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Aerobic Epoxidation of Olefins Catalysed by Square-Planar Cobalt(III) Complexes of Bis-*N,N'*-disubstituted Oxamides and Related Ligands

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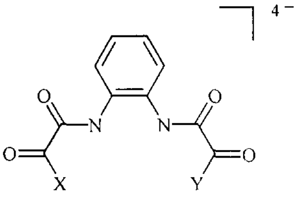
Abstract: Three new monomeric square-planar cobalt(III) complexes of bis-*N,N'*-disubstituted oxamides and related ligands have been prepared. These complexes catalyse the epoxidation of tri- and di-substituted olefins with molecular oxygen/pivalaldehyde with very good yields.

Olefin epoxidation stands as one of the most useful functional group manipulations in organic synthesis because the formed epoxides are intermediates that can be converted to a variety of products. The use of transition-metal complexes as catalysts for epoxidation has received increasing attention during the last decade and a variety of catalytic systems are avalaible today. This variety arises from the posibility to use several transition-metals ions, organic ligands and terminal oxidants. For instance, cobalt and manganese complexes are included among the most effective catalysts for the oxidation of different types of organic substrates. Thus, several (salen)manganese(III) complexes have been efficiently utilized by Jacobsen[1] and Katsuki[2] for olefin epoxidation. Recently we have also reported an epoxidation catalysed by a new (salen)Mn(III) complex bearing a sesquiterpene salicylaldehyde moiety.[3] Several square planar or pyramidal Co(II)[4-9] and octahedral Co (III)[5,10] complexes have been reported to be efficient catalysts for epoxidation of olefins. However, square planar Co(III) complexes are very scarce and they have only been used by Collins[11-12] for olefin epoxidation.

Bis-*N,N'*-disubstituted oxamides and related ligands have been recently shown by some of us[13] to be useful ligands in the stabilization of unusual tervalent oxidation state complexes of copper and nickel, owing to the high donor capacity of the deprotonated amido group. In this Letter we report on the synthesis and general characterization of the corresponding Co(III) complexes with this new family of ligands and their use as catalysts in epoxidation reactions of unfunctionalized olefins.

The monomeric Co(III) complexes of general formula $(NMe_4)[CoL]\cdot 2H_2O\cdot CH_3CN$, where NMe_4 is the tetramethylammonium cation and L stands for *ortho*-phenylenebis(oxamate) (opba) **1**, *ortho*-phenylene(*N'*-methyloxamidate)oxamate (Meopba) **2** and *ortho*-phenylenebis(*N'*-methyloxamidate) (Me_2opba) **3**, were prepared by reaction of $Co(ClO_4)_2\cdot 6H_2O$ with one equivalent of the corresponding ligand[13] and an excess of NMe_4OH in methanol under aerobic conditions at room temperature. Complexes **1**, **2** and **3** were obtained as very hygroscopic brownish powdered solids after solvent elimination and treatment with acetonitrile of the resulting oil during a few hours.[14] These complexes are sparingly soluble in aprotic solvents such as acetonitrile or fluorobenzene but very soluble in methanol and water, affording dark-brown solutions. Solidstate variable-temperature magnetic susceptibility measurement for **1-3** over the temperature range 80-300 K showed paramagnetic Curie behaviour with an estimated magnetic moment of about 1.0 cm^3 K mol^{-1} at 298 K. These data are consistent with an intermediate spin-triplet (S = 1) ground state, suggesting that **1-3** were four coordinated complexes as their related Cu(III) or Ni(III) analogues.[13] In fact, square-planar Co(III) complexes although rare, have been structurally characterized for thiolate,[15] biuret[16] and other ligands incorporating amido-donor groups.[17]



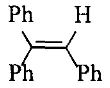
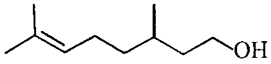
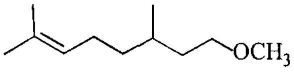
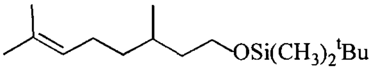
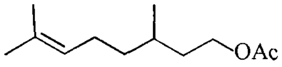
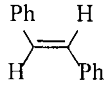
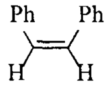
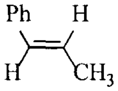
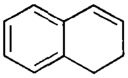
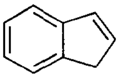
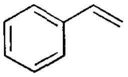
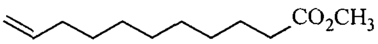
X	Y	Ligand
O	O	opba
O	NCH_3	Meopba
NCH_3	NCH_3	Me_2opba

The epoxidation of some representative substituted olefins using **1**, **2** and **3** as catalyst was next examined. Epoxidation of dihydronaphthalene was firstly carried under a variety of conditions in order to screen various terminal oxidants and to establish the optimal reaction protocol. Thus, we used several common oxidants like iodosylbenzene, sodium hypochlorite (in Jacobsen's conditions), hydrogen peroxide, *tert*-butylhydroperoxide, oxone, sodium and tetra-*n*-butylammonium periodate and oxygen/pivalaldehyde in the adequate solvents. Molecular oxygen in presence of aldehyde (Mukaiyama's conditions) was found to be the only one but very effective oxidant. The reaction proceeded smoothly at ambient temperature to give the corresponding epoxide in good yield. However, contrary to the case of analogues Collins' complexes,[11] no epoxidation was observed when iodosylbenzene was used as terminal oxidant and even with the other oxidants above mentioned.

The above procedure of combined use of pivalaldehyde and molecular oxygen catalyzed by **1**, **2** or **3** in fluorobenzene as solvent was successfully applied to various olefins, as shown in Table for complex **3**. Similar results were obtained with complexes **1** and **2**. Aromatic and aliphatic trisubstituted olefins were smoothly transformed in the corresponding epoxides in high yields. Olefins bearing ether, ester, hydroxy or silyloxy groups were converted into the corresponding epoxides in good to high yields without undesirable decomposition of these functional groups. Olefins with other different substitution patterns were also epoxidized by this procedure, though the chemical yields were diminished to some extent. Thus, while *trans*-stilbene oxide and *trans*-β-methylstyrene oxide were obtained in good yield (95% and 80% respectively), epoxidation of *cis*-stilbene stopped half-way giving the *trans*-epoxide in moderate yield. Cyclic olefins as 1,2-dihydronaphthalene and indene were also converted into the corresponding epoxides with high yields. The highly reactive toward oxygenation styrene, was converted into styrene oxide with good yield without any carbon-carbon bond cleavage. Finally, epoxidation of methyl undecylenate (terminal olefin) stopped half-way yielding the corresponding epoxide in moderate yield. The mechanism of the reaction probably involves an acylperoxo-cobalt(III) species as the active epoxidizing agent as suggested earlier,[18] even if a higher oxidation state cannot be ruled out.[11]

In conclusion, the new complexes **1**, **2** and **3** catalyse the epoxidation of unfunctionalized tri- and di-substituted olefins with molecular oxygen/pivalaldehyde with very good yields. The high selectivity of this mild and effective catalytic system offers a convenient and promising methodology for synthetic purposes.

Table. Epoxidation of Olefins with Oxygen/ pivalaldehyde Catalyzed by Co(III)

Entry	Olefin	Time	Conversion(%)	Yield(%) [a,b]
1		2h	100[c]	98
2		2h30min	100	95
3		1h30min	100	97
4		1h15min	100	95
5		1h15min	100	96
6		2h	100[c]	95
7		4h[d]	50[c]	45[e]
8		1h15min	100	80
9		1h	100	90
10		1h	100	90
11		2h	100	95
12		4h[d]	60[c]	50

[a] Yields refer to isolated and pure compounds (column chromatography on silicagel). In entries 4, and 8-11 column chromatography was carried out on neutral alumina. All compounds exhibited spectral data consistent with their structures.

[b] In absence of catalyst some extension of epoxidation was observed.

[c] Pivalaldehyde (0.66 mmol, 6 eq.) was used in two portions.

[d] With reaction times of 24 hours the conversion was identical.

[e] The reaction product was all *trans*-epoxide.

Typical experimental procedure: A solution of olefin (0.11 mmol) in 0.2 mL of fluorobenzene was added to a stirred mixture of catalyst (6.5 10^{-3} mmol) and pivalaldehyde (0.33 mmol) in 0.2 mL of fluorobenzene under dioxygen atmosphere. The mixture was stirred at room temperature for the indicated time in table and consumption of the starting olefins and formation of epoxide were monitored by TLC. The obtained epoxide and unreacted olefin were separated by flash column chromatography on silicagel or neutral alumina.

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