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Mendeleev Commun., 1993, **3(2)**, 43–45
Mendeleev Communications

1,2- and 1,4-Addition Reactions of α-Metallated (η^6-Alkylarene)tricarbonylchromium Complexes to Carbonyl Compounds

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A [η^6-benzylcopper(I)]tricarbonylchromium complex has been obtained and its 1,4-addition reaction with methyl vinyl ketone carried out, while a convenient method for the 1,2-addition of benzyllithium derivatives of (η^6-alkylarene)tricarbonylchromium complexes to carbonyl compounds has been elaborated.

Benzylic functionalization of alkylarenes is of great interest for organic synthesis; however, the direct introduction of substituents into the benzylic position is often rather difficult to achieve. Complexation of alkylarene ligands to the tricarbonylchromium group enhances the acidity of the benzylic protons and allows the metallation of (η^6-alkylarene)tricarbonylchromium complexes at the α-position.[1,2]

The α-metallated derivatives thus obtained undergo reactions with different substrates. The benzyl-substituted alkylarenes can be easily liberated from the complexes above by the methods described earlier.[1,2]

We have earlier elaborated convenient methods of metallation of (η^6-alkylarene)tricarbonylchromium complexes at the benzylic position using sodium amide in liquid NH_3[3] or lithium amides in THF[4] and the preparative introduction of carboxy[5] and carboxymethyl[3] groups into the benzylic position of the carbanions thus obtained.

It is known that α-metallated derivatives of (η^6-alkylarene)-tricarbonylchromium complexes add to activated carbonyl groups in formaldehyde,[6,7] benzaldehyde[7,8] and diethyl oxalate[9]. However, the products were obtained in some cases in poor yields,[7,8] and additional products were not obtained if the carbonyl compounds were susceptible to enolization.[7,10]

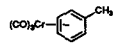
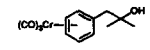
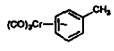
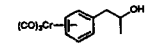
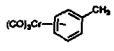
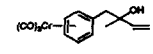
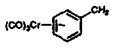
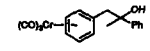
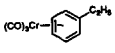
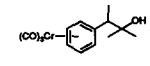
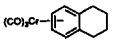
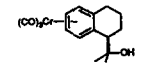
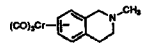
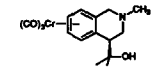
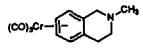
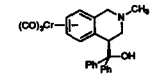
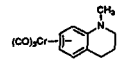
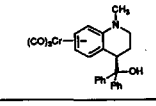
We found that with benzyllithium derivatives the tricarbonylchromium complexes added smoothly to the carbonyl compounds to give the corresponding carbinol complexes in good yields, Scheme 1.

The complexes obtained and their yields and melting points are given in Table 1. The data demonstrate that both aldehydes and ketones of different types easily undergo the 1,2-addition reaction in high yields.

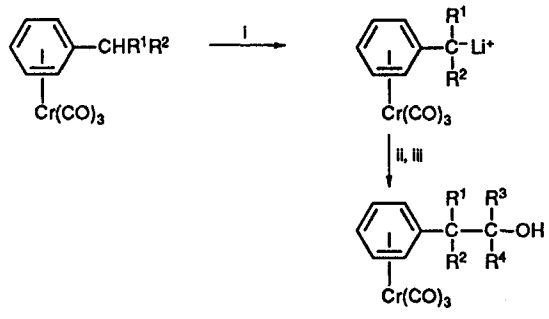
Two isomers, *exo* and *endo*, may be formed from bicyclic (η^6-alkylarene)tricarbonylchromium complexes in these reactions (runs 5–9). However, we obtained really only one product and according to the literature data[1,2] it should have an *exo*-structure.

In the present work we also demonstrate that the benzyllithium derivative of (η^6-toluene)tricarbonylchromium readily enters into a transmetallation reaction with copper(I) halides to give the benzylcopper(I) derivative. This is the first example of a benzylcopper(I) compound bearing a tricarbonylchromium group.

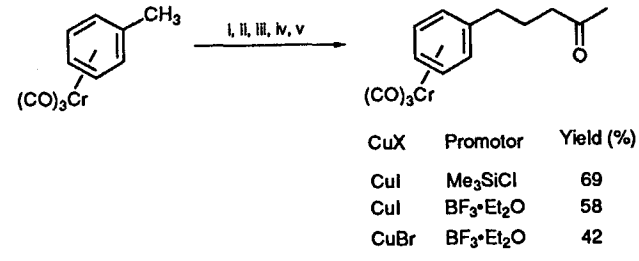
Table 1

Run no.	Starting material	Ketone	Product[a,b]	Yield (%)	M.p./°C
1				80	72.0–73.5
2				62	69.5–70.0
3				69	76.0–77.0
4				63	89.0–89.5
5				67	46.0–47.0
6				82	110.0–111.0
7				72	143.0–144.5
8				85	187.0–188.0
9				71	165.0–166.0

[a] *Reagents and conditions*: Reactions were carried out in an argon atmosphere using THF as solvent. Bu^{n}Li (1.5 mmol) in hexane was added to a solution of Et_2NH (1.5 mmol) in 20 ml THF. After being stirred for 5 min at 20 °C the starting complex was added. After being stirred for 3–10 min the mixture was cooled to −30 °C and Bu^{n}Li (1.0 mmol) was added. The mixture was stirred again for 5 min at −30 °C and cooled to −70 °C. The appropriate carbonyl compound was added and the mixture was stirred at this temperature for 30 min. The mixture was allowed to warm to 20 °C and was quenched with a saturated aqueous solution of NH_4Cl. The products were chromatographed on Al_2O_3 followed by recrystallization from ether–hexane (1:1). [b] The structures of the products obtained were determined by ^{1}H NMR spectroscopy and elemental analysis.



Scheme 1 *Reagents and conditions*: i, Et_2NLi, r.t., THF; ii, R^3COR^4, −78 °C, THF; iii, H^+



CuX	Promotor	Yield (%)
CuI	Me_3SiCl	69
CuI	BF_3•Et_2O	58
CuBr	BF_3•Et_2O	42

Scheme 2 *Reagents and conditions*: i, 1.5 equiv. Et_2NLi, 0 °C, 10 min; ii, 1.0 equiv. Bu^{n}Li, −30 °C, 5 min; iii, 5 equiv. CuX, 20 °C, 10 min; iv, 10 equiv. CH_2=$CHCOCH_3$, promotor, −78 °C, 2 h; v, 10% HCl

In contrast to the usual benzylcopper(I) compounds, the benzylcopper(I) derivative of (η^6-toluene)tricarbonylchromium has increased stability and this makes it possible to use it in the 1,4-addition reaction with methyl vinyl ketone.

A yellow solution of the benzyllithium derivative of (η^6-toluene)tricarbonylchromium in THF turned black on addition of a two-fold excess of copper(I) halide. The mixture became yellow again when methyl vinyl ketone and the promotor (Me_3SiCl or $BF_3 \cdot Et_2O$) were added. Acidic treatment of the reaction mixture gave the 1,4-addition product of [η^6-benzylcopper(I)]tricarbonylchromium complex to methyl vinyl ketone.

It must be noted that in contrast to [η^6-benzylcopper(I)]tricarbonylchromium, the corresponding lithium derivatives only enter a 1,2-addition reaction with methyl vinyl ketone (run 3).

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Received: Moscow, 29th October 1992
Cambridge, 25th November 1992; Com. 2/05826J