Journal of Organometallic Chemistry, 302 (1986) 265–267
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

ASYMMETRIC TRANSFER HYDROGENATION OF KETONES CATALYZED BY CHIRAL PHOSPHINEIRIDIUM COMPLEXES

H.W. KRAUSE and A.K. BHATNAGAR

Academy of Sciences of GDR, Central Institute of Organic Chemistry, Division of Complex Catalysis, Rostock (G.D.R.) and Indian Institute of Petroleum, Dehra Dun (India)

(Received September 25th, 1985)

Summary

The complexes formed in situ from Ir(COD)acac and chiral menthylphenylphosphines proved to be active catalysts in the hydrogen transfer reaction from isopropanol to prochiral ketones. When acetophenone was used, optical yields of up to 42% were achieved, the configuration of the carbinols being dependent on the bulkiness of the phosphine employed. Concerning the reaction rate, the activation process and the P/Ir ratio, the two menthyl-substituted phenylphosphines display different behaviour.

Introduction

Only a few examples have been published concerning asymmetric transfer hydrogenation catalyzed by chiral metal complexes [1–4]. In all cases the enantioselectivity is poor or moderate and obviously strongly dependent on the reactants used. The best results were obtained upon applying the monodentate neomenthyldiphenylphosphine (NMDPP)[Ir(COD)Cl] system, which gave rise to optical yields of 20% and some diphosphines, for example PROPHOS, with an enantiomeric excess (ee) up to 30% [4].

Results and discussion

We used menthyldiphenylphosphine (MDPP) and the bulkier dimenthylphenylphosphine (DMPP) as ligands for the Ir complex-catalyzed transfer hydrogenation of prochiral ketones according to eq. 1.

$$ArCOR + (CH_3)_2CHOH \xrightarrow[\substack{83°C,KOH\ activation \\ 30\ min}]{Ir(COD)acac + L + HBF_4} ArCHOH\ R + CH_3COCH_3 \qquad (1)$$

The experimental results reveal that the cationic complexes prepared in situ are catalyst precursors which effectively reduce ketones, giving rise to comparably high

0022-328X/86/$03.50

TABLE 1
ASYMMETRIC TRANSFER HYDROGENATION OF KETONES WITH CATIONIC PHOSPHINEIRIDIUM COMPLEXES

Run	Phosphine	Ketone	Time (h)	Conversion (%) [a]	ee [b] (%)	Conf.
1	MDPP	acetophenone	8	54.4	39.4	(*R*)-(+)
2	MDPP	acetophenone	8	87.4 [c]	42.4	(*R*)-(+)
3	DMPP	acetophenone	16	81.6	39.5	(*S*)-(−)
4	DMPP	acetophenone	16	78.3	36.4 [d]	(*S*)-(−)
5	DMPP	propiophenone	34	36.1	35.1	(*S*)-(−)
6	DMPP	2,5-dimethyl-acetophenone			No reaction	
7	MDPP	acetophenone	188	29.9	47.8 [e]	(*R*)-(+)
8	MDPP	acetophenone	11	76.5	29.7 [f]	(*R*)-(+)
9	NMDPP	acetophenone	33	50.5	14.0 [f]	(*R*)-(+)
10	DMPP	acetophenone	12	79.9	13.3 [f]	(*S*)-(−)

[a] Reactions were carried out in refluxing i-PrOH(40 ml) under argon, [Ir(COD)acac] 4×10^{-5} *M* for DMPP, 2×10^{-5} *M* for MDPP, [P]/[Ir] = 2, [Ir]/[HBF_4] = 1, [KOH]/[Ir] = 4, runs 1 and 2 = 15, [substrate]/[catalyst] = 535. [b] $[\alpha]_D^{23}$ −52.5° (*c* 2.27, CH_2Cl_2) [5] for (*S*)-1-phenylethanol, $[\alpha]_D^{17-20}$ +40° (*c* 5, benzene) [6] for (*R*)-1-phenylpropanol. [c] [P]/[Ir] = 10. [d] Reproduction of run 3. [e] Room temp., [P]/[Ir] = 10. [f] Using $[Ir(COD)_2]BF_4$.

optical yields (Tables 1 and 2). Catalytic activity is achieved only by activation with alkali [4]. The data from Table 1 (runs 1–4) show that both ligands give optical yields of up to 40% at conversions greater than 80%. The behaviour of MDPP and DMPP differs in some respects. If the P/Ir ratio is increased, the reaction rate is influenced markedly only by MDPP (run 2), we assume because of steric conditions in the coordination sphere. Both ligands behave in opposite ways concerning the configuration of the carbinols formed (runs 1 and 3). This indicates quite different diastereomeric intermediates which again can be related to the bulkiness of the ligands, especially DMPP. Lowering the reaction temperature causes the optical yield to increase (run 7). Although the conversion is only approximately 30%, and there is an inverse dependence of ee on the degree of conversion, as pointed out by Zassinovich et al. [3], in our case the enantiomeric excess actually increases despite the extremely long reaction time during which normally some racemization is presumed. Only the cationic complexes formed in situ from MDPP and DMPP are effective and enantioselective catalyst precursors.

TABLE 2
ASYMMETRIC TRANSFER HYDROGENATION OF ACETOPHENONE WITHOUT FORMATION OF CATIONIC COMPLEXES

Phosphine	Time (h)	[Substrate]/[Ir]	Conversion (%) [a]	ee (%)	Config.
MDPP	10	850	64.8	36.2	(*R*)-(+)
DMPP	35	535	44.5	3.1	(*S*)-(−)
NMDPP	5	425	9.5	26.0 [b]	(*R*)-(+)

[a] Reactions were carried out as reported in Table 1, [KOH]/[Ir] = 7. [b] [P]/[Ir] = 10.

When the crystalline $[Ir(COD)_2]BF_4$ complex and the phosphines, including NMDPP, are employed, the rate remains unchanged but the stereoselectivity is lowered (runs 8–10).

Other ketones such as propiophenone are reduced at a lower rate (run 5), but the reaction with 2,5-dimethylacetophenone (run 6) fails reflecting strong steric hindrance by the methyl groups. The activation of the in situ phosphineiridium complexes without preformation of the cationic complexes influences only the DMPP complex considerably (Table 2, run 2) whereas MDPP does not appreciably change its activity and selectivity. Probably the same intermediate has been formed. The NMDPP complex shows a relatively low reaction rate even at a higher P/Ir ratio, and the configuration is surprisingly (*R*)-(+), as found for MDPP.

Experimental

All reactions were carried out under argon. Isopropanol was purified by fractional distillation from NaOH, standing over molecular sieves A5, and additional fractional distillation discarding the previous run. The ligands were obtained by published methods from menthyl chloride [7] or using the menthylmagnesium chloride, respectively [8]. Ir(COD)acac and $[Ir(COD)_2]BF_4$ were prepared analogously to the Rh complexes.

The reaction was followed by GLC (Chromatron-GC 18.3, temperature 140°C, 3 m column, 15% OV 210 on chromosorb W/AW-DMCS, 60 to 80 mesh). Optical rotation was measured with a Polamat A instrument (Carl Zeiss, Jena).

Acknowledgements

We thank Mrs. I. Stahr, R. Dehne and K. Kortus for assistance and technical help.

References

1 M. Bianchi, U. Matteoli, G. Menchi, P. Frediani, S. Pratesi, F. Piacenti and C. Botteghi, J. Organomet. Chem., 198 (1980) 73.
2 K. Ohkubo, I. Terada, K. Sugahara and K. Yoshinaga, J. Mol. Catal., 7 (1980) 421.
3 G. Zassinovich, C. Del Bianco and G. Mestroni, J. Organomet. Chem., 222 (1981) 323.
4 R. Spogliarich, G. Zassinovich, J. Kaspar and M. Graziani, J. Mol. Catal., 16 (1982) 359.
5 U. Nagai, T. Shishido, R. Chiba and H. Mitsuhashi, Tetrahedron, 21 (1965) 1701.
6 I. Kenyon, S.M. Partridge and H. Phillips, J. Chem. Soc., (1937) 207.
7 J.D. Morrison and W.F. Masler, J. Org. Chem., 39 (1974) 270.
8 H.W. Krause and A. Kinting, J. Prakt. Chem., 322 (1980) 485.