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Tricarbonyl(η^5-cyclopentadienyl)manganese(I) Complexes

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Since the initial preparation of CpMn(CO)_3 by Fischer and Jira in 1954\(^1\) many methods have been developed for the synthesis of this compound and its C\(_5\) substituted derivatives.\(^2\) Interestingly, each of these preparations has at least one significant drawback from a preparative perspective (e.g. employing thallium reagents, high pressures, poor yields, or reagents that require significant preparative investment).

Surprisingly missing from this collection of preparative methods is the direct reaction between commercially available Mn(CO)_5Br and NaCp. This suggests that the reaction proceeds in poor yields, consistent with our experience. In 1988, Smart and co-workers found Mn(CO)_3(pyridine)_2Br to be an effective reagent in making a substituted indacenylmanganese tricarbonyl complex.\(^3\) This compound also provides an effective manganese starting material for high yield syntheses of cymantrene compounds bearing substituents that can tolerate formation of cyclopentadienyl anions (e.g. (C\(_5\)H\(_5\))Mn(CO)_3 and (C\(_5\)Me\(_5\))Mn(CO)_3).

A. Tricarbonyl(η^5-cyclopentadienyl)manganese(I)

Procedure

Under an inert atmosphere place 0.400 g Mn(CO)_3(pyridine)_2Br\(^4\) and 0.230 g Na(C\(_5\)H\(_5\))•DME\(^5\) in a Schlenk flask equipped with a magnetic stir bar. Stopper the flask and add 10 mL dry, deoxygenated THF. After stirring overnight, remove the THF \textit{in vacuo}, being
careful to place the residue under a nitrogen atmosphere as soon as the mixture is dry. Against a counterstream of nitrogen, insert a water-cooled sublimation head. Evacuate and seal the flask. Warm the flask in a 50 °C water bath for two hours. After refilling the flask with nitrogen, remove the sublimation head and scrape off the CpMn(CO)₃ in the air. Yield: 0.165 g (73%).

*Properties

Tricarbonyl(η⁵-cyclopentadienyl)manganese(I) is a yellow, air-stable solid that sublimes at room temperature.⁶ It dissolves in many non-polar and moderately polar solvents (e.g. hexane, toluene, CH₂Cl₂, and acetone). The solution IR spectrum displays ν(C≡O) at 2024 (medium, sharp) and 1937 (strong, broad) cm⁻¹ in dichloromethane or 2029 and 1947 cm⁻¹ in hexane.⁷ The ¹H NMR spectrum displays a single resonance at 4.75 ppm in CDCl₃.⁸

B. Tricarbonyl(η⁵-pentamethylcyclopentadienyl)manganese(I)

*Procedure

Under an inert atmosphere place 0.400 g Mn(CO)₃(pyridine)₂Br⁴ and 0.18 g Li(C₅Me₅) in a Schlenk flask equipped with a magnetic stir bar. Stopper the flask and add 10 mL dry, deoxygenated THF. After stirring overnight, remove the THF in vacuo. Against a counterstream of nitrogen, insert a water-cooled sublimation head. Evacuate and seal the flask. Warm the flask in a 90-95 °C water bath for 3 hours. After refilling the flask with nitrogen, remove the sublimation head and scrape off the (C₅Me₅)Mn(CO)₃ in the air. Yield: 0.158 g (52%).†

†Properties

Tricarbonyl(η⁵-pentamethylcyclopentadienyl)manganese(I) is a yellow, air-stable solid that sublimes at elevated temperatures. It dissolves in many non-polar and moderately polar solvents (e.g. hexane, toluene, CH₂Cl₂, and acetone). The solution IR spectrum displays ν(C≡O) at 2002 and 1913 cm⁻¹ in dichloromethane. The ¹H NMR spectrum displays a single resonance at 1.88 ppm in CDCl₃.⁸
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References and Notes


6. This is why one should not dry the solid under vacuum for long periods of time and should perform sublimations under static vacuum.


*Checkers report a 51% yield.
†Checkers report a 47% yield.