

## **Experiment 2**

### **The Synthesis of Arenetricarbonylchromium (0) Complexes**

## EXPERIMENT 2:

### THE SYNTHESIS OF $\eta^6$ -ARENETRICARBONYLCHROMIUM(0) COMPLEXES

#### Aims of the experiment

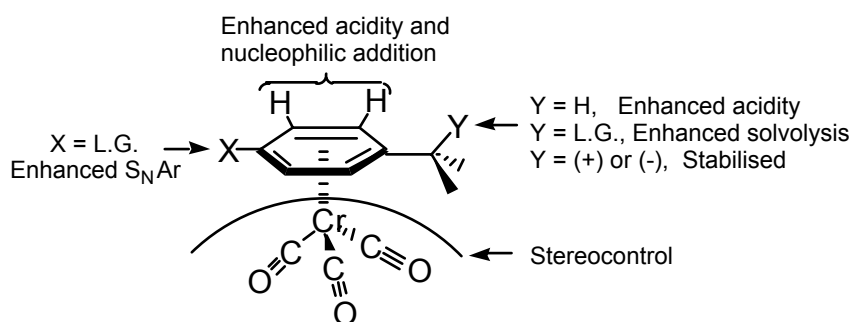
To use vacuum line techniques to prepare sensitive arenetricarbonylchromium (0) complex.

#### Techniques used/learned:

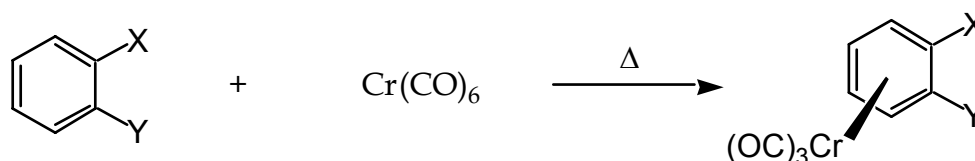
The use of vacuum line techniques for synthesis under anaerobic conditions.

#### Introduction

The exploitation of the modification of reactivity of an organic molecule by complexation to a metal is one of the major areas of development in organic synthesis in recent times<sup>1</sup>. One particular area is the study of the enhanced reactivity of arenes upon complexation by Group VI metal and manganese carbonyls. Among these by far the most studied are the aren chromium tricarbonyl complexes<sup>2</sup>. The effect of the metal moiety on the arene ring is an apparent electron withdrawal from the  $\pi$ -system and this manifests itself in a variety of ways as shown below:



It is important for the ease of use of such complexes that they should be readily prepared and efficiently decomplexed. This experiment demonstrates the most convenient method of preparation using a simple vacuum line/nitrogen manifold. The complexes are synthesised by the direct reaction between the arene and chromium hexacarbonyl in an ether solvent mixture (Bu<sub>2</sub>O-THF 10-1)<sup>3</sup>.



The need for the Schlenk line arises from the fact that the intermediates generated during the synthesis, the coordinatively unsaturated chromium carbonyl species, are very oxygen sensitive and rigorously anaerobic conditions are essential. Once formed the arene complexes are air stable in the solid state and can be handled without difficulty by conventional techniques.

## **HAZARD DATA - READ THIS BEFORE GOING ANY FURTHER!**

### **DIBUTYL ETHER:**

#### **IRRITATING TO EYES, SKIN, AND RESPIRATORY TRACT FORMS EXPLOSIVE PEROXIDES FLAMMABLE**

Colourless liquid; b.p. 142°C; immiscible with water. Liable to form explosive peroxides on exposure to light/air. Peroxides removed by treatment with aqueous sodium metabisulfite. Avoid breathing vapour. avoid skin/eye contact.

- Toxic effects:** The vapour is somewhat irritating to the respiratory system. The liquid irritates the eyes and is hazardous by skin absorption.
- Hazardous reactions:** Peroxide formation can result in subsequent explosion. Powerful oxidants can cause explosion.
- Fire Hazard:** Flash point 25°C, ignition temp. 194°C; extinguish fire with CO<sub>2</sub>.
- Spillage & disposal:** Wear face shield, goggles and gloves. Absorb bulk quantities on sand, shovel into containers and remove to a chemical disposal skip. Wash site of spillage with plenty of water and detergent.

### **TETRAHYDROFURAN:**

#### **IRRITATING TO EYES AND RESPIRATORY TRACT MAY FORM EXPLOSIVE PEROXIDES HIGHLY FLAMMABLE**

Colourless volatile liquid with ethereal odour; b.p. 66°C; miscible with water. Liable to form explosive peroxides on exposure to light/air. Peroxides removed by treatment with aqueous sodium metabisulfite. Avoid breathing vapour, eye and skin contact. OEL 295 mgm<sup>-3</sup>.

- Toxic effects:** The vapour irritates eyes and respiratory system; high concentrations have narcotic effect. Absorption or ingestion may cause liver damage.
- Hazardous reactions:** Explosive peroxides formed on exposure to air/light. NaOH/KOH can cause explosion with peroxidised material.
- Fire hazard:** Flash point -17°C; ignition temp. 321°C; extinguish fire with CO<sub>2</sub>.
- Spillage & disposal:** Clear area, shut off all sources of ignition. Wear goggles, gloves, and laboratory coat. Mop up with plenty of water and run to waste. Organise effective ventilation and evaporate remaining liquid.

### **FLUOROBENZENE:**

#### **HIGHLY FLAMMABLE**

Colourless liquid, benzene like odour; b.p. 85°C; m.p. -45°C; immiscible with water.

- Toxic effects:** Harmful by inhalation and skin contact. May be harmful by ingestion. Irritating to eyes.
- Hazardous reactions:** Can react with oxidising reagents
- Fire Hazard:** Flash point -15°C, extinguish with CO<sub>2</sub>
- Spillage & disposal:** Wear face shield, goggles and gloves. Absorb bulk quantities on sand, shovel into containers and remove to a chemical disposal skip. Wash site of spillage with plenty of water and detergent.

### **CHLOROBENZENE:**

#### **FLAMMABLE HARMFUL BY INHALATION**

Colourless liquid, faint almond odour; b.p. 132°C; m.p. -56°C; immiscible with water. Avoid skin or eye contact. Avoid breathing vapour. OEL 230 mgm<sup>-3</sup>

- Toxic effects:** Harmful by ingestion and inhalation. Irritating to skin and eyes.
- Hazardous reactions:** Can react with oxidising reagents
- Fire hazard:** Flash point 29°C, extinguish with CO<sub>2</sub>
- Spillage & disposal:** Wear face shield, goggles and gloves. Absorb bulk quantities on sand, shovel into containers and remove to a chemical disposal skip. Wash site of spillage with plenty of water and detergent.

### **ANISOLE:**

#### **FLAMMABLE**

### IRRITATING TO EYES, SKIN, AND RESPIRATORY TRACT

Pale yellow liquid, aromatic odour; b.p. 155°C; m.p. -37°C; immiscible with water. Avoid inhalation of vapour

- Toxic effects:** Harmful by ingestion and inhalation. Irritating to skin and eyes
- Hazardous reactions:** Can react with oxidising reagents
- Fire Hazard:** Flash point 41°C, extinguish with CO<sub>2</sub>
- Spillage & disposal:** Wear face shield, goggles and gloves. Absorb bulk quantities on sand, shovel into containers and remove to a chemical disposal skip. Wash site of spillage with plenty of water and detergent.

### CHROMIUM HEXACARBONYL:

#### HIGHLY TOXIC BY INGESTION, INHALATION MAY CAUSE CANCER

Colourless volatile crystals, m.p. 150°C (dec); immiscible with water. Avoid skin/eye contact. Avoid breathing vapour. OEL 0.24 mgm<sup>-3</sup> [assessed as Ni(CO)<sub>4</sub>]

- Toxic effects:** Highly toxic by inhalation. Avoid all exposure. Handle only in an efficient fume cupboard.
- Spillage & disposal:** Do not attempt to deal with a spillage. ***Call a Demonstrator or Technician immediately.***

### DIETHYL ETHER:

#### HARMFUL BY INHALATION, AND INGESTION MAY FORM EXPLOSIVE PEROXIDES EXTREMELY FLAMMABLE

Colourless highly volatile liquid with characteristic odour; b.p. 34°C; immiscible with water. Liable to form explosive peroxides on exposure to light/air. Peroxides removed by treatment with aqueous sodium metabisulfite. Avoid breathing vapour. OEL 1200 mgm<sup>-3</sup>.

- Toxic effects:** Inhalation of the vapour may cause drowsiness, dizziness, mental confusion, faintness and, in high concentrations, unconsciousness. Ingestion may also produce these effects. Continued inhalation of low concentrations may cause loss of appetite, dizziness, fatigue and nausea.
- Hazardous reactions** Peroxide formation can result in subsequent explosion. Powerful oxidants can cause explosion. Reacts vigorously with sulfuryl chloride.
- Fire Hazard** Flash point -45°C, ignition temp. 180°C; extinguish fire with CO<sub>2</sub>.
- Spillage & disposal** Clear area, shut off all sources of ignition. Organise effective ventilation and allow to evaporate. Diethyl ether should be placed in the non-chlorinated waste container for central disposal.

## Experimental Procedure

**IMPORTANT! SAFETY NOTE:** Chromium hexacarbonyl and the chromium complexes you prepare are extremely toxic and may cause cancer. Chromium hexacarbonyl is a volatile solid, which must be handled and weighed out within a fume hood, wearing nitrile gloves. The evaporation step must be carried out on a rotary evaporator situated in a fume hood.

A mixture of anhydrous di-*n*-butyl ether [Aldrich Sure-Seal<sup>®</sup> (60ml)],<sup>4</sup> THF [Aldrich Sure-Seal<sup>®</sup> (6ml)],<sup>4</sup> the arene you have been assigned (10ml) and chromium hexacarbonyl (1.0g) are placed, together with a magnetic stirrer bar, in a 100ml round bottomed flask and a reflux condenser fitted. The assembly is connected to the vacuum line/nitrogen manifold using semipressure tubing and a magnetic stirrer and a heating bath on a lab jack, placed beneath the round bottomed flask.

Check that all joints are sealed then evacuate the apparatus by carefully turning the 3-way tap on the frame (see APPENDIX for the vacuum line/nitrogen manifold system). As soon as the solvent begins to boil, let in the dry, oxygen free nitrogen *via* the 3-way tap. Repeat this cycle nine more times to ensure that the system is completely anaerobic. With the system maintained under a slight positive pressure of nitrogen by the manifold commence stirring and heating the contents of the flask. Maintain the solution at a steady reflux for ~ 24 h.

At the end of this time, the flask is cooled then detached from the apparatus. The solvent is evaporated off **using a cardice Büchi evaporator situated in a fume hood** with minimal bath heating. In the fume hood, the residue is taken up in diethyl ether and the solution is chromatographed over a short (~5cm) column of silica gel 60 using diethyl ether to complete the elution of the yellow/orange complex. Evaporation of the solvents, again **using a cardice Büchi evaporator situated in a fume hood** with minimal bath heating, yields the product.

Record the m.p. of your product and record and interpret the i.r. and n.m.r. spectra.

**NOTE** - the product complex is **unstable** in solution. If possible, make up the NMR sample just before the samples are collected to be run. Cover the sample tube in foil to protect the solution from light, and indicate on the NMR queue sheet that the sample is sensitive.

## Write Up

The write up should conform to *Organic and Biomolecular Chemistry* style (Title, Abstract, Introduction, Results and Discussion, Experimental, References). Your introduction must include discussion of the following points:

1. One recent (2003 or later) example of a synthetic application of arenetricarbonylchromium complexes from the primary literature.
2. One other recent (2003 or later) example from the primary literature of the use of other types of metal carbonyl complex in organic synthesis (*ie* NOT arenetricarbonylchromium complexes). No extra marks for excessive length or detail in description).

## References and Notes

1. For broad surveys see: "*Comprehensive Organometallic Chemistry*" Eds G.Wilkinson, F.G.A.Stone and E.W.Abel, Pergamon Press, Oxford, 1982, Vols 7 and 8; S.G.Davies, "*Organotransition metal Chemistry: Applications to Organic Synthesis*" Pergamon Press, Oxford, 1982; "*Organometallics in Organic Synthesis*" by E.-I. Negishi, Wiley-Interscience, New York, 1980.
2. M.F.Semmelhack, G.R.Clark, J.L.Garcia J.J.Harrison, Y.Thebtaranonth, W.Wulff, and A.Yamashita, *Tetrahedron*, 1981, **37**, 3957; G.Jaouen, *Ann.N.Y.Acad.Sci.*, 1977, **295**, 59; M.F.Semmelhack, *ibid.*, p. 36; D.A. Widdowson, *Phil. Trans. Roy. Soc. Lond.*, 1988, **A 326**, 595.
3. This solvent mixture has been determined empirically to give the optimum reaction temperature and a good backwash of the volatilised chromium hexacarbonyl. See C.A.L. Mahaffy and P.L.Pauson, *Inorg. Syntheses*, 1979, **19**, 154.
4. Dry, distilled solvents are supplied - consult a Demonstrator or Simon Mann **BEFORE** you use them.

## Appendix

The line is simple to use, but note carefully the following points:-

1. Study the frame before you use it and make sure that you understand its operation. If in doubt, **ASK** a Demonstrator!
2. During the flask evacuation / filling sequence, the tap to the oil bubbler should be closed so that the mercury bubbler is in operation. Once the evacuation / filling is over, and you are ready to leave the reaction overnight, open the tap to the oil bubbler and adjust the nitrogen pressure to give a gentle flow through the oil bubbler.
3. Turn taps slowly and carefully. Make sure that you understand the consequences before you turn any tap.
4. Always top up the liquid nitrogen trap in the vacuum line before starting to use the frame. It is essential that you protect the vacuum pump in this way; we cannot afford replacements.
5. Once you have finished using the vacuum line, remember that you must **NEVER** open an active vacuum line to air with the liquid nitrogen trap in place, since this may cause condensation of liquid oxygen with disastrous (and potentially explosive) consequences. Always remove the trap immediately prior to venting the system to air.