A Simple Synthesis of Cyclopentadienylindium(I)

By **Clovis Peppe, Dennis G. Tuck,** and **Luis Victoriano,** Department of Chemistry, University of Windsor, Windsor, Ontario, Canada N9B 3P4

Cyclopentadienylindium(I) can be prepared by the metathetical reaction of Li[C_5H_5] with a slurry of indium(I) chloride in diethyl ether. This method represents a significant improvement on previous syntheses.

CYCLOPENTADIENYLINDIUM(I) has a number of intrinsic features of interest in addition to the fact that it is one of the very few known organoindium(I) compounds. The half-sandwich structure established by electron diffraction methods[1] implies the presence of a donor pair of electrons, which can take part in addition[2] or insertion[3] reactions. Furthermore, it has long been the only soluble indium(I) compound, and as such has served as the starting point for the synthesis of neutral[4] and anionic[5] indium(I) complexes.

The standard preparation of [In(η-C_5H_5)] has been by the method of Fischer and Hofmann,[6] involving the reaction of $InCl_3$ with excess sodium cyclopentadienide; the probable course of this reaction has been discussed elsewhere.[7] A more direct but somewhat specialised route is by condensing metal vapour onto a frozen matrix of cyclopentadiene.[8] We have recently found that indium monobromide and monoiodide are soluble in toluene in the presence of certain neutral donors such as *NNN'N'*-tetramethylethylenediamine, and that such solutions can be used in the synthesis of lower oxidation-state indium compounds. In exploring these systems, we noted that slurries of indium monochloride in diethyl ether react smoothly with lithium cyclopentadienide to give [In(η-C_5H_5)] in good yields in a convenient one-step synthesis.

EXPERIMENTAL

General.—The preparation of indium(I) halides, solvent purification, and analytical and spectroscopic procedures, were as described elsewhere.[9] All operations were carried out under nitrogen or *in vacuo*, and light was excluded in the latter stages of the synthesis since [In(η-C_5H_5)] is photosensitive.

Lithium Cyclopentadienide.—Diethyl ether solutions of cyclopentadiene and methyl-lithium (*ca.* 0.1 mol quantities, total volume *ca.* 100 cm^3) were mixed together at room temperature. The resultant slurry was evaporated to dryness to give Li[C_5H_5] in almost quantitative yields.

Cyclopentadienylindium(I).—Indium(I) chloride (1.55 g, 10.3 mmol) and a five-fold excess of Li[C_5H_5] were suspended in diethyl ether (100 cm^3), and the mixture stirred for 12 h at room temperature. The solvent was then removed and the resultant off-white solid purified by vacuum sublimation (1 h, 100 °C). The product was identified by analysis (Found: In, 63.6%. Calc. for C_5H_5In: In, 63.9%), and by i.r. spectroscopy (*cf.* refs. 7 and 10). Yield 1.34 g, 72% based on indium(I) chloride.

DISCUSSION

The above reaction is novel and surprising, given the generally low reactivity of indium(I) halides, and the tendency of indium(I) species to undergo disproportionation in the presence of basic solvents to In^{III} and indium metal. It may well be that the mild reaction conditions are important in preventing disproportionation, since we noted that product yields were consistently lower when higher temperatures were used. The yields were also reduced if the reactants were taken in stoicheiometric ratio, or if indium(I) chloride was replaced by the bromide; no [In(η-C_5H_5)] was obtained when indium(I) iodide was the starting material. The effect of reactant ratio may be explained by an equilibrium (see below) in which

$$\mathrm{InX} + \mathrm{Li}[\mathrm{C_5H_5}] \rightleftharpoons \mathrm{Li}[\mathrm{In}(\eta\text{-}\mathrm{C_5H_5})\mathrm{X}]$$

the product is a soluble anionic indium(I) complex which subsequently dissociates to LiX and [In(η-C_5H_5)], but the effect of temperature and halide remain unexplained at present.

This work was supported by a grant from the Indium Corporation of America. One of us (C. P.) thanks the Conselho Nacional de Desenvolvimento Cientifico e Technológico, Brasil, for the award of a scholarship.

[1/670 *Received, 27th April,* 1981]

REFERENCES

[1] S. Shibata, L. S. Bartell, and R. M. Gavin, *J. Chem. Phys.*, 1964, **41**, 717.

[2] J. G. Contreras and D. G. Tuck, *Inorg. Chem.*, 1973, **12**, 2596.

[3] A. F. Berniaz and D. G. Tuck, *J. Organomet. Chem.*, 1973, **51**, 113; J. G. Contreras and D. G. Tuck, *ibid.*, 1974, **66**, 405.

[4] J. J. Habeeb and D. G. Tuck, *J. Chem. Soc., Dalton Trans.*, 1975, 1815.

[5] J. J. Habeeb and D. G. Tuck, *J. Chem. Soc., Chem. Commun.*, 1975, 600; *J. Chem. Soc., Dalton Trans.*, 1976, 866.

[6] E. O. Fischer and H. P. Hofmann, *Angew. Chem.*, 1957, **69**, 639.

[7] J. S. Poland and D. G. Tuck, *J. Organomet. Chem.*, 1972, **42**, 307.

[8] G. M. Kuz'yants, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1976, 1895.

[9] B. H. Freeland, J. L. Hencher, D. G. Tuck, and J. G. Contreras, *Inorg. Chem.*, 1976, **15**, 2144.

[10] H. P. Fritz, *Adv. Organomet. Chem.*, 1964, **1**, 240.