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Preliminary communication

RING METALLATION OF THIOPHENECHROMIUM TRICARBONYL WITH BUTYLLITHIUM

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Summary

It has been found that the α-hydrogen atoms in thiophenechromium tricarbonyl are extremely readily substituted by Li under the action of n-butyllithium in THF at —50° C. This reaction is used for producing dideutero-, trimethylsilyl- and bis(trimethylsilyl)-thiophenechromium tricarbonyl.

At present, a large body of literature exists devoted to the methods of synthesis and the physico-chemical characteristics of thiophenechromium tricarbonyl (TCT) and its derivatives (see, for instance, [1] and references therein).

But very little is known of the chemical reactions of TCT, only the electrophilic isotopic exchange of hydrogen has been described [2] and there is an indication for the possibility of mercuration [3].

We have found that TCT is very readily metallated with n-butyllithium. In a THF solution at —50° C the reaction proceeds practically instantaneously and quantitatively. When using a 2.5 to 3-fold excess of BuLi and decomposing the reaction mixture with D_2O, dideutero-TCT is formed (99% d_2 according to the mass-spectral data). The PMR spectrum of this compound displays only a singlet signal of β-hydrogens, δ 4.3 ppm. Thus, with excess BuLi both α hydrogen atoms of TCT are totally substituted by Li. Accordingly, treating the reaction mixture with trimethylchlorosilane we have obtained bis(trimethylsilyl)-TCT with a quantitative yield. With an equimolar ratio of reagents only one hydrogen α-atom is substituted. After treating the reaction mixture with trimethylchlorosilane we have isolated mono(trimethylsilyl)-TCT (about 30% of the initial TCT remains unreacted).

It is known that when transition metal carbonyl complexes are treated with BuLi both metallation and addition to the carbonyl ligand may take place; in some cases substitution of THF by ether changes completely the direction of

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reaction [4]. Interaction of BuLi with TCT in ether at −50°C followed by treatment with trimethylchlorosilane leads to a good yield of bis(trimethylsilyl)-TCT, as was the case with THF. However, at room temperature metallation in ether proceeds to a small extent, mainly insoluble products of decomposition being formed.

It should be noted that in the case of thiophene substitution of one α-hydrogen atom when treated by BuLi also proceeds very readily, but much more rigid conditions (boiling with excess reagent [5] or application of tetramethylethylenediamine [6]) are required to introduce a second Li atom. Thus a chromium tricarbonyl group increases the acidity of the ligand α-hydrogens.

Experimental

Metallation was carried out under an argon atmosphere; solvents were distilled in argon over $LiAlH_4$ just before use.

Bis(trimethylsilyl)-TCT

To a stirred solution of 0.22 g (1 mmol) TCT in 20 ml THF cooled to −50°C was added 2.8 mmol of BuLi in 3.5 ml hexane with a syringe. After 10 min at −50°C 1 ml of trimethylchlorosilane was added and the reaction mixture was allowed to warm up to room temperature under stirring. The addition of BuLi results in the immediate disappearance of the orange-red color of TCT, which gradually returns after treating with trimethylchlorosilane. The mixture was then decomposed with water, extracted with benzene; 0.39 g of bis(trimethylsilyl)-TCT, contaminated by a small amount of a colourless oil insoluble in heptane, was isolated from the benzene solution; crystallized from heptane the compound shows a satisfactory element analysis, m.p. 149–150°C (decomp.). The substance is stable in air for some long period of time. Its mass spectrum shows a peak of the molecular ion P^+, *m/e* 364, $P^+ - 2CO$, $P^+ - 3CO$ (the most abundant), and also $C_4H_2S(SiMe_3)_2^+$, $C_4H_2SSiMe_3^+$ and so on. The PMR spectrum in C_6D_6 displays a singlet of the ring β-hydrogens, δ 5.0 ppm, and a signal of methyl hydrogens coinciding with HMDS; in CS_2 5.4 and 0.3 ppm, respectively. $\nu(CO)$ 1875, 1895 and 1965 cm^{-1}.

Trimethylsilyl-TCT

In a similar way with a TCT:BuLi ratio of 1:1.3 trimethylsilyl-TCT was obtained in a mixture with the initial compound, and with a TCT:BuLi ratio of 1:1.8 trimethylsilyl-TCT was obtained in the mixture with bis(trimethylsilyl)-TCT. The pure substance was obtained by crystallization from heptane. Chromatographic separation is complicated by the fact that during long contact with neutral Al_2O_3 or with silica gel partial elimination of trimethylsilyl groups occurs. For analytical purposes TLC on silica gel is suitable. Trimethylsilyl-TCT, m.p. 107–108°C, is stable in air. In the mass-spectrum the peaks P^+, *m/e* 294, $P^+ - 2CO$, $P^+ - 3CO$, $C_4H_3SSiMe_3^+$, $C_4H_3SSiMe_2^+$ and so on can be seen. In the PMR spectrum in C_6D_6 the multiplet of the ring protons, δ 4.7–4.5 ppm, and a singlet of methyl hydrogens at 0.1 ppm and in CS_2 the unsplit signal of ring protons at 5.5 ppm and a singlet at 0.3 ppm can be seen.

Dideutero-TCT

TCT was metallated with a three-fold excess of BuLi, as was described above, then 1 ml of D_2O was added at −50°C and the reaction mixture was allowed to warm to room temperature, the solvent was removed in a vacuum, and the residue was extracted with benzene. From the benzene solution dideutero-TCT was isolated with ca. 50% yield. If the reaction mixture is treated with water, as was described above, partial loss of the isotope occurs due to exchange with the medium catalyzed by alkali.

TCT lithiation in ether at −50°C is carried out in a similar fashion, except that dilithium-TCT precipitates from the solution as brown flakes.

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