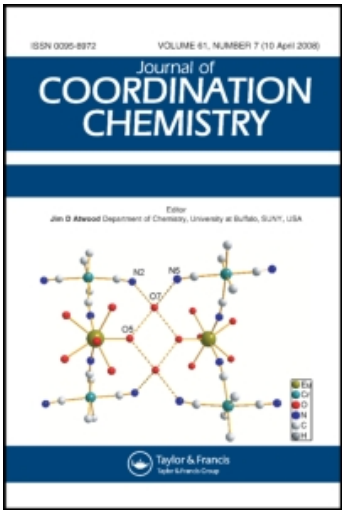


Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Induced Molecular Asymmetry in the Coordination of Olefins to Rhodium(I) and Ruthenium(II) Chiral Phosphine Complexes

Katsutoshi Ohkubo[a]; Kehchi Hirata[a]; Tsutomu Ohgushi[a]; Kohji Yoshinaga[a]
[a] Department of Synthetic Chemistry, Faculty of Engineering, Kumamoto University, Kumamoto, Japan

To cite this Article Ohkubo, Katsutoshi , Hirata, Kehchi , Ohgushi, Tsutomu and Yoshinaga, Kohji(1977) 'Induced Molecular Asymmetry in the Coordination of Olefins to Rhodium(I) and Ruthenium(II) Chiral Phosphine Complexes', Journal of Coordination Chemistry, 6: 3, 185 — 187
To link to this Article: DOI: 10.1080/00958977708079908
URL: http://dx.doi.org/10.1080/00958977708079908

J. Coord. Chem.
1977, vol. 6 pp. 185–187

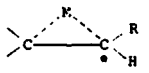
SHORT COMMUNICATION
Induced Molecular Asymmetry in the Coordination of Olefins to Rhodium(I) and Ruthenium(II) Chiral Phosphine Complexes

KATSUTOSHI OHKUBO, KEIICHI HIRATA, TSUTOMU OHGUSHI, and KOHJI YOSHINAGA

Department of Synthetic Chemistry, Faculty of Engineering, Kumamoto University, Kumamoto 860, Japan

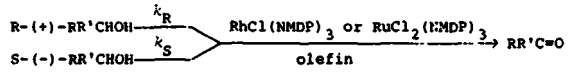
(Received June 3, 1976)

Although the enantioface selection of prochiral olefins has recently been received considerable attention in their hydrogenation by Rh(I) chiral phosphine complexes,[1] the induced molecular asymmetry in the coordination of olefins to transition-metal complexes has been the object of only limited investigation. A small number of investigations have been documented on the induced molecular asymmetry of olefins coordinated with platinum(II) amine complexes.[2]



The present authors report, here, on the importance of the molecular asymmetry induced by olefins in the enhancement of the enantioselective dehydrogenation of racemic alcohols ($RR'CHOH$) catalyzed by $RhCl(NMDP)_3^3$ or $RuCl_2(NMDP)_3^3$ (NMDP = (+)-neomenthyldiphenylphosphine) prepared *in situ* by the reaction of NMDP[4] with $[RhCl(C_2H_4)_2]_2$ or $RuCl_2(PPh_3)_3$ respectively.

When the enantioselective dehydrogenation of 1-phenylethanol, I, was carried out with the above chiral phosphine complexes at 165–195°C in the presence or absence of olefins, the alcohol I obtained by fractional distillation without any other contaminants possessing optical rotation indicated a small but reproducible enantioselectivity, and the optical purity (O.P.) of I enriched in the S-(−) conformer increased with increasing conversion,[5] obeying a pseudo-first-order rate law:



The results of a representative series of the experiments are shown in Table I. The magnitude of the selectivity (defined by k_R/k_S), which shows no direct correlationship with the dehydrogenation rate, was obviously enhanced by the unsaturated additives in comparison with that in the system without olefins and varied from olefin to olefin. Thus, the molecular asymmetry induced by the olefin by its coordination to the metal complex was observed, and the magnitude of its contribution to the selectivity was almost constant in the Rh(I) and Ru(II) complex systems including the same olefins.

Among the olefins tested, two unsaturated ketons of PhCH=CHR (R=acetyl and benzoyl) were most effective in terms of the enhancement of the selectivity, though PhCH=CHR (R=phenyl) was markedly less effective than the above ketones. Hence, one could suppose that, with the particular olefins (the ketones) chosen, the formation of phsophobetaine can be expected from the reaction of the above ketone with the chiral ligand[6] and the phosphobetaine ($R'_3{}^+PCH(Ph)CH=C(R)\bar{O}$) is then bound in the metal complex as a new chiral ligand. Secobarbital containing an asymmetric center in its stereochemically bulky fragment was next to the unsaturated ketones in terms of the enhancement of the selectivity, while methacrylate esters except 2-ethylhexyl methacrylate possessing an asymmetric carbon center were found to be relatively less effective than PhCH=CHR probably because the negatively charged oxygen binds the ester to the metal and disturbs the coordination of the chiral ligand.

The effect of the induced molecular asymmetry on the selectivity was also dependent of the temperature and substantially decreased with elevating the temperature in spite of an increase in the conversion of I. This is presumably due to the change in the magnitude of the molecular asymmetry by the

TABLE I.
Variation of Enantioselectivity in the dehydrogenation of I with molecular asymmetry induced by olefins coordinated to $RhCl(NMDP)_3$ or $RuCl_2(NMDP)_3$[a]

olefin	Temp. (°C)	Time (hr.)	Conv. (%)	$-[\alpha]_D^{23}$[b] (deg.)	O.P. (%)	$10^5 k_R$ (sec^{-1})	$10^5 k_S$ (sec^{-1})	k_R/k_S	ΔΔH‡ (kcal/mol)	ΔΔS‡ (e.u.)
Benzal-	165	5	18.7	0.616	1.174	1.212	1.082	1.121		
acetone	(160)	(36)	(7.9)	(0.274)	(0.512)	(0.0677)	(0.0597)	(1.135)		
	170	5	27.9	0.892	1.699	1.912	1.723	1.110		
	(170)	(30)	(10.9)	(0.322)	(0.613)	(0.1130)	(0.1016)	(1.112)	1.03	2.13
	180	5	38.2	1.199	2.283	2.803	2.548	1.100	(0.87)	(1.76)
	(180)	(30)	(18.5)	(0.390)	(0.743)	(0.1961)	(0.1823)	(1.076)		
	190	5	60.3	1.106	2.109	5.244	5.009	1.047		
	(190)	(30)	(22.5)	(0.434)	(0.827)	(0.3648)	(0.3419)	(1.067)		
Benzalaceto-	180	8	17.3	1.055	2.010	0.7284	0.5892	1.273		
phenone	(180)	(30)	(12.4)	(0.331)	(0.631)	(0.1287)	(0.1170)	(1.100)		
	190	8	46.4	2.264	4.313	2.319	2.019	1.148	4.22	8.86
	195	8	81.2	2.514	4.788	5.980	5.648	1.059		
trans-	180	8	26.2	0.053	0.100	1.089	1.051	1.036		
Stilbene	(180)	(30)	(6.4)	(0.077)	(0.147)	(0.0623)	(0.0596)	(1.045)	0.96[c]	2.03[c]
	195	8	41.8	0.026	0.050	1.882	1.878	1.002		
Ethyl	165	8	7.6	0.046	0.088	0.2778	0.2717	1.036		
cinnamate	180	8	36.1	0.050	0.095	1.558	1.552	1.003	0.47[c]	1.03[c]
	(180)	(30)	(11.0)	(0.035)	(0.066)	(0.1087)	(0.1075)	(1.010)		
n-Dodecyl methacrylate	180	5	34.2	0.065	0.124	2.333	2.319	1.006		
2-Ethylhexyl methacrylate	180	8	11.0	0.289	0.570	0.4151	0.3968	1.051		
n-Hexyl	180	8	13.7	0.073	0.138	0.5161	0.5064	1.019		
methacrylate	(180)	(30)	(23.2)	(0.031)	(0.059)	(0.2454)	(0.2443)	(1.005)		
Secobarbital	180	5	18.9	0.376	0.715	1.464	1.385	1.057		
None	165	5	11.3	0.035	0.067	0.6725	0.6650	1.011		
	(170)	(30)	(12.1)	(0.070)	(0.133)	(0.1210)	(0.1185)	(1.021)	0.19[c]	0.41[c]
	180	5	19.4	0.023	0.044	1.199	1.194	1.004	(0.36)	(0.78)
	(180)	(24)	(29.4)	(0.025)	(0.048)	(0.4027)	(0.4016)	(1.003)		
	(190)	(22)	(45.1)	(0.048)	(0.091)	(0.7571)	(0.7548)	(1.003)		

Values are for $RuCl_2(NMDP)_3$ and those in parentheses are for $RhCl(NMDP)_3$.
[a] $([RhCl(C_2H_4)_2]_2)_0$ = 5 mM and $(NMDP)_0$ = 30 mM; $(RuCl_2(PPh_3)_3)_0$ = 8 mM and $(NMDP)_0$ = 48 mM; $(olefin)_0/(I)_0$ = 0.84.
[b] $[\alpha]_D^{23}$ −52.5° (c 2.27, CH_2Cl_2)[7].
[c] Roughly estimated value.

epimerization or mutarotation[2] or the change in the interacting motion of the complex and the olefin (and/or the alcohol). The difference between the entropies of activation, ΔΔS‡, which was derived from the linear Arrhenius dependence of each rate constant (k_R or k_S), indicates a substantial relationship with the selectivity; that is, at the same temperature, the high selectivity can be expected from the olefin involving stereochemically effective bulkiness which results in the large ΔΔS‡ value. Unexpectedly, the ΔΔS‡ value becomes large in parallel with the ΔΔH‡ value which inevitably indicates the activation-energy difference of the rate determining step of the dehydrogenation of each conformer. It is deduced, therefore, that the more stereochemically effective bulkiness of the substituents in the olefins elevates the activation barriers of the coordination process (during this process, the dehydrogenation may occur simultaneously in the coordination sphere) of the S-(−) conformer of I to the metal complex with an enhancement of the selectivity.

In the absence of olefins, no transfer hydrogenation from I to an olefin promotes the formation of racemic or meso bis(1-phenyethyl) ether in its comparable amount with that of acetophenone.

$$RR'CHOH + (M) \xrightarrow{-H^\bullet} [RR'\overset{H}{C}-O--(M)] \longrightarrow [RR'C{=}O--(M{-}H)] \longrightarrow RR'C{=}O$$

$$RR'CHOH + H^+ \longrightarrow RR'CHOH_2^+ \xrightarrow{[RR'CHO--(M)]} (RR'CH)_2O$$

where (M) and (M–H) denote the metal complex and the metal hydride complex respectively.

The detailed investigation of the induced molecular asymmetry and the present reaction mechanism is now in progress.

REFERENCES

1. R. E. Horman, S. K. Gupta, and J. Brown, *Chemical Rev.*, **73**, 21 (1973), and references therein.
2. G. Paiaro and A. Panunzi, *J. Amer. Chem. Soc.*, **86**, 5148 (1964); A. Panunzi and G. Paiaro, *J. Amer. Chem. Soc.*, **88**, 4843 (1966); R. Lazzaroni and P. Salvadori, *Chem. Comm.*, 1164 (1970).
3. Strictly speaking, the structure of the complex ($RhCl(NMDP)_3$ or $RuCl_2(NMDP)_3$) is uncertain.
4. J. D. Morrison and W. F. Masler, *J. Org. Chem.*, **39**, 270 (1974).
5. K. Ohkubo, K. Hirata, K. Yoshinaga, and M. Okada, *Chem. Lett.*, 183 (1976).
6. L. Marko and B. Heil, *Catalysis Rev.*, **8**, 269 (1973).
7. U. Nagai, T. Shishido, R. Chiba, and H. Mitsuhashi, *Tetrahedron*, **21**, 1701 (1965).