Use of a Titanium Metallocene as a Colorimetric Indicator for Learning Inert Atmosphere Techniques

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We have recently discovered that titanium(III) metallocene compounds provide a very useful visual aid for students learning standard Schlenk vacuum line techniques (*1*). Our process for training students in these procedures begins by demonstrating various anaerobic techniques such as solvent degassing, solution transfer through a cannula, and filtering through frits or immersion filters (*2*). The students are then instructed to practice these techniques using a solution of a Ti^{3+} metallocene (preparation described below). A striking blue to yellow color change provides an immediate signal that helps students to judge whether they performed an operation correctly. This experience accelerates the learning process and rapidly increases their self-confidence to work independently on the vacuum line. Both undergraduate and graduate students new to the research lab have benefited from this exercise and have gained respect for the care needed to successfully accomplish operations with rigorous exclusion of dioxygen gas.

A solution of the reactive Ti(III) metallocene indicator can be easily prepared in situ in a Schlenk flask attached to a Schlenk vacuum line. Dicyclopentadienyltitanium(IV) dichloride (cyclopentadienyl, C_5H_5, hereafter referred to as *Cp*; available from Aldrich Chemical Co. as *titanocene dichloride*, catalog #23,482-6) is dissolved in deaerated acetonitrile followed by addition of zinc dust.[1] A slow reduction reaction[2] can be followed visually through a series of color changes. The initially orange-red solution of $TiCp_2Cl_2$ turns green as the dimer $(TiCp_2)_2(\mu\text{-}Cl)_2$ is formed (Fig. 1).[3] The appearance of a deep blue solution signals the formation of $[TiCp_2(NCCH_3)_2]^+$, a result of facile dimer cleavage in the coordinating solvent acetonitrile (*3*). When this is exposed to O_2, the deep blue color of $[TiCp_2(NCCH_3)_2]^+$ is rapidly bleached to yellow as Ti^{3+} is oxidized back to Ti^{4+}.

After preparation of the blue $[TiCp_2(NCCH_3)_2]^+$ solution in Schlenkware, students practice a variety of operations in which the reactive blue $[TiCp_2(NCCH_3)_2]^+$ solution will quickly indicate errors of technique. One common operation is the anaerobic transfer of solutions from one flask to another through a steel tube or cannula. Neglecting to purge the cannula of air by passing through inert atmosphere for several minutes or insufficient purging of the receiving flask by repetitive evacuation and N_2-refill cycles will be exposed to the student when the blue solution turns yellow during the transfer operation. As a second example, this colorimetric method helps students judge the nitrogen gas flow needed to permit the successful exchange of a rubber septum for a reflux column, glass stopper, or another piece of apparatus when the flask is opened.

We have also used the solution of $[TiCp_2(NCCH_3)_2]^+$ as a colorimetric indicator for oxygen contamination in inert-atmosphere glove boxes. Small quantities of the blue solution are conveniently prepared by dissolving small (mg) amounts of $TiCp_2Cl_2$ in acetonitrile in a scintillation vial, adding zinc dust, and capping. Aliquots of this solution may be removed by disposable pipet and transferred to an open vial. Inspection of the aliquot gives a qualitative indication of the dioxygen level in the glove box. As the solution is exposed to trace dioxygen the solution color changes from blue to green and ultimately, under higher dioxygen concentrations, to yellow.

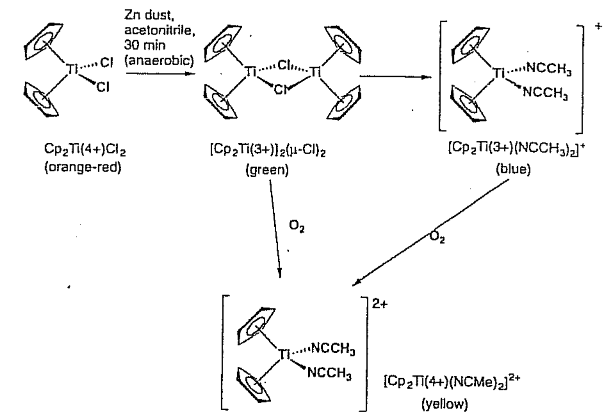

Figure 1. Reaction scheme for synthesis of the colorimetric indicator $[TiCp_2(NCCH_3)_2]^+$ and its reaction with dioxygen.

Acknowledgment

We thank John Bercaw for helpful comments regarding the bis(cyclopentadienyl)titanium chemistry.

Notes

1. Example quantities are 8 mg $TiCp_2Cl_2$ in 20 mL acetonitrile to which is added 6 g of zinc dust.

2. The reduction typically requires at least 15 min and is complete within 30 min.

3. If the reduction is carried out in tetrahydrofuran (THF) solution the reaction stops after formation of green $[TiCp_2]_2(\mu\text{-}Cl)_2$ and no blue species appears even after prolonged reaction times.

Literature Cited

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2. An excellent text describing modern methods and equipment used in anaerobic work is *Experimental Organometallic Chemistry*; Wayda, A. L.; Darensbourg, M. Y., Eds.; ACS Symposium Series No. 357; American Chemical Society: Washington, D C, 1987.
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Use of a Titanocene Complex as a Colorimetic Indicator for Learning Inert Atmosphere Techniques

Before beginning a full-scale preparation, you must first conduct the following simple test to determine your synthetic skills in handling air-sensitive compounds. This simple experiment will give you a quick and easy indication of whether you can manipulate an oxygen-sensitive compound through a variety of steps such as filtration, cannula transfer, and short-term storage. Note that the compound you're making is not water sensitive.

Procedure

Stir 0.1 g of Cp_2TiCl_2 in 20 mL of acetonitrile in a 100 mL Schlenk flask using a magentic stirrer. Bubble nitrogen through the solution via a cannula inserted through a Suba Seal inserted in the 24/40 joint (you'll also need to insert a vent).

Under a nitrogen counterflow, add a few grams of Zn *dust* and continue stirring. Periodically stop the stirrer and examine the solution.

When you have a nice blue/purple solution on settling, filter this into a Schlenk tube using a cannula with a Whatman #1 filter paper wired to it.

Practice manipulating the resulting solution:

- Put a few drops in a test tube in air to see how quickly it changes color (decomposes!).
- Use a syringe to see how well you can transfer the solution without decomposition
- Add some non-degassed acetonitrile to see the effect of dissolved oxygen.
- Stopper some of the solution to see how long your sample survives – compare with your neigbors.

When you can routinely handle these solutions, you're ready to move on to the experiments in the rest of Group A.

0.1 g Cp_2TiCl_2 in 20 mL CH_3CN = 0.02 M

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A method is described to aid the instruction of undergraduate and graduate students in inert atmosphere techniques. A highly oxygen-sensitive organometallic compound, a titanium metallocene, changes color form blue to yellow when exposed to dioxygen contaminant, thereby providing an easily visualized monitor for students learning to manipulate the special glassware and operations typical of inert atmosphere reactions.

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First, the box was purged with argon for one hour. A dark blue solution of [Cp2TiClCl]ZnCl2*2THF was then prepared and syringed onto a glass plate within the dry-box. After 10 min, during evaporation of the THF, the solution became olive green, indicating >5 ppm of oxygen. After 20 min the solution became deep orange, indicating a >20 ppm oxygen content. Since the moisture test indicated the absence of water for more than three days whereas the oxygen test indicated the presence of oxygen within 20 min, the gloves must be semipermeable to oxygen but impermeable to water. Therefore, an improvement in this box would be to incorporate neoprene or equivalent dry-box gloves. These range in price from $100 to $200.