

The Electronic Structure of Cobalt Jacobsen's Catalyst

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Cobalt salen related systems have a wide range of applications: they are used as catalysts for the oxygenation of organic molecules; they can act as antiviral agents, due to their ability to interact with proteins and nucleic acids; and they have been used to mimic biological co-factors, such as cobalamin. Recently, E. Jacobsen et al. discovered a new Cobalt salen catalyst (**1**) (Cobalt Jacobsen), which can be used for the hydrolytic kinetic resolution (HKR) of terminal epoxides and the enantioselective catalytic ring opening of meso epoxides [1]. The HKR technique is widely used to produce epoxides and diols with a high enantioselectivity (around 98 %) and a high chemical yield. The synthesis of the cobalt Jacobsen's complex occurs in two steps. In the first step cobalt salen complex (**2**) is synthesized which is subsequently activated (to **1**) by exposure to air and addition of acetic acid. In this work, we present an analysis of both cobalt salen complexes (**1** and **2**), by means of CW and pulsed Electron Paramagnetic Resonance (EPR). The *g* and cobalt hyperfine values of the not activated complex **2** show that we are dealing with a low-spin Co(II) complex with a $|yz, ^2A_2\rangle$ groundstate. The X- and W-band EPR spectra of the activated complex **1** bear the characteristics of an organic radical interacting with a cobalt nucleus. X-band HSCORE experiments reveal the hyperfine and nuclear-quadrupole couplings of the nearest nitrogens. Large changes are observed in both the nitrogen and proton HSCORE spectra upon activation of the complex. The EPR data will be discussed in function of the electronic structure of both complexes and related to known work on Co(II) complexes.

References:

[1] Tokunaga, M.; Larrow, J.F.; Kakiuchi, F.; Jacobsen, E.N., *Science*, 277, 936 (1997)

