Abstract

Ozonation of some transition-metal organometallic hydrides

The reactions of C−H, Si−H and Ge−H bonds of carbon, silicon and germanium compounds with ozone and the formation of hydrotrioxide intermediates have been well described in the literature. In my dissertation, I focused on the investigation of the ozonation of M−H bonds of some organometallic hydrides of transition metals, in particular the organometallic pincer complexes of nickel, palladium and platinum.

Since the pincer complexes of these metals are not commercially available, I prepared them from commercially available metal precursors and ligands according to modified literature procedures. The organometallic halides obtained from these reactions were then reduced to M−H bonds. I also prepared the corresponding M−OH and M−OCO_2H pincer complexes to characterize the products of the ozone oxidation reaction. All were characterized by NMR spectroscopy and some were also crystallized and analyzed by X-ray diffraction.

The ozonation of organometallic hydrides has proven to be very difficult because the resulting intermediates are not stable at room temperature. I was therefore limited to a very low temperature range (−70 °C > T > −90 °C), which still allows NMR experiments in the liquid phase. I found that ozonation of organometallic hydrides in the presence of CO_2 leads to the formation of hydrogencarbonate complexes, which can be formed either directly from the hydrotrioxide intermediate or from the hydroxide as oxidation end product. Despite great efforts to avoid the presence of CO_2 altogether, this has proven impossible, as ozone also oxidizes the pincer complexes to some extent already in the reaction mixture, causing them to decompose and partially form carbon dioxide. I indirectly confirmed the formation of the unstable oxidized intermediate by ^{1}H, ^{31}P, and ^{17}O NMR spectroscopy. However, I could not conclusively confirm the structure of the detected intermediate by low-temperature crystallization and X-ray structure analysis because this intermediate is too unstable to crystallize at low temperatures. Furthermore, I could not detect the characteristic M−OOO<u>H</u> absorption for the hydrotrioxide proton by ^{1}H NMR spectroscopy.

I also found that $^{t\text{-Bu}}$(PCP)Pd−OH catalyzes the keto-enol tautomerism of acetone and other carbonyl compounds. Therefore, I used this property in experiments on catalytic reactions in catalysis. I found that as little as 1.5 mol% of the above complex catalyzed the Michael condensation reaction between acetylacetone and nitrostyrene in the presence of a minimal amount of solvent.

Key words: pincer complexes, reduction, ozone, hydrotrioxides, aldol condensation