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# Regioselective Nucleophilic Additions to (η⁶-Benzyl alcohol)tricarbonylchromium: Isolation and *X*-Ray Crystal Structure of the Intermediate (η⁶-5-Methylene-6-*exo*-t-butylcyclohexa-1,3-diene)tricarbonylchromium

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Treatment of ($\eta^6$-benzyl alcohol)tricarbonylchromium with alkyl-lithium compounds (Bu$^t$Li; MeLi–tetramethylethylenediamine; Bu$^n$Li; PhLi) regioselectively generates the corresponding $\eta^6$-5-methylene-6-*exo*-alkylcyclohexa-1,3-diene complexes which undergo proton catalysed isomerisations to give ($\eta^6$-*ortho*-alkyltoluene)tricarbonylchromium complexes.

Arenes are activated towards nucleophilic attack on co-ordination to tricarbonylchromium.[1] Thus, for example, addition of carbanions to (benzene)tricarbonylchromium generates an intermediate 6-*exo*-substituted cyclohexadienyltricarbonylchromium anion which on oxidation or protonation generates the corresponding uncomplexed substituted arenes or cyclohexadienes respectively.[2] Addition of carbanions to (alkylbenzene)tricarbonylchromium complexes occurs predominantly in the *meta* position.[3] We report here a novel chelation controlled nucleophilic addition of carbanions to ($\eta^6$-benzyl alcohol)tricarbonylchromium (**1**) which subsequently leads to the formation of *ortho*-substituted toluenetricarbonylchromium complexes.

Treatment of the yellow ($\eta^6$-benzyl alcohol)Cr(CO)$_3$ (**1**)[4] in tetrahydrofuran at −78 °C with at least two equivalents of t-butyl-lithium and warming to room temperature gave a stable crimson solution. Addition of methanol, chromatography, and crystallisation from n-pentane gave red needles (49%) for which the spectroscopic data was consistent with the formation of ($\eta^6$-5-methylene-6-*exo*-t-butylcyclohexa-1,3-

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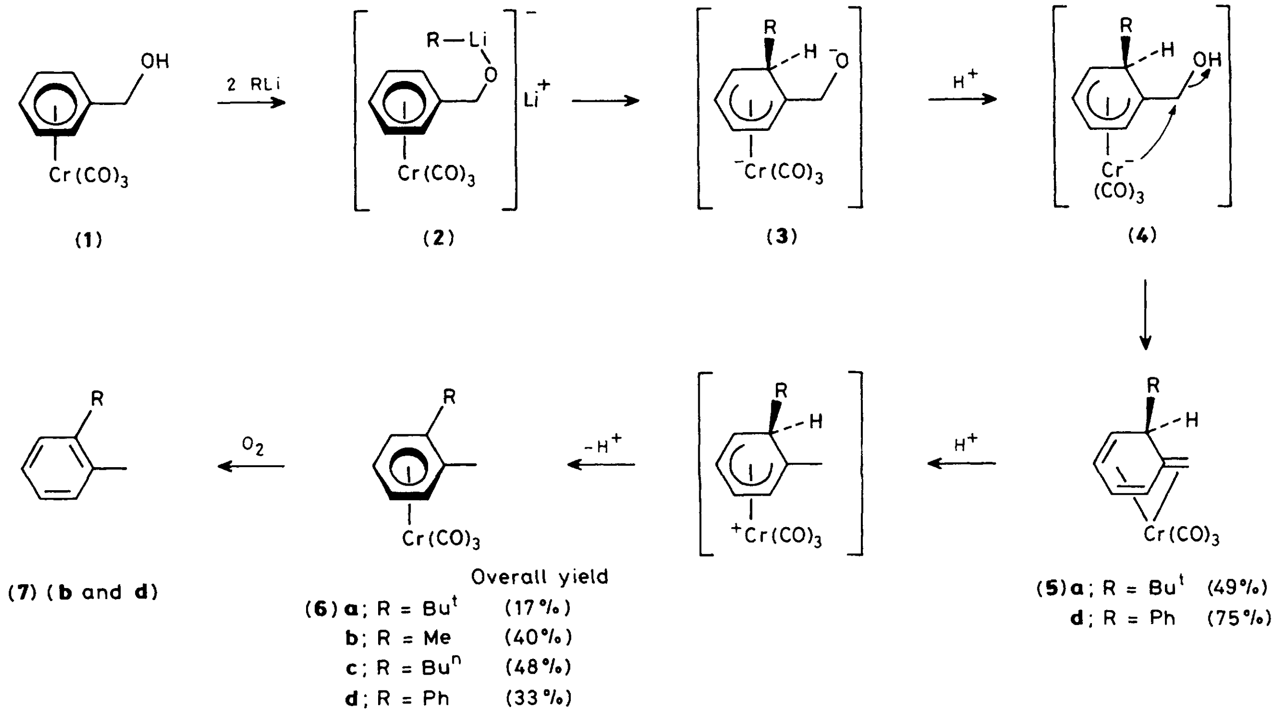

Scheme 1

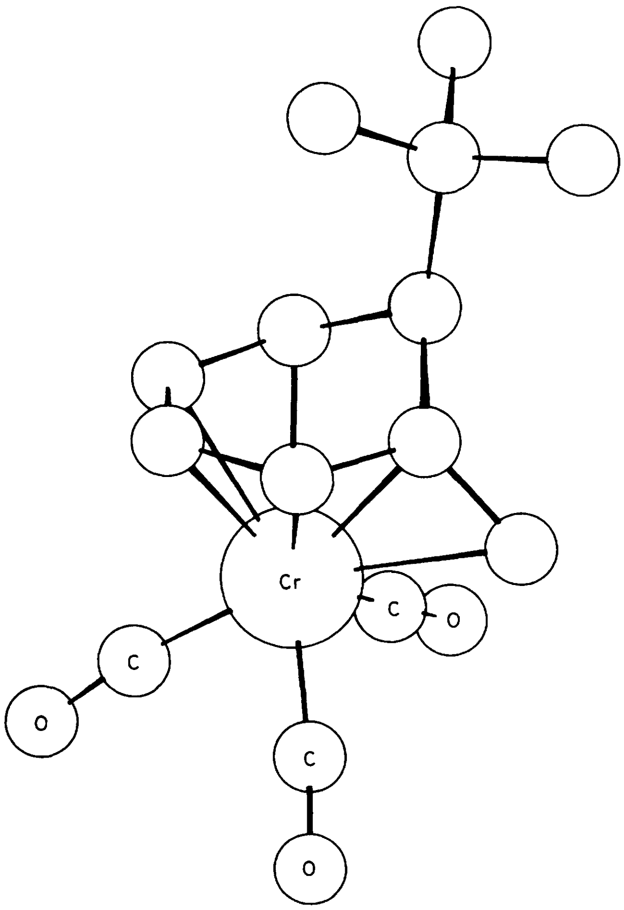

**Figure 1.** *X*-Ray crystal structure of (**5a**).

diene)tricarbonylchromium (**5a**). This assignment was confirmed by an *X*-ray crystal structure analysis of (**5a**)† (Figure 1).

On warming in neutral or acidic methanol, a red solution of (**5a**) became yellow. Work up led to the isolation of (*ortho*-t-butyltoluene)tricarbonylchromium (**6a**). Treatment of (**5a**) with $CD_3OD$–$D_2O$ gave α-monodeuteriated (**6a**) consistent with (**6a**) being formed by a protonation–deprotonation mechanism rather than *via* a rearrangement.

Treatment of (**1**) with at least two equivalents of methyl-lithium–tetramethylethylenediamine, n-butyl-lithium, or phenyl-lithium gave the corresponding red complexes (**5b**), (**5c**), and (**5d**) respectively. Complexes (**5b**) and (**5c**) were unstable isomerising to (**6b**) and (**6c**) on chromatography whereas the conversion of (**5d**) to (**6d**) required methanol treatment. Complex (**6b**) was identical in all respects with an authentic sample prepared from *o*-xylene and hexacarbonylchromium. Decomplexation of (**6b**) and (**6d**) by standing a diethyl ether solution in air and sunlight gave quantitatively *o*-xylene (**7b**) and *o*-methylbiphenyl (**7d**) identical in all respects with authentic samples.

A mechanism consistent with the above results is shown in Scheme 1. Initial formation of alkoxide (**2**) followed by the

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† *Crystal data* for (**5a**): $C_{14}H_{16}O_3Cr$, $M = 284.28$, orthorhombic, space-group *Pbca*, $a = 17.038(3)$, $b = 12.988(2)$, $c = 12.572(2)$ Å, $U = 2782$ Å$^3$, $Z = 8$, $D_c = 1.36$ Mg m$^{-3}$, $\mu$(Cu-$K_\alpha$) 68.6 cm$^{-1}$, $F(000)$ 1184. The structure was solved by direct methods and refined by full-matrix least-squares methods. 1356 Independent reflections for which $I > 3\sigma(I)$ were refined to conventional values of $R = 0.052$, $R_w = 0.066$, and GOF = 1.01. Cell parameters and reflection intensities were measured with graphite monochromated Cu-$K_\alpha$ radiation on an Enraf–Nonius CAD-4F diffractometer operating in the ω–2θ scan mode for a crystal having approximate dimensions 0.51 × 0.59 × 0.82 mm. The data were corrected for Lorentz, polarisation, and absorption effects. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1, 1986.

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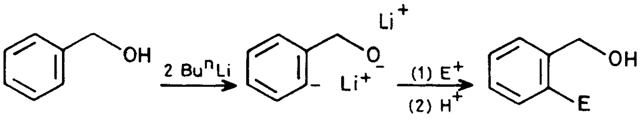

**(8)** **(9)**

chelation controlled addition of the carbanion regioselectively to an *ortho* position would give the dianion (**3**). Protonation of (**3**) followed by loss of the α-oxygen substituent would generate the intermediate (**5**). Proton catalysed isomerisation of (**5**) would give (**6**) and after decomplexation (**7**). Intercepting the intermediate (**3d**) with iodine gave 2-phenylbenzyl alcohol (58%), identical with an authentic sample. The reactivity of (**1**) described above complements that previously reported for benzyl alcohol and n-butyl-lithium where intermediate *ortho*-lithiated species (**8**) could be trapped by electrophiles to give *ortho*-substituted benzyl alcohols (**9**).[5]

We thank Glaxo Group Research Ltd (Ware) and the S.E.R.C. for a CASE award (to J. B.), the S.E.R.C. for financial support (to K. H. S.), and Dr. Keith Prout of the Chemical Crystallography Laboratory, Oxford.

*Received, 20th May 1986; Com. 680*

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