COMPARISON OF $[CpMo(CO)_3]_2$ AND $[CpMo(CO)_2]_2$.

ABSTRACT
This experiment is described for a senior level student. It requires the student to read (but not necessarily search for) the primary literature. The synthesis uses molybdenum hexacarbonyl and freshly-cracked dicyclopentadiene as the precursors.

Equipment
The techniques employ basic Schlenk line/inert atmosphere procedures. Characterization is by IR, NMR and mass spectroscopy. The use of a viewing program for crystal structures is encouraged. All reactions should be done in a fumehood.

Safety Hazards
$Mo(CO)_6$ is toxic and dicyclopentadiene is harmful and an irritant and is toxic to aquatic organisms. Halogenated solvents are carcinogenic.

Year Level: 400

Student time required: three to four 3-hour lab periods.

Teaching notes? Available only to instructors upon request.

Contact: Dave Berry (berryde@uvic.ca)

University of Victoria
British Columbia • Canada

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Molybdenum and tungsten are very unusual in that they form two types of dimer as cyclopentadienyl carbonyl complexes. Some interesting conclusions can be drawn from the structures of these two compounds.

You are required to prepare the two dimers of molybdenum. The dicarbonyl dimer is synthesized from the tricarbonyl. A method is suggested below, but adaptions from it, or alternatives from the literature are also possible.

Procedure:
Preparation of $[CpMo(CO)_3]_2$:

$$Mo(CO)_6 \xrightarrow[CH_3CN]{\Delta} Mo(CO)_3(CH_3CN)_3 \xrightarrow[C_5H_6]{\Delta} (C_5H_5)_2Mo_2(CO)_6$$

In advance of the first lab period, ask the instructor to set up a still for acetonitrile. Ask for the cyclopentadiene still to be put on prior to the second lab period.

Reflux molybdenum hexacarbonyl (3.0 g, 11.4 mmol) (**Caution:** volatile and toxic. Weigh in a closed vessel) under nitrogen in dry acetonitrile (30 mL) for 2 h. During the reflux, knock any sublimed molybdenum hexacarbonyl from the condenser back into the reaction flask with a long wire.

Cool the solution and remove the solvent under vacuum to give a solid residue of $[Mo(CO)_3(CH_3CN)_3]$. Record the ir spectrum.

Add freshly distilled cyclopentadiene (10 mL) to the solid $[Mo(CO)_3(CH_3CN)_3]$ and warm the suspension slowly to 90° for 2 h. On cooling, $[CpMo(CO)_3]_2$ starts to precipitate. Reduce the volume of solvent under vacuum to about 5 mL. Decant the supernatant liquid and dry the solid. More product can be obtained by placing the supernatant liquid in the freezer overnight. Sublime on to a cold probe unreacted $[Mo(CO)_6]$ from the solid using a water bath of 40°. Record the yield, ir (CH_2Cl_2), nmr ($CDCl_3$) and electron impact mass spectra.

Preparation of $[CpMo(CO)_2]_2$:
This part of the experiment must be planned based on the literature. Draft a plan and set aside some time to discuss it with the instructor. It will be necessary to prepare well in advance, as some solvents may need to be pre-dried. Allow yourself plenty of time!

Reaction of $[CpMo(CO)_2]_2$:
Use a nucelophilic ligand that will allow you to prepare $[CpMo(CO)_2L]_2$.

The data from the crystal structure determination has been put into a file accessible by *Mercury* (available as a free download from the Cambridge Crystallographc Data Centre home page http://www.ccdc.cam.ac.uk/).

References:
Dobson, G.R.; Amr El Sayed, M.F.; Stolz, I.W.; Sheline, R.K. *Inorg. Chem.*, **1962**, *1*, 526.
Ross, B.L.; Grasselli, J.G.; Ritchey, W.M.; Kaesz, H.D. *Inorg. Chem.*, **1963**, *2*, 1023.
Adams, R.D.; Collins, D.M.; Cotton, F.A. *Inorg. Chem.*, **1974**, *13*, 1086.
Ginley, D.S.; Wrighton, M.S.; *J. Amer. Chem. Soc.*, **1975**, *97*, 3533.
Klingler, R.J.; Butler, W.M.; Curtis, M.D.; *J. Amer. Chem. Soc.*, **1975**, *97*, 3535
Ginley, D.S.; Bock, C.R.; Wrighton, M.S. *Inorg. Chim. Acta.*, **1977**, *23*. 85.
Curtis, M.D.; Klingler, R.L. *J. Organomet. Chem.*, **1978**, *161*, 23.
Klingler, R.J.; Butler, W.M.; Curtis, M.D.; *J. Amer. Chem. Soc.*, **1978**, *100*, 5034.
Cotton, F.A.; Walton, R.A. *Multiple Bonds Between Metal Atoms*, John Wiley & Sons: New York, 1982; pp 245-249.
Gould, R.O.; Barker, J.; Kilner, M. *Acta Cryst., Sect C, Comm.*, **1988**, *44*, 461.
Sargent, A.L.; Hall, M.B. *J. Amer. Chem. Soc.*, **1989**, *111*, 1563.
Curtis, M.D.; Hay, M.S. *Inorg. Synth.*, **1990**, *28*, 150.
Ardon, M.; Hogarth, G.; Oscroft, D.T.W. *J. Organomet. Chem.*, **2004**, *689*, 2429.