Hydroformylation of epoxides catalyzed by cobalt and hemilabile P–O ligands

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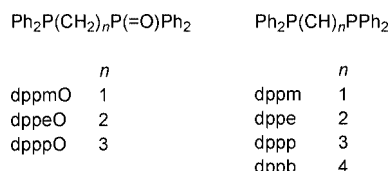
Complexes of cobalt efficiently catalyze the hydroformylation of epoxides in the presence of hemilabile P–O chelating ligands to give β-hydroxyaldehydes in high selectivities and yields.

The hydroformylation of epoxides provides an elegant and inexpensive pathway to β-hydroxyaldehydes which may easily be hydrogenated to 1,3-diols which have a wide variety of uses.[1] Lately propane-1,3-diol has attracted considerable industrial interest as an intermediate in the production of polyester fibers and films.[2]

For the hydroformylation of epoxides, special catalysts and ligands are needed to suppress side reactions such as isomerization and hydrogenation.

Previously, chelating diphosphine ligands have been reported for the cobalt catalyzed hydroformylation of epoxides.[3] For the rhodium catalyzed hydroformylation of olefins and for carbonylation reactions P–O ligands have been found to be superior to their phosphine analogues.[4] This fact prompted us to apply P–O ligands to the hydroformylation of epoxides. To the best of our knowledge, P–O ligands have not been reported for the hydroformylation of epoxides, whereas various diphosphine ligands such as dppm, dppe, dppp and dppb have been reported for this process (Scheme 1).

$$Ph_2P(CH_2)_nP(=O)Ph_2 \qquad Ph_2P(CH)_nPPh_2$$

	n		*n*
dppmO	1	dppm	1
dppeO	2	dppe	2
dpppO	3	dppp	3
		dppb	4

Scheme 1 Structures of investigated ligands.

Using a catalyst prepared *in situ* under the applied reaction conditions from $Co_2(CO)_8$ and dppmO (for abbreviations see Scheme 1) in toluene, ethylene oxide **1** was converted to 3-hydroxypropanal **2** with 89% selectivity. Hydrogenation of **2** yielded 32% of propane-1,3-diol (1,3-PDO), **3** (Scheme 2).†

Scheme 2
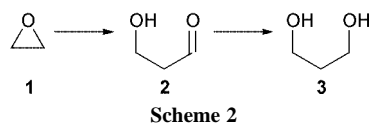
In comparison to dppe (Table 1, run 2) the dppmO system proved to be much more efficient in terms of higher selectivities and yields. The reaction with diphosphines strongly depends on the solvents applied. Performing the reaction in a mixture of toluene and chlorobenzene, which is known to yield the best results for dppe, we could only achieve a 17% maximum yield of 1,3-PDO under the conditions selected.

To examine the role of the chelate effect of the ligands, the reaction was run with monodentate triphenylphosphine ($Co:PPh_3 = 1:2$) and with triphenylphosphine and diphenylmethylphosphine oxide ($Co:PPh_3:Ph_2MeP(O) = 1:1:1$) as ligands (Table 1, runs 3 and 4). Scarcely any 1,3-PDO was observed after hydrogenation. Obviously, the presence of a chelating ligand is an important condition for a catalytically active system.

The use of dppeO and dpppO (Table 1, runs 5 and 6) as ligands led to a significant decrease in selectivity and yield, indicating that ligands which are capable of forming a five-membered chelate ring are preferred. A similar trend was observed employing dppm, dppp and dppb (Table 1, runs 7, 8, 9) as ligands.

As is well known in homogeneous catalysis, the variation of the ligand to metal ratio can have a strong influence on the activity and selectivity of the reaction. We thus varied the dppmO to cobalt ratio (Table 1, runs 10–14) and found that an increase of the amount of dppmO employed led to a steady enhancement of the 1,3-PDO yield, whereas an inverse relationship was observed for dppe.[5] The maximum yield of 1,3-PDO was obtained for a 1:1 ratio of dppe to cobalt and increasing the ligand to cobalt ratio resulted in a dramatic loss of activity. An explanation for the different behavior of the dppmO–Co system may be understood from ^{31}P NMR investigations of the reaction mixture after a pre-formation period. For a dppmO to cobalt ratio > 1, free ligand can be detected. It is known that triphenylphosphine oxide is used as a promoter for the hydroformylation of ethylene oxide[6] and excess dppmO may act in a similar manner. By increasing the amount of the free ligand the activity of the system is improved and therefore, dppmO can act as ligand and promoter at the same time.

We were able to isolate a stable cobalt complex [(dppmO)-$Co(CO)_3]_2$, a single crystal X-ray analysis of which confirmed the dimeric structure (Fig. 1). The coordination geometry around cobalt is trigonal bipyramidal.‡

A comparison of the catalytic behavior of the isolated complex (Table 1, run 15) to the *in situ* system gave nearly

Table 1 Cobalt catalyzed hydroformylation of ethylene oxide **1**

Run	Ligand	Ligand:Co	GC yield of **3**[a](%)	Selectivity toward **2**[b] (%)
1	dppmO	1:1	32	89
2	dppe	1:1	10	76
3	PPh_3	2:1	< 1	—
4	PPh_3, Ph_2MeP(O)	1:1:1	≈ 2	—
5	dppeO	1:1	9	63
6	dpppO	1:1	5	51
7	dppm	1:1	—	—
8	dppp	1:1	4	52
9	dppb	1:1	3	58
10	—	—	3	—
11	dppmO	1:2	22	59
12	dppmO	3:4	26	89
13	dppmO	3:2	47	84
14	dppmO	2:1	54	84
15	[(dppmO)Co(CO)_3]_2	1:1	31	90

[a] Yields are based on the substrate and were determined by gas chromatography with standard compounds. For simpler GC detection all samples were hydrogenated. [b] Selectivity = products/(by-products + products).
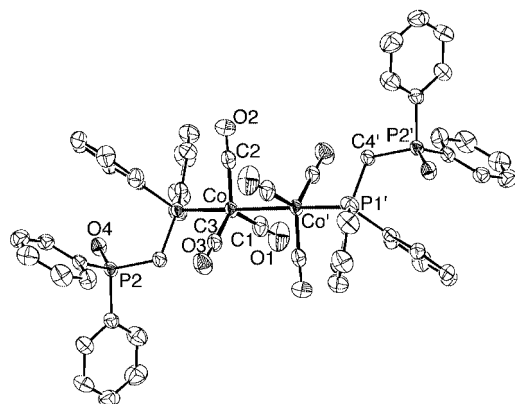
Fig. 1 Displacement ellipsoid plot (PLATON[11]) of the molecular structure of [(dppmO)Co(CO)$_3$]$_2$ in the crystal. Ellipsoids are drawn at 50% probability with hydrogen atoms omitted. Primed atoms are related to unprimed ones by the symmetry operation $-x$, $-y$, $-z$. Selected bond distances (Å) and angles (°): Co–Co′ 2.660(1), Co–P1 2.185(1), P1–C4 1.836(3), C4–P2 1.818(3), P2–O4 1.481(2); Co–Co′–P1′ 178.45(4), P1–C4–P2 121.6(2).

identical results and thus it can be assumed that for both runs the same catalytically active species are formed. The reaction sequence shown in Scheme 3 is proposed for this catalytic system.

$$2 \ dppmO + Co_2(CO)_8 \longrightarrow [(dppmO)Co(CO)_3]_2 \xrightarrow{CO/H_2} (dppmO)Co(CO)_2H$$

active complex
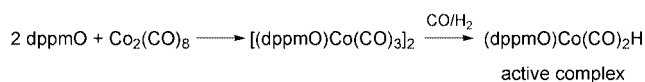
Scheme 3 Proposed catalytic sequence.

Cobalt catalyzed hydroformylation with dppmO as ligand can be readily applied to other epoxides affording the corresponding 1,3-diols after hydrogenation of the 3-hydroxy-aldehydes (Table 2).

Propylene oxide and *trans*-2,3-epoxybutane (Table 2, runs 1, 2) are especially suitable for hydroformylation. The poorer results for styrene oxide and cyclohexene oxide can be explained in terms of increased isomerization to the corresponding aldehydes. It is known that Co$_2$(CO)$_8$ may catalyze those isomerization reactions.[7] Assuming that the isomerization occurs *via* an ionic mechanism and that the stabilization of the

Table 2 Cobalt catalyzed hydroformylation of different epoxides with dppmO

Run	Epoxide	Yield of 1,3-diol[a] (%)	Selectivity toward 3-hydroxyaldhyde[b] (%)
1	Propylene oxide	30	75
2	*trans*-2,3-butene oxide	66	79
3	Cyclohexene oxide	39	52
4	Styrene oxide	7	4

[a] Yields are based on the substrate and were determined by gas chromatography with standard compounds. For simpler GC detection all samples were hydrogenated. [b] Selectivity = products/(by-products + products).

intermediate carbocation is of importance, the extent of the isomerization of styrene oxide becomes understandable.

In conclusion, the hydroformylation of epoxides employing hemilabile P–O ligands and cobalt metal salts has been successfully carried out for the first time. Suitable hemilabile ligands must be able to form a chelate ring with cobalt, preferably a five membered-ring chelate. An excess of the hemilabile ligands further enhances the yield of the β-hydroxyaldehydes. The reaction can be extended to different epoxides establishing a new route to synthesize 1,3-diols or 3-hydroxyaldehydes.

Notes and references

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