. For such alkenes the use of dichloromethane and nitrogen-based adducts of MTO (1 : 1) can be a useful alternative for achieving efficient epoxidations.

Chiral Epoxidations

In an attempt to achieve chirality, we prepared different chiral rhenium(VII) adducts by adding (*S*)-(+)-2-aminomethylpyrrolidine, (*R*)-(+)-phenyl ethylamine, and L-prolinamide to different solutions of MTO. Addition of these chiral auxiliaries induced enantioselective and diastereoselective oxidation of several prochiral olefins with low-to-moderate levels of stereoinduction (see Table 3) (21, 28). Indeed, the results collected in Table 3 show that the enantiomeric excess obtained in the asymmetric epoxidation of 1-methylcyclohexene was rather low at −5°C. As may be expected, when lowering temperature to −55°C the epoxides were obtained with a significant improvement in enantioselectivity (Table 3).

For styrene derivatives, the reactions were performed at −5°C since conversions at −55°C were almost negligible. Nevertheless, even at this temperature the enantioselectivities were the highest found among all the alkenes studied (35 and 36 ee (%) for *cis*-*β*-methylstyrene with H_2O_2 and H_2O_2–urea as stoichiometric oxidants, respectively). The possibility that the dynamic equilibrium would not be completely shifted to a coordinated amine could account for the moderate enantioselectivity values measured for these chiral complexes. To check this hypothesis, an equimolar deuterated chloroform solution of (*R*)-(+)-phenyl ethylamine and MTO was prepared at room temperature. The mixture turned immediately yellow (a strong indication that the adduct had been formed) and the ^{1}H NMR spectrum was recorded at ambient temperature. The spectrum was undoubtedly assigned to the (*R*)-(+)-phenyl ethylamine–MTO adduct based in the appearance of a significant sharp singlet to approximately 2.1 ppm (Re–CH_3) and the downfield shiftings of the amine protons. The fact that the spectrum did not show any trace of free MTO ($\delta_{CH_3} = 2.65$ ppm) strongly suggested that the dynamic equilibrium was completely shifted to a coordinated amine. The same spectrum could be obtained even when the spectrum was recorded at −40°C, confirming the fact that the complex had been effectively formed even at the low temperature of the epoxidation experiments. This fact corroborates the fact that the moderate enantiomeric excess obtained (at least in this case) should not be attributed to a lack of full coordination of the amine to MTO, but to the intrinsical stereochemical features of the newly formed chiral complex.

Finally, we studied the applicability of chiral rhenium(VII) catalysts for the epoxidation of the terpenic

TABLE 2

Epoxidation of 1-Hexene by MTO/Pyridine in Different Solvents at 25°C

MTO/pyridine (mmol)	Solvent	Conversion (mol %)[a]		Selectivity (mol %)			T.O.N.[b]
		1-Hexene[c]	H_2O_2[d]	H_2O_2[e]	Epoxide	Glicol	
1/1	Trifluoroethanol	99	96	97	100	0	40
1/1	Dichloromethane	73	99	74	99	1	29
1/1	Nitromethane	67	99	69	96	4	26

[a] Reaction conditions: 8 mmol of 1-hexene, 2 mmol of H_2O_2, 0.05 mmol of MTO, 0.05 mmol of pyridine, 10 ml of solvent, $T^a = 25$°C, time = 7 h.

[b] Calculated as moles of product obtained/mole of catalyst.

[c] Calculated as percentage of the maximum amount of 1-hexene that can be converted.

[d] Calculated as percentage of the initial amount of oxidant.

[e] Moles of oxidized products/mole of $H_2O_2 \times 100$.

TABLE 3

Asymmetric Epoxidation of Alkenes Catalyzed by MTO–Amine Quiral Complexes and H_2O_2 as Stoichiometric Oxidant

Substrate	Amine	T (°C)	Conv. (%)[a,b,c]	Selectivity (%)[c]		ee (%)[d]
				Epoxide	Diol	
1-Methylcyclohexene	L-Prolinamide[e]	−5	12	35	65	4
	(+)-2-Aminomethylpyrrolidine[e]	−5	18	80	20	5
1-Methylcyclohexene	L-Prolinamide[e]	−35	59	96	4	8
	(+)-2-Aminomethylpyrrolidine[e]	−35	29	70	30	13
1-Methylcyclohexene	L-Prolinamide[e,f]	−55	15	85	15	9
	(+)-2-Aminomethylpyrrolidine[e,f]	−55	48	78	22	20
cis-β-Methylstyrene	(*R*)-(+)-1-Phenyl ethylamine[e,f]	−5	10	77	16	35
		−5	9	82	11	36
trans-β-Methylstyrene	(*R*)-(+)-1-Phenylethylamine[e,f]	−5	10	80	19	20
		−5	11	82	17	15
α-Pinene	(+)-2-Aminomethylpyrrolidine[e,f]	−5	11	57	25	41 (% de)[g]

[a] Conversion calculated as percentage of the maximum amount of alkene that can be epoxidized.
[b] Reaction conditions: 8 mmol of substrate; 2 mmol of H_2O_2; 0.2 mmol of catalyst; 0.2 mmol of amine; 10 ml of dichloromethane; time = 7 h at −5°C, 45 h at −35°C, and 48 h at −55°C.
[c] Calculated by capillary GC.
[d] Calculated by quiral capillary GC.
[e] MTO–amine adduct prepared *in situ* in the catalysis solution.
[f] Performed with the H_2O_2–urea adduct as oxidant in dichloromethane.
[g] de, Diastereomeric excess.

α-pinene olefin since the corresponding terpenic oxide is a valuable starting material for the synthesis of fragrances. Again the reaction was rather slow at −5°C, although a diasteromeric excess of 41% could be obtained with the auxiliary (+)-2-aminomethylpyrrolidine (Table 3).

Even if the level of chiral induction obtained is far from optimum, these results open possibilities for preparing new types of chiral metal catalysts, in which the stereoselectivity relies on nonbonding interactions. The importance of this feature is that contrary to other complexes, the pool of potential substrates can be enlarged to the category of nonfunctionalized olefins with catalysts that at the same time are able to make efficient use of the environmentally friendly oxidant H_2O_2.

CONCLUSION

Addition of selected monodentate and bidentate nitrogen bases to solutions of methyltrioxorhenium(VII) formed nitrogen-donor adducts sufficiently stable in most cases to be characterized spectroscopically by ^{1}H NMR. In general the newly formed complexes were highly efficient for the catalytic epoxidation of 1-hexene. As previously observed, a systematic investigation with amines of different basic strength showed that strong N-donor ligands induced good activity and selectivity in the epoxidation of 1-hexene. Interestingly, mono- and polihalogenated pyridines behaved as excellent stable catalyst for the epoxidation of 1-hexene, giving high selectivities and good catalytic turnovers. This experimental fact has been attributed to a stabilization of the resulting complex by a combination of hydrophobic and electronic effects.

In addition to this, moderate values of stereoinduction could be obtained when epoxidations were carried out with chiral rhenium complexes formed with the amines: (*S*)-2-aminomethylpyrrolidine, (*R*)-(+)-phenyl ethylamine, and L-prolinamide.

ACKNOWLEDGMENTS

Financial support by the Spanish CICYT (MAT2000-1392) and by Generalitat Valenciana (M.J.S, GVDOC99-0203) is gratefully acknowledged. We thank Mrs. María A. Pasamar for her technical assistance.

REFERENCES

1. (a) Zhang, W., Loebach, J. L., Wilson, S. R., and Jacobsen, E. N., *J. Am. Chem. Soc.* **112**, 2801 (1990); (b) Chang, S., Galvin, J. M., and Jacobsen, E. N., *J. Am. Chem. Soc.* **116**, 6937 (1994); (c) Irie, R., Noda, K., Ito, Y., Matsumoto, N., and Katsuki, T., *Tetrahedron Lett.* 7345 (1990).
2. (a) Wang, Z. X., Tu, Y., Frohn, M., Zhang, J.-R., and Shi, Y., *J. Am. Chem. Soc.* **119**, 11224 (1997); (b) Tu, Y., Wang, Z.-X., and Shi, Y., *J. Am. Chem. Soc.* **118**, 9806 (1996).
3. (a) Wong, M.-K., Ho, L.-M., Zheng, Y.-S., Ho, C.-Y., and Yang, D., *Org. Lett.* **3**, 2587 (2001); (b) Page, P. C. B., Rassias, G. A., Barros, D., Ardakani, A., Buckley, B., Bethell, D., Smith, T. A. D., and Alexandra, A. M. Z., *J. Org. Chem.* **66**, 6926 (2001).
4. Taramasso, M., Perego, G., and Notari, B., U.S. Patent 4,410,501 (1983).
5. Arends, I. W. C. E., Sheldon, R. A., Wallau, M., and Schuchardt, U., *Angew. Chem. Int. Ed. Engl.* **36**, 1144 (1997).
6. Corma, A., *Chem. Rev.* **97**, 2373 (1997).
7. (a) Corma, A., Esteve, P., and Martinez, A., *J. Catal.* **161**, 11 (1996); (b) Corma, A., Díaz, U., Fornés, V., Jordá, J. L., Domine, M., and Rey, F., *Chem. Commun.* 779 (1999).

8. Corma, A., Navarro, M. T., and Pérez-Pariente, J., *J. Chem. Soc. Chem. Commun.* 197 (1994).
9. Camblor, M. A., Corma, A., Martinez, A., and Pérez-Pariente, J., *J. Chem. Soc. Chem. Commun.* 589 (1992).
10. van Vliet, M. C. A., Arends, I. W. C. E., and Sheldon, R. A., *Chem. Commun.* 821 (1999).
11. (a) Herrmann, W. A., Kuchler, J. G., Felixberger, J. K., Herdtweck, E., and Wagner, W., *Angew. Chem. Int. Ed. Engl.* **27**, 394 (1988); (b) Herrmann, W. A., Fritz-Meyer-Weg, D. M., Wagner, W., Kuchler, J. G., Weichselbaumer, G., and Fischer, R., U.S. Patent 5,155,247 (1992).
12. Herrmann, W. A., and Wang, M., *Angew. Chem. Int. Ed. Engl.* **30**, 1641 (1991).
13. Adam, W., Herrmann, W. A., Saha-Möller, C. R., and Shimizu, M., *J. Mol. Catal.* **97**, 15 (1995).
14. Huston, P., Espenson, J. H., and Bakac, A., *Inorg. Chem.* **32**, 4517 (1993).
15. Yamazaki, S., Espenson, J. H., and Huston, P., *Inorg. Chem.* **32**, 4683 (1993).
16. Herrmann, W. A., Fischer, R. W., Scherer, W., and Rauch, M. U., *Angew. Chem. Int. Ed. Engl.* **32**, 157 (1993).
17. (a) Adam, W., and Mitchell, C. M., *Angew. Chem.* **108**, 578 (1996); (b) Boelow, T. D., and Spilling, C. D., *Tetrahedron Lett.* **37**, 2717 (1996).
18. Herrmann, W. A., Kün, F. E., Mattner, M. R., Artus, G. R. J., Geisberger, M. R., and Correia, J. D. G., *J. Organomet. Chem.* **538**, 203 (1997).
19. Herrmann, W. A., Kühn, F. E., Rauch, M. U., Correia, J. D. G., and Artus, G., *Inorg. Chem.* **34**, 2914 (1995).
20. Rudolph, J., Reddy, K. L., Chiang, J. P., and Sharpless, K. B., *J. Am. Chem. Soc.* **119**, 6189 (1997).
21. Coperet, C., Adolfsson, H., and Sharpless, K. B., *Chem. Commun.* 1565 (1997).
22. de Villa, P., A. L., De Vos, D. E., de Montes, C., and Jacobs, P. A., *Tetrahedron Lett.* **39**, 8521 (1998).
23. Herrmann, W. A., Kuchler, J. G., Weichselbaumer, G., Herdtweck, E., and Kiprof, P., *J. Organomet. Chem.* **372**, 351 (1989).
24. Herrmann, W. A., Fischer, R. W., Rauch, M. U., and Scherer, W., *J. Mol. Catal.* **86**, 243 (1994).
25. Copéret, C., Adolfsson, H., Chiang, J. P., Khuong, T.-A. V., Yudin, A. K., and Sharpless, K. B., *J. Org. Chem.* **63**, 1740 (1998).
26. Copéret, C., Adolfsson, H., Chiang, J. P., Yudin, A. K., and Sharpless, K. B., *Tetrahedron Lett.* **39**, 761 (1998).
27. Herrmann, W. A., and Fischer, R. W., *J. Am. Chem. Soc.* **117**, 3223 (1995).
28. Tucker, C. E., and Davenport, K. G., U.S. Patent 5,618,958 (1997).