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# **BIS[HALOTETRACARBONYLMANGANESE(I)]**

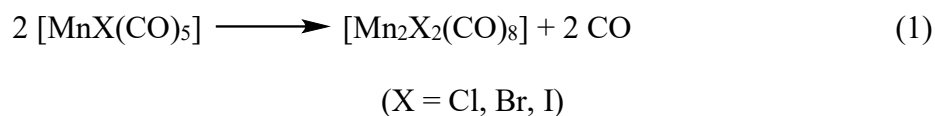
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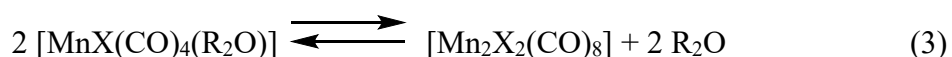
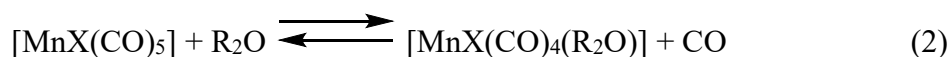
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These compounds were originally prepared by Abel and Wilkinson<sup>1</sup> by way of thermal dissociation of coordinated carbon monoxide from the monomeric halopentacarbonyl derivatives of manganese(I), according to the following stoichiometry:



For reaction (1), the authors used an inert solvent, namely a mixture of saturated hydrocarbons boiling in the 100-120° range. The reported yields are about 40% due to partial decomposition.

The bromo- and iodo-derivatives, which are more frequently used due to their higher thermal stability with respect to the chloro analog, can be conveniently prepared in a poorly coordinating solvent such as diisopropyl ether, which boils at 68-69°. Presumably, the ether solvent stabilizes the tetracarbonyl intermediate arising from CO dissociation before it dimerizes to the final product. The stabilizing effect of the ether solvent, the low temperature, and the low partial pressure of carbon monoxide during the experiment (due to the elevated vapor pressure of the solvent) all contribute favorably to minimizing the formation of the undesired decomposition products  $\text{Mn}_2(\text{CO})_{10}$  and  $\text{MnX}_2$ , and to give excellent yields of the dimeric halo-carbonyl complexes.



### *Procedure*

- **Caution.** *Carbon monoxide and carbonyl compounds are extremely toxic and all reactions must be carried out in an efficient fume hood. Diisopropyl ether is very peroxidizable and must be handled with extreme care. Excess solvent should be discarded as soon as possible.*

A 100-mL reaction flask equipped with an inert gas inlet and connected to another flask of the same volume through a fine, sintered-glass filter is used.\* Under an atmosphere of purified dinitrogen, 2.91 g of  $[\text{MnBr}(\text{CO})_5]$  (10.59 mmoles) and 50 mL of *i*-Pr<sub>2</sub>O freshly distilled over Li[AlH<sub>4</sub>] are introduced into the reaction flask. The suspension is refluxed (the walls of the filter (or condenser) are used as a refluxing chamber) under an initially slightly reduced pressure, and the reaction flask is then connected periodically and briefly to a vacuum line, while the temperature of the external bath is at about 80°. The reaction is monitored by infrared spectroscopy in the carbonyl stretching region, and, after two to three hours, no  $[\text{MnBr}(\text{CO})_5]$  is observed in solution, while the slightly-soluble, brick-red  $[\text{Mn}_2\text{Br}_2(\text{CO})_8]$  is present as a precipitate. The dimeric bromo derivative is filtered at room temperature, washed with water (to remove MnBr<sub>2</sub>), and then with *i*-Pr<sub>2</sub>O, and finally dried under vacuum at room temperature for several hours (yield: 2.2 g; 84.1%).

The product obtained by this procedure is analytically and spectroscopically pure according to the published spectrum<sup>2</sup> and does not require further purification for most chemical purposes. Operating under similar conditions, except for the longer reaction time (about 6 hr), a 90% yield of  $[\text{Mn}_2\text{I}_2(\text{CO})_8]$  is similarly obtained. The longer reaction time required is in agreement with the observed<sup>3</sup> slower kinetics for CO substitution from  $[\text{MnI}(\text{CO})_5]$  compared to  $[\text{MnBr}(\text{CO})_5]$ .

It was found that for both the bromo- and the iodo-derivatives, prolonged refluxing in *i*-Pr<sub>2</sub>O leads to decomposition to  $[\text{Mn}_2(\text{CO})_{10}]$  and MnX<sub>2</sub>.

\* The checkers report that a water-cooled condenser may be used in place of the sintered-glass filter.

### References

1. E. W. Abel and G. Wilkinson. *J. Chem. Soc.*, 1501 (1959).
2. M. A. El-Sayed and H. D. Kaesz, *Inorg. Chem.*, **2**, 158 (1963).
3. A. Wojcicki and F. Basolo, *J. Am. Chem. Soc.*, **83**, 525 (1961).