

## An Unexplained Observation

### Which intermediate product causes the blue colouring in a Grignard reaction involving zirconium chelates?

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While working on the doctoral thesis about chelates of zirconium and hafnium – cf. [1] for preparation of the ligands and [2] for preparation of the chelates – we made an observation which could not be explained and therefore was only described in the doctoral thesis of Christof Tröltzsch, Leipzig, 1960, in the following way:

After adding 1 mmol tris(1,3-diphenyl-1,3-propane-dionato)-zirconium chloride to a solution of 10 mmol cyclopentadienyl magnesium chloride [3] in dry diethyl ether under dry pure nitrogen at room temperature, an intensive green colour was immediately observed, which later changed to dark brown under evolution of minute gas bubbles. At room temperature, the same observations were made for the reaction with ethyl magnesium bromide.

At -20°C the green colour appeared slowly. At temperatures below -5°C the green color was stable for more than 24 hours under inert conditions. When the temperature rose to 0°C or higher, the brown colour appeared under gas evolution. Phenyl magnesium bromide showed the same behaviour. A similar phenomenon was observed in the reaction of ethyl magnesium bromide with tris(1,3-diphenyl-1,3-propane-dionato)-zirconium bromide, tetrakis(1,3-diphenyl-1,3-propane-dionato)-zirconium, tetrakis(1,2,3-triphenyl-1,3-propane-dionato)-zirconium and tetrakis(1,3-bis(*p*-biphenyl)-1,3-propane-dionato)-zirconium, but in these cases the colour was an intensive blue-green.

We suspect that the colour of the unknown reaction product is blue and that the blue-green shade is the result of a mixture with yellow chelates. In some cases the blue-green colour changed via yellow to brown when heated to temperatures above 0°C. An analogous reaction under the same conditions with tetrakis(2,4-pentane-dionato)-zirconium at -15°C instantaneously showed a yellow colour, which then changed to brown. No green or blue-green intermediate colouring was observed.

We suppose that the blue colour is caused by the reduction of zirconium(IV) to zirconium(III), which is only stable when the unpaired electron of zirconium(III) is stabilized by conjugation of the chelate ring with aromatic systems. Further stabilization can be reached by voluminous aromatic substituents.

All experiments were conducted in a flask, which priorly had been used to prepare the Grignard reagent, thus unreacted magnesium was still present. Besides the Grignard reagents the magnesium could also act as reducing agent.

B. N. Chakravarti [4] prepared tris(2,4-pentane-dionato)-titanium which

dissolves in benzene with intensive blue colour. Titanium dihalides and titanium trihalides are much more stable than the corresponding zirconium and hafnium halides. [5-8] This explains why a titanium(III) chelate only slowly reacts with oxygen, while a zirconium(III) chelate is solely stable under inert conditions, low temperature, stabilisation by mesomerism and perhaps steric shielding.

We tried to produce the corresponding chelate from zirconium trichloride – prepared according to [5] – and 1,3-diphenyl-1,3-propane-dionato sodium, but the reaction failed. The preparation of 1,3-diphenyl-propane-1,3-dion itself does not lead to the desired result, because the released hydrogen chloride immediately reacts with zirconium trichloride, which results in zirconium tetrachloride and hydrogen.

To test the magnetism of the unknown intermediate, a sample of the green solution, which was as concentrated as possible and prepared by the reaction of ethyl magnesium bromide with tris(1,3-diphenyl-1,3-propane-dionato)-zirconium chloride in diethyl ether, was filled into a Quinke tube [9] with cooling jacket and put into an inhomogeneous magnetic field of max. 20000 Gauss. All procedures were carried out well below 0°C. The solution showed diamagnetism, but an approximate calculation indicated that the diamagnetism of the solvent can be dominant.

We suppose the zirconium(III) chelate with 1,3-bis(*p*-biphenyl)-1,3-propanedione to be most stable, but this ligand will not be commercially available and should be prepared according to Ref. [1]. We think that ESR measurements could solve the introductory question. Despite my habilitation in 1967 I was not free in deciding the direction of my research activities and after 1990 other work was much more important. I would be very glad if someone in the scientific community could solve this old problem.

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