

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

Julian Blagg, Stephen G. Davies,* Craig L. Goodfellow, and Kevin H. Sutton

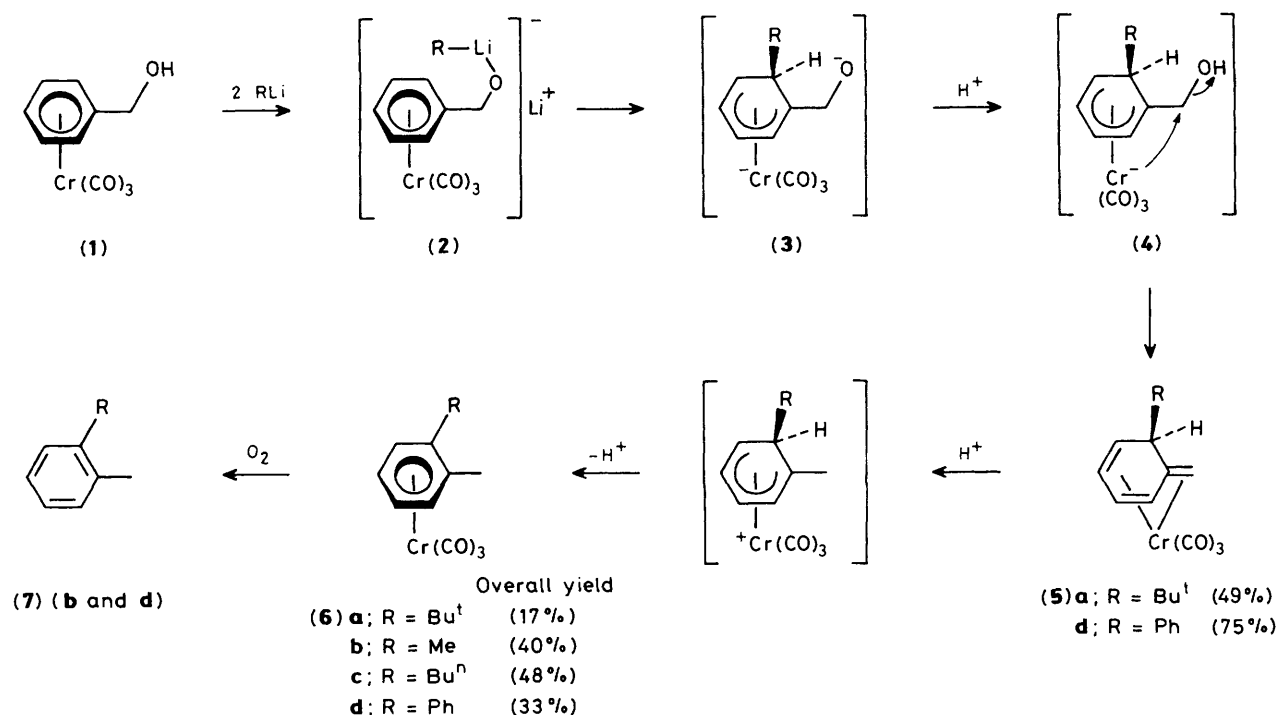
The Dyson Perrins Laboratory, South Parks Road, Oxford OX1 3QY, U.K.

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

Arenes are activated towards nucleophilic attack on coordination to tricarbonylchromium.¹ Thus, for example, addition of carbanions to (benzene)tricarbonylchromium generates an intermediate 6-*exo*-substituted cyclohexadienyl-tricarbonylchromium 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

(η^6 -benzyl alcohol)tricarbonylchromium (**1**) which subsequently leads to the formation of *ortho*-substituted toluenetricarbonylchromium complexes.

Treatment of the yellow (η^6 -benzyl alcohol) $\text{Cr}(\text{CO})_3$ (**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 (η^6 -5-methylene-6-*exo*-*t*-butylcyclohexa-1,3-



Scheme 1

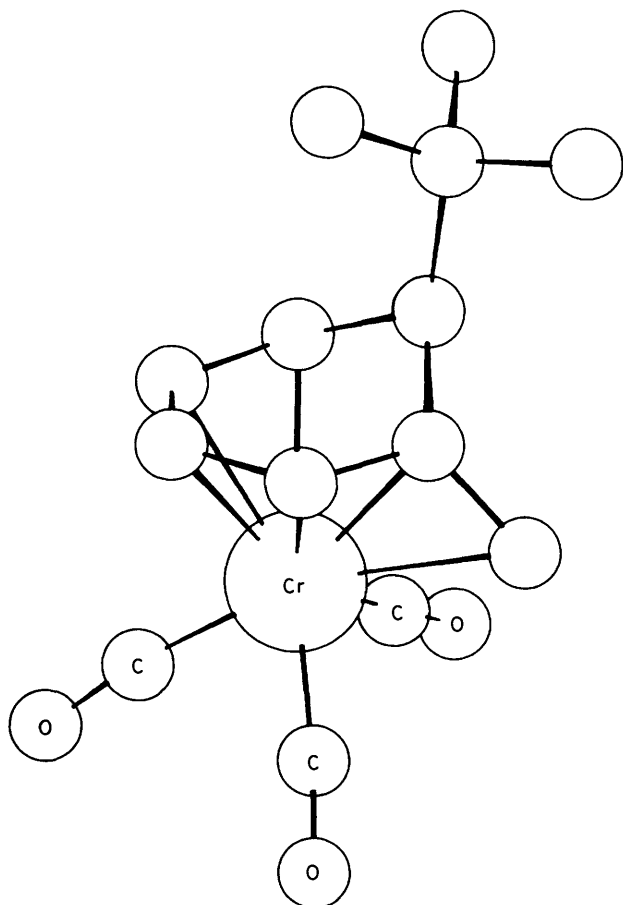


Figure 1. X-Ray crystal structure of (5a).

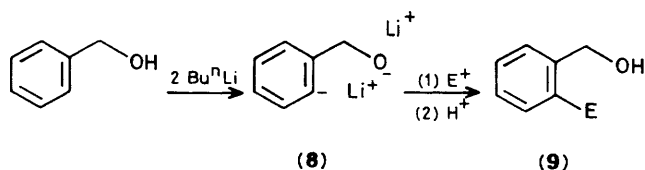
diene)tricarbylchromium (5a). This assignment was confirmed by an X-ray crystal structure analysis of (5a)[†] (Figure 1).

On warming in neutral or acidic methanol, a red solution of (5a) became yellow. Work up led to the isolation of (*ortho*-*t*-butyltoluene)tricarbylchromium (6a). Treatment of (5a) with CD₃OD-D₂O gave α -monodeuterated (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

[†] Crystal data for (5a): C₁₄H₁₆O₃Cr, *M* = 284.28, orthorhombic, space-group *Pbca*, *a* = 17.038(3), *b* = 12.988(2), *c* = 12.572(2) Å, *U* = 2782 Å³, *Z* = 8, *D*_c = 1.36 Mg m⁻³, μ (Cu-K α) 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 σ (*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 α radiation on an Enraf-Nonius CAD-4F diffractometer operating in the ω -2 θ 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.



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

References

- 1 S. G. Davies, 'Organotransition Metal Chemistry: Applications to Organic Synthesis,' Pergamon Press, Oxford, 1982; A. J. Pearson, 'Metallo-Organic Chemistry,' John Wiley & Sons, New York, 1985; M. F. Semmelhack, *Ann. N.Y. Acad. Sci.*, 1977, **36**; G. Jaouen, 'Transition Metal Organometallics in Organic Synthesis,' ed. H. Alper, Academic Press, London, 1978, vol. II, p. 105; M. Gharshov and D. A. Widdowson, *J. Chem. Soc., Perkin Trans. 1*, 1983, 3065; E. P. Kundig and D. P. Simmons, *J. Chem. Soc., Chem. Commun.*, 1983, 1320; A. Alemagna, C. Baldoli, P. Del Buttero, E. Licandro, and S. Maiorana, *ibid.*, 1985, 417; C. Baldoli, P. Del Buttero, S. Maiorana, and A. Papagni, *ibid.*, 1985, 1181; J.-C. Boutonnet, F. Rose-Munch, and E. Rose, *Tetrahedron Lett.*, 1985, **26**, 3989.
- 2 M. F. Semmelhack, H. T. Hall, R. Farina, M. Yoshifuji, G. Clarke, T. Bargar, K. Hirotsu, and J. Clardy, *J. Am. Chem. Soc.*, 1979, **101**, 3535; M. F. Semmelhack, G. R. Clarke, J. J. Harrison, Y. Thebtaranonth, W. Wulff, and A. Yamashita, *Tetrahedron*, 1981, **37**, 3957.
- 3 R. J. Card and W. S. Trahanovsky, *Tetrahedron Lett.*, 1973, 3823; *J. Org. Chem.*, 1980, **45**, 2560.
- 4 Prepared in 81% yield by thermolysis, under a nitrogen atmosphere, of benzyl alcohol (3 g, 28 mmol) and hexacarbonylchromium (7 g, 32 mmol) in a mixture of di-*n*-butyl ether (90 ml) and tetrahydrofuran (9 ml). See also B. Nicholls and M. C. Whiting, *J. Chem. Soc.*, 1959, 551.
- 5 N. Meyer and D. Seebach, *Angew. Chem., Int. Ed. Engl.*, 1978, **17**, 521; H. W. Gschwend and H. R. Rodriguez, *Org. React.*, 1979, **26**, 1; M. Reuman and A. I. Meyers, *Tetrahedron*, 1985, **41**, 837.