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Materials Science
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Oxygen sensitive rhodium NHC complexes with a vibrant range of colours

Novel Rh-NHC complexes were developed which show remarkably high sensitivity to oxygen. The drastic colour change that these complexes undergo when oxidized makes them a promising candidate as efficient colourometric oxygen sensors.

From a similar set of structures, Olena Zenkina and associates at Queens University were able to synthesize compounds which demonstrate a remarkably high sensitivity to oxygen and yield a range of colours. When exposed to oxygen, the synthesized compounds undergo drastic and beautiful colour changes. The obvious visual changes these compounds undergo when exposed to oxygen make them exceptionally applicable in the field of colourmetric oxygen sensors. The synthesized compounds are coordination rhodium NCH complexes. This research was encouraged by the need for inexpensive oxygen sensors required by the food industry. This article was published in 2012 and the patent for the developed materials is still pending.

With the growing global population, proper preservation of food has become increasingly important. Food may spoil for a variety of reasons including growth of microorganisms, the decomposition due to enzymes and oxidation of the food by atmospheric oxygen. The process of vacuum sealing food is an effective method for reducing these effects. Removing oxygen reduces the growth of obligate anaerobic microorganisms and reduces the activity of decomposing enzymes. It also reduces the possibility of oxidation of the food. When a food is vacuum sealed, it is essential for the safety of the consumers to ensure that the product has not come into contact with oxygen. If the vacuum sealing fails, and the product is subjected to oxygen, the food could spoil and could then be dangerous to consume. This is where the application of the colourometric oxygen sensors would be applied. A compound which changes colour when exposed to oxygen could be placed on the inside of the packaging. This could be easily used to see if the vacuum sealing has failed, and oxygen has entered the packaging. For this compound to be useful, many factors must be considered. Since one of the main applications is in the food safety, it should not be toxic in small amounts. It should be sensitive to small amounts of oxygen and the colour change should be sufficiently drastic so that the change is obvious. The compound should be stable until exposed to oxygen so that it does not decompose before exposed to oxygen. All of these considerations have been met by the complexes produced by the research of Zekina and associates.

The oxygen sensitive complexes which were developed are coordination rhodium complexes with NHC ligands, to now be referred to the RhNHC complexes. Coordination complexes are the general group of chemicals used to describe a complex with a central atom, usually metallic, with different surrounding bound moieties. Ligand is the term used to describe the moieties bound to the metal centre. Ligands bring positive or negative charges which will affect the oxidation state of the metal centre. Though this is the general definition of a coordination complex, coordination complexes may have two or more metal centres, as in the case of the RhNHC complexes developed in this experiment. When there are two metal centres, the complex is referred to as a dimer, compared to when there is one metal centre, the complex is referred to as a monomer. Just as copper goes from a gold to a green when oxidized, many other metal complexes will undergo a colour change when oxidized. This is the reason for the drastic change in colour of the RhNHC complexes when exposed to oxygen; the metal centre became oxidized. Oxidation in this context is the process of the metal centre increasing its oxidation state. In the case of the RhNHC complexes, as will be shown, the oxidation state will increase from I to III with the association of oxygen, a negative ligand.

In this article, 11 complexes were synthesized. The synthesis of all of these compounds revolved around reactions starting with complex 1 (Figure 1) was the key to such successful reactions: the metal centres are highly reactive due to their high level of unsaturation. Rhodium (0) has d^9 valence electron configuration and, with one negatively charged chloride ligand, the metal becomes rhodium (I) now with d^8 electron configuration. Transition metals such as rhodium are most stable when their electron count is 18, complex 1 has an electron count of 14, making it highly reactive as it will readily accept more ligands. Complex 1 was reacted with pyridine and, in a separate reaction, with lutadine, to produce complexes 3 and 4 respectively. Complex 3 was a bright yellow and complex 4 was an orange-yellow. Complex 1 was also reacted with BiPy and, in a separate reaction, Phen to form complexes five and six respectively, shown in Figure 4 and 5. Complex 6 was a dark purple colour and complex 5, a dark blue. This reaction schema is shown in Figure 2. The reaction of a comparable to complex 1 monomer under these same conditions did not yield any detectable amount of product 5 or 6. This suggests that complex one could also be a superior catalyst for other reactions not studied in this paper. The reactions of complex 5 and 6 with oxygen were then

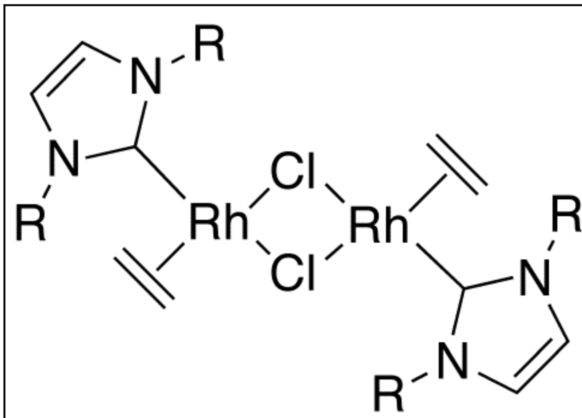

Figure 1: Complex 1

studied. When exposed to oxygen, dark green compound 5 reacted to form bright yellow compound 9, and deep purple complex 6 decomposed to form yellow-orange complex 10. Both complex 9 and 10 decomposed to form complex 11. It was considered that it could be a problem that complexes 9 and 10 decomposed. Zenkina was asked about this, she said that the desired applications of the RhNCH complexes only require them to permanently change when exposed to oxygen and the fact that they decomposed to form complex 11 was actually a good thing since it shows that they are not going to react in the opposite direction to form back complex 6 or 7.

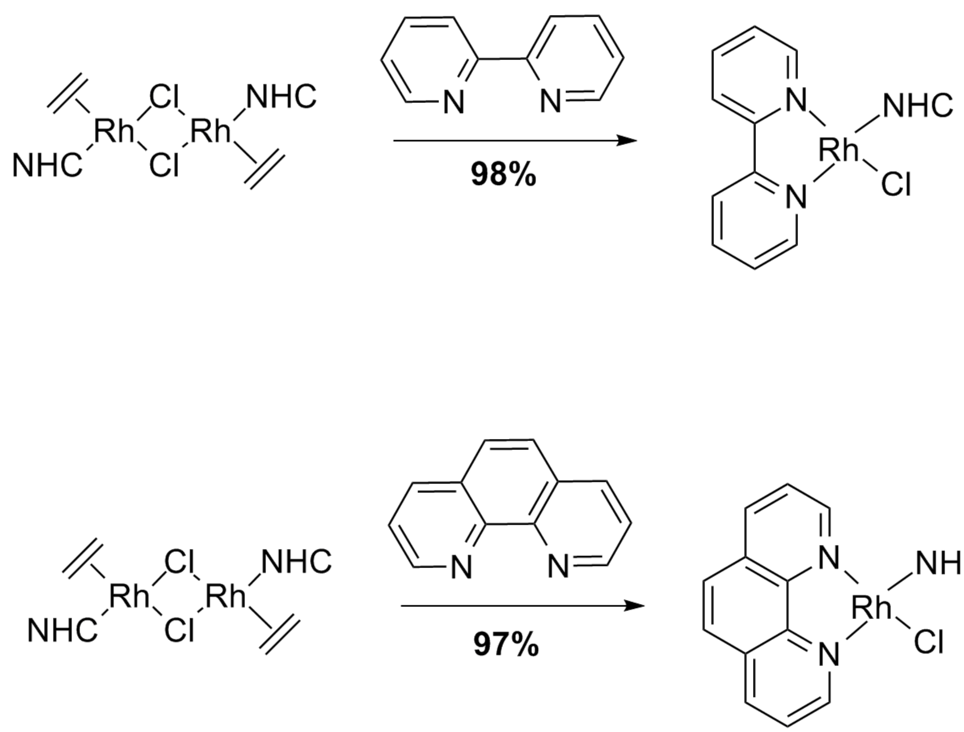

Figure 2: Reaction Schema to synthesize complex 5 (top) and complex 6 (bottom)

In order to be able to report on any of the complexes produced in this study, structural information had to be gathered. Throughout the experiment, x-ray crystallography and NMR data was used to gather information regarding the structure of the complexes. For most complexes, this was not an issue, however some issues arose when the structures displayed fluxional behaviour. Fluxional behavior was a particular issue for complex three. The fluxional behaviour is due to the free rotation of the NHC ligand. To combat this, Zenkina reduced the fluxional behavior of the NCH ligand by replacing the two hydrogens on the NHC complex with two methyl groups which greatly hindered any rotational motion. This was further stabilized by gathering structural information at lower temperatures.

There is an exciting research in the future of the RhNHC complexes. Complex 6 shows the most promising results. When considering the applications of these complexes, it is desirable to use the smallest possible quantity for health and financial reason. Complex 6 has such a deep purple colour that the colour is visible in microscopic quantities and more importantly, the colour change when complex 6 is oxidized to form complex 10 and then decomposed to form complex 11 is sufficiently drastic that it can be noticed in such small quantities. Because of these promising results, complex 6 will be focused on. Since the applications of this research mostly revolve around using the complexes as a colourometric oxygen sensor in food packaging, attaching the complex to the surface of plastic is of considerable interest. Zenkina said that further research regarding the attachment of complex 6 has already been commenced and that the research is promising. Zenkina has already shown how the complex may be attached as a monolayer on a polymer and it remains highly effective at detecting oxygen. Having only a monolayer required, a sufficient amount of this complex would only costs cents and have no toxic effect. Zenkina's research could greatly improve the detection of oxygen contaminated products.