4-2014

(η5-Cyclopentadienyl)Tricarbonylmanganese(I) Complexes

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Recommended Citation

Kirk, P. N., Castellani, M. P., Rizzo, M. and Atwood, J. D. (2014). (η5-Cyclopentadienyl)Tricarbonylmanganese(I) Complexes. In Inorganic Syntheses: Volume 36 (eds G. S. Girolami and A. P. Sattelberger). doi:10.1002/9781118744994.ch13

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. $(C_5H_5)Mn(CO)_3$ and $(C_5Me_5)Mn(CO)_3$).

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 $Na(C_5H_5)$•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 *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 ºC 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(η^5-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, CH_2Cl_2, 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 $CDCl_3$.[8]

B. Tricarbonyl(η^5-pentamethylcyclopentadienyl)manganese(I)

Procedure

Under an inert atmosphere place 0.400 g $Mn(CO)_3(pyridine)_2Br$[4] and 0.18 g $Li(C_5Me_5)$ 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 *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 ºC water bath for 3 hours. After refilling the flask with nitrogen, remove the sublimation head and scrape off the $(C_5Me_5)Mn(CO)_3$ in the air. Yield: 0.158 g (52%).†

Properties

Tricarbonyl(η^5-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, CH_2Cl_2, 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 $CDCl_3$.[8]

Acknowledgements

PNK thanks the WV EPSCoR – Research Challenge Fund for support in the form of a SURE Summer Fellowship.

References and Notes

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*Checkers report a 51% yield.

†Checkers report a 47% yield.