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AN ORGANOLITHIUM ROUTE TO SUBSTITUTED η^4-CYCLOBUTADIENECOBALT COMPLEXES

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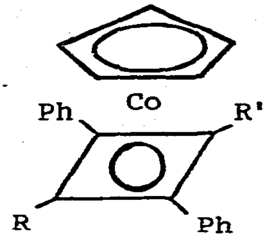
SUMMARY

The reaction of η^5-cyclopentadienyl-η^4-1,3-bis(triphenylstannyl)-2,4-diphenylcyclobutadienecobalt with phenyllithium in tetrahydrofuran gave an organolithium reagent in which one Ph_3Sn substituent was replaced by lithium. Reaction of this reagent with trimethylchlorosilane gave the expected trimethylsilyl derivative. The Ph_3Sn group in this product could be replaced by lithium in a second reaction with phenyllithium, but a dilithio derivative could not be prepared directly from the bis(triphenylstannyl) compound in a single step.

INTRODUCTION

While the reactions of a suitable η^5-cyclopentadienylcobalt compound with acetylenes provide η^5-cyclopentadienyl-η^4-cyclobutadiene complexes with various substituents on the cyclobutadiene ligand,[1] it was of interest to prepare such cobalt complexes by other than acetylene-based routes. The known η^5-cyclopentadienyl-η^4-1,3-bis(triphenylstannyl)-2,4-diphenylcyclobutadienecobalt (Ia)[2] in principle provides the means of preparing compounds of type I by reaction sequences in which Li/Sn transmetalation is the initial step. (The transmetalation



I a, R = R' = Ph_3Sn
b, R = R' = Li
c, R = Li; R' = Ph_3Sn
d, R = Me_3Si; R' = Ph_3Sn
e, R = Me_3Si; R' = CH_3

reaction between organotin compounds and organolithium reagents is a useful route for the preparation of organolithium compounds which are difficult to prepare by other means.³) We have tested the feasibility of this approach.

Ideally, treatment of Ia with two molar equivalents of phenyllithium might be expected to give the novel dilithium reagent Ib, whose reactions would be of considerable interest and which might be useful in the preparation of interesting cobalt-containing polymers via condensations with suitable difunctional substrates. In practise, this approach could not be realized.

RESULTS AND DISCUSSION

Treatment of a THF solution of Ia with two molar equivalents of phenyllithium at room temperature resulted in precipitation of tetraphenyltin. Addition of this reaction mixture to an excess of trimethylchlorosilane gave η^5-cyclopentadienyl-η^4-1-trimethylsilyl-3-triphenylstannyl-2,4-diphenylcyclobutadienecobalt (Id) in 74% yield. The tetraphenyltin yield, based on available Ph_3Sn groups, was correspondingly low, only 35%. Thus, under standard transmetalation conditions, the dithium species is not formed and the reaction stops with the formation of the monolithium reagent Ic, leaving one molar equivalent of phenyllithium unconsumed.

In spite of this limitation, it is possible to introduce two substituents in replacement of the two triphenylstannyl groups in Ia in stepwise fashion. This is shown by the preparation of Ie in 80% yield in a sequence in which monolithium reagent Ic was prepared first by reaction of Ia with one molar equivalent of phenyllithium. It then was allowed to react with one molar equivalent of trimethylchlorosilane, giving Id. This product was not isolated, rather the reaction mixture at that point was treated successively with one molar equivalent each of phenyllithium and dimethyl sulfate to produce Ie.

It is clear that this simple one-pot procedure will serve nicely in the preparation of a wide variety of cobalt complexes of type I in which the R and R' substituents may be the same or different organic or organometallic groups.

EXPERIMENTAL

Preparation and Characterization of η^5-Cyclopentadienyl-η^4-1-trimethylsilyl-3-triphenylstannyl-2,4-diphenylcyclobutadienecobalt.

A 200 ml, round-bottomed, three necked flask, which was equipped with a magnetic stirring unit, a no-air stopper and a nitrogen inlet tube, was flamed dry under a stream of nitrogen and charged with 3.65 g (3.55 mmol) of cobalt complex Ia (prepared according to ref. 2, mp 170-171°; lit.[2] mp 174-175°C) and 100 ml of dry tetrahydrofuran (THF). To the resulting solution was added rapidly in one portion, with stirring, 6.4 ml of 1.14<u>M</u> phenyllithium (7.30 mmol) in diethyl ether. The reaction mixture was stirred at room temperature under nitrogen for 1 hr. A similarly equipped 300 ml three-necked flask was flamed dry and charged with 1.77

ml (14 mmol) of trimethylchlorosilane (Union Carbide Corp.) and 25 ml of dry THF. The lithium reagent solution then was added by cannula to the chlorosilane, slowly over a period of 15 min. The resulting mixture was stirred at room temperature overnight and then was hydrolyzed by addition of 200 ml of water. The organic layer was dried ($MgSO_4$) and evaporated at reduced pressure. The residue was extracted with 10 ml of dry THF, leaving 1.1 g (35%) of tetraphenyltin, mp 224-225°C (lit.[4] mp 225°C). The filtrate was evaporated at reduced pressure and the solid residue was purified by column chromatography (yellow band on 4 cm x 30 cm alumina column, 20% dichloromethane in pentane eluent) and recrystallization from hexane to give 2.01 g (74%) of dark yellow crystals of the title compound, mp 146-148°C. NMR (Varian T60; CCl_4/CH_2Cl_2): δ 0.27 (s, 9H, Me_3Si), 4.63 (s, 5H, C_5H_5) and 6.87-7.44 ppm (complex m with maxima at 7.02 and 7.25, 25H, C_6H_5).
Anal.: Calcd. for $C_{42}H_{39}SiSnCo$: C, 67.31; H, 5.25. Found: C, 67.13; H, 5.26.

Preparation and Characterization of η^5-Cyclopentadienyl-η^4-1-methyl-3-trimethylsilyl-2,4-diphenylcyclobutadiene-cobalt.

A 300 ml, round-bottomed flask, equipped as described above, was charged with 3.91 g (3.80 mmol) of Ia and 150 ml of dry THF. Then 5.35 ml of 0.73M phenyllithium (3.91 mmol) in diethyl ether was added by syringe. The reagent solution was stirred under nitrogen at room temperature for 90 min. and then was treated with 3.97 mmol of trimethylchlorosilane. After the resulting mixture had been stirred for 60 min., another 5.35 ml (3.91 mmol) of phenyllithium solution was added. After a further 90 min. period of stirring, 0.40 ml of dimethyl sulfate was added. The reaction mixture was

stirred at room temperature overnight, hydrolyzed with 200 ml of water, and the organic layer was dried and evaporated at reduced pressure. The solid residue was extracted with 10 ml of dry THF, giving a yellow solution and a 2.64 g (79%) residue of tetraphenyltin. The filtrate was evaporated and the residue was purified by column chromatography (alumina column, pentane eluent) and recrystallization from hexane. The title compound was obtained in 80% yield (1.26 g), mp 130-131°C.
NMR (Varian T60; CCl_4/CH_2Cl_2): δ 0.32 (s, 9H, Me_3Si), 2.05 (s, 3H, CH_3) 4.64 (s, 5H, C_5H_5) and 7.04-7.47 ppm (m, 7.24 maximum, 10H, C_6H_5).
Anal. Calcd. for $C_{25}H_{29}SiCo$: C, 72.44; H, 6.57.
Found: C, 72.21; H, 6.50.

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