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ASYMMETRIC HYDROFORMYLATION OF OLEFINS USING CHIRAL PLATINUM COMPLEX CATALYSTS

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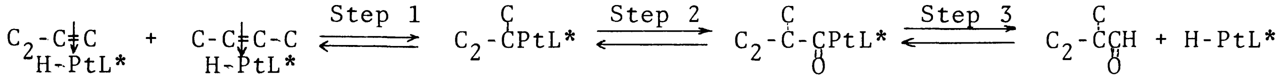
Hydroformylation of butenes and styrene were studied using $[(-)\text{-DIOP}]PtCl_2\text{-}SnCl_2$ catalyst system. Contrary to the reported results, each butene isomer gave 2-methylbutanal of inherent optical purity and prevailing chirality as in the case of rhodium-catalyzed reaction. The result indicates that asymmetric induction takes place before the making up of the diastereomeric alkyl-Pt intermediates.

Recently, Consiglio and Pino[1)] reported that, in the asymmetric hydroformylation of butenes by use of $[(-)\text{-DIOP}]PtCl_2\text{-}SnCl_2$ catalyst system; all the resulting 2-methylbutanals showed the same prevailing (S)-configuration with the same optical purity (1.2 %) irrespective of the sort of starting butene isomers. The result is markedly different from that of the rhodium-catalyzed reaction, where the three 2-methylbutanals arising from each butene isomer had different optical purities. On the basis of the results, they proposed that the asymmetric induction should take place in a step after the alkyl-Pt intermediate 2 in the following equation.



$$\underset{\text{H-PtL*}}{C_2\text{-C}\ddagger\text{C}} + \underset{\text{H-PtL*}}{\text{C-C}\ddagger\text{C-C}} \xrightleftharpoons{\text{Step 1}} C_2\text{-}\overset{\text{C}}{\text{C}}\text{PtL*} \xrightleftharpoons{\text{Step 2}} C_2\text{-}\overset{\text{C}}{\text{C}}\text{-}\underset{\text{O}}{\text{C}}\text{PtL*} \xrightleftharpoons{\text{Step 3}} C_2\text{-}\overset{\text{C}}{\text{C}}\underset{\text{O}}{\text{C}}\text{H} + \text{H-PtL*}$$

1 2 3 L*: Chiral ligand

The report prompted us to study the same reaction, however, by use of DBP-DIOP, an analog of DIOP whose PPh_2 group was substituted by 5H-dibenzophospholyl group (DBP), instead of DIOP by the following consideration. As we reported previously,[2)] a marked increase in the reaction rate and the optical yield was observed in the rhodium-chiral phosphine-catalyzed asymmetric hydroformylation of butenes and styrene when DBP-DIOP were used instead of DIOP. The rate enhancement has been widely observed with other phosphines bearing DBP and also when they were used with cobalt- or platinum-catalysts;[3)] e.g., 1-butene is hydroformylated about ten times faster by the $[\text{DBP-Ph}]_2\text{-}PtCl_2\text{-}SnCl_2$ catalyst system than by the PPh_3 system. If the rate enhancement is caused by the acceleration of the step 2 and thereafter, the use of $[\text{DBP-DIOP}]PtCl_2$ instead of $[\text{DIOP}]PtCl_2$ may accelerate these steps and the energy differences between the π-butene-Pt intermediates in state 1 should be more or less reflected in the asymmetric induction. Actually, we could obtained different optical yields with different butene isomers as shown in Table. However, in this case, the use of DBP-DIOP resulted in a rather slower overall reaction rate than the use of DIOP. Nevertheless, the formation of more branched aldehyde from 2-butenes suggests that the CO-insertion step 2 has been accelerated by DBP group. Unfortunately, however, the blank experiments by use of DIOP did not reproduce the reported results as shown in Table;

Table Hydroformylation of olefins with [(-)-DIOP]PtCl$_2$ or [DBP-DIOP]PtCl$_2$a)

Run	Olefin	Catalyst	Press.b) (atm)	Time c) (h)	Aldehyde				
					yield (%)	straight/ branched	[α]$_D$ (°)	O.Y.d)	Conf.
1	1-butene	[DIOP]PtCl$_2$	100	1	50	86/14	-0.88	2.8	R
2	cis-butene	[DIOP]PtCl$_2$	100	3	40	44/56	+3.08	9.9	S
3	trans-butene	[DIOP]PtCl$_2$	100	3.5	65	46/54	+3.98	12.8	S
4	1-butene	[DBP-DIOP]PtCl$_2$	100	3	50	65/35	+3.79	12.1	S
5	cis-butene	[DBP-DIOP]PtCl$_2$	100	8	60	29/71	-0.19	0.6	R
6	trans-butene	[DBP-DIOP]PtCl$_2$	100	9	45	29/71	-0.55	1.8	R
7	styrene	[DIOP]PtCl$_2$	250	1	60	43/57	+28.92	18.1	S
8	styrene	[DBP-DIOP]PtCl$_2$	235	1	50	23/77	+35.37	22.1	S

a) Pt-complex(3.2x10^{-5}mole), SnCl$_2$·2H$_2$O(1.6x10^{-4}mole, mp:43°C), solvent(6ml, ethylbenzene for Run 1-6 or benzene for Run 7,8), and olefin(3ml) were introduced in this order into a 50 ml stainless steel (SUS-27) autoclave under N$_2$. Reaction temp.: 100°C. b) Pressure at 0°C($P_{H_2}=P_{CO}$) c) Heating time untill gas uptake creased. d) Calculated taken for the optically pure [R]-2-methylbutanal and [S]-2-phenylpropanal show [α]$_D$ -31.2° and +160°, respectively.

three butenes suffered different asymmetric induction. The results indicate that the asymmetric induction took place before the formation of alkyl-metal intermediate also in this [DIOP]PtCl$_2$-SnCl$_2$-catalyzed reaction as in the rhodium-catalyzed one.

The Table shows that the 2-methylbutanals obtained from butenes by use of the DBP-DIOP catalyst and by use of the DIOP one, respectively, had opposite prevailing chirality, as in the case4) of rhodium-catalyzed reactions. On the contrary, the 2-phenylpropanals obtained from styrene using DBP-DIOP and DIOP in the platinum-catalyzed reactions had the same prevailing (S)-configuration. These results indicate that the prediction of the ligand effect with respect to asymmetric induction and rate control is very difficult.

[(-)-DIOP]PtCl$_2$ was prepared by addition of a (-)-DIOP-benzene solution (100mg/5 ml)to a refluxing solution of Pt(PhCN)$_2$Cl$_2$-benzene (95mg/10ml) under dinitrogen; white precipitate separated out gradually. After further refluxing for 1 h, the precipitates were separated from the solution by filtration at room temperature, and washed with benzene (3mlx2); yield 118mg (79%). mp. 301.5-302.0°C (decopm. under N$_2$). [Anal. Found: C, 48.95; H, 4.23; Cl, 9.37% Calcd. for $C_{31}H_{32}O_2P_2Cl_2Pt$: C, 48.70; H, 4.22; Cl, 9.27%]. [DBP-DIOP]PtCl$_2$ was also prepared in a similar manner; yield 94%. mp. 288.0-289.0°C (decomp. under N$_2$) [Anal. Found: C, 48.83; H, 3.72; Cl, 9.25% Calcd. for $C_{31}H_{28}O_2P_2Cl_2Pt$; C, 48.96; H, 3.71; Cl, 9.32%].

References

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