cine-Substitution† in Halogenobenzenetricarbonylchromium Complexes

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cine-Substitution of the chloro group of chlorobenzenetricarbonylchromium complexes by a carbon nucleophile has been observed.

Reaction of chlorobenzenetricarbonylchromium with 2-lithioisobutyronitrile has been reported to yield phenylisobutyronitrile[1]‡ after iodine oxidation. If acid is added prior to iodine oxidation, then chlorosubstituted cyclohexadienes (**1**) (at least five isomers) and *o*-chlorophenylisobutyronitrile are observed as major products in addition to phenylisobutyronitrile. We report herein our results concerning the reactions of carbon nucleophiles with *p*-chlorotoluenetricarbonylchromium (**2**), which follow different pathways depending on the experimental conditions and on the nature of the nucleophile.

Complex (**2**) was treated at −78 °C with 2-lithioisobutyronitrile to give, upon treatment with CF_3CO_2H, *m*-2-cyanopropan-2-yltoluenetricarbonylchromium (**7a**)§ as the major product (42% yield) (Scheme 1). This reaction clearly shows that addition of the carbanion occurred *ortho* to the chloro leaving group and *meta* to the methyl group. This corresponds to a *cine*-substitution.† When CF_3CO_2D is used, the deuterio complex (**7b**)§ is obtained.

2-Lithio-2-phenyl-1,3-dithiane, another carbanion which adds reversibly to arenetricarbonylchromium complexes, was treated at −78 °C with the same complex (**2**) to give, after treatment with CF_3CO_2H, a single cyclohexadiene isomer (**9c**)§ as the major product (70% yield) along with arene complexes (**7c**)§ (18% yield). Using CF_3CO_2D, deuteriocyclohexadiene (**9d**)§ is obtained: the deuteriocomplex (**7d**)§ is produced as a minor product. The formation of the products (**7d**) and (**9d**) can be explained by the intermediacy of complex (**4d**).

Several features of these reactions are noteworthy. When the hydride of complex (**4d**) migrates to the carbon which is *ortho* to the methyl group and *meta* to the chloro group, the reaction stops at this stage,[3] affording complex (**6d**). Apparently, hydrogen abstraction does not occur to give the η^5-cyclohexadienyl complex (**8d**) which is the precursor of the other cyclohexadiene isomers. This could be attributed to the steric bulk of the 2-phenyl-1,3-dithianyl group in complex (**6d**) as well as the affinity of the sulphur atoms for complexation with chromium which could lead to loss of the $Cr(CO)_3$ entity from the cyclohexadiene ligand in order to yield the organic product (**9d**).¶

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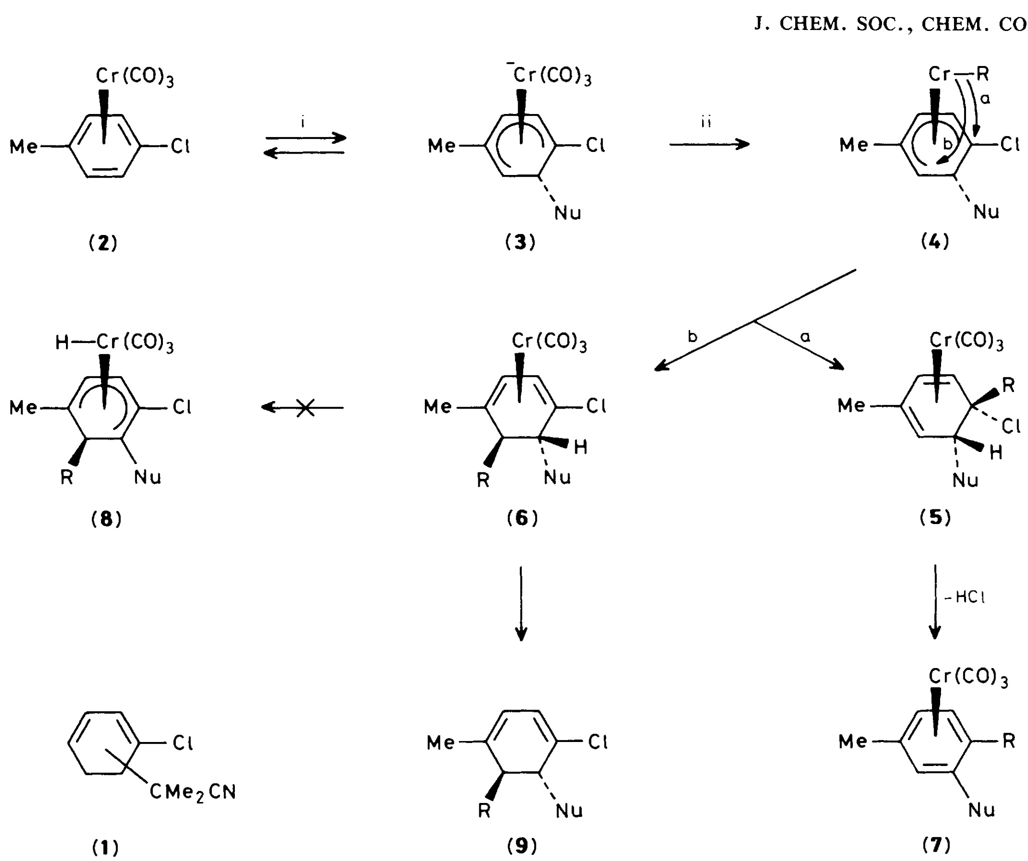
† The term '*cine*-substitution' is used in accordance with IUPAC recommendations to denote reactions in which the entering group takes up a position *ortho* to the leaving group. 'Glossary of Terms used in Physical Organic Chemistry,' ed. V. Gold, *Pure Appl. Chem.*, 1979, **51**, 1725.

‡ With *p*-chlorotoluenetricarbonylchromium, *p*-methylphenylisobutyronitrile has been obtained (ref. 2).

§ Satisfactory spectral and analytical data have been obtained for all new compounds. (**7a**): δ 5.68 (ArH, 4H, m), 2.25 (Me, 3H, s), 1.76 (Me, 6H, s). (**7b**): δ 5.68 (ArH, 3H, m), 2.25 (Me, 3H, s), 1.76 (Me, 6H, s). (**7c**): δ 8.17 (ArH *ortho*, 2H, m); 7.40 (ArH *meta* + *para*, 3H, m), 5.60 (5-H and 2-H, 2H, m), 5.32 (4-H and 6-H, 2H, m), 2.75 (SCH_2, 4H, m), 2.10 (Me, 3H, s), 2.00 (SCH_2CH_2, 2H, m). (**7d**): δ 5.64 (5-H, 1H, d, J 5.91 Hz), 5.60 (2-H, 1H, s), 5.35 (6-H, 1H, d, J 5.91 Hz). (**9c**) ($CDCl_3$, J in Hz): δ 7.92 (ArH *ortho*, 2H, m), 7.29 (ArH *meta* + *para*, 3H, m), 6.02 (3-H, 1H, ddm, $J_{2,3}$ 5.78, $J_{3,Me}$ 0.54), 5.13 (2-H ddq, $J_{2,3}$ 5.78, $J_{2,Me}$ 1.61), 2.70 (S–CH_2, 4H, CH allyl, 3H, m), 1.84 (SCH_2–CH_2, 2H, m), 1.60 (Me, 3H, br s). (**9d**): deuterium was present at the 6-position *cis* to the $Cr(CO)_3$ entity, δ 6.02 (3-H, 1H, d br t, $J_{2,3}$ 5.77, $J_{3,Me}$ 0.60), 5.13 (2-H, dq, $J_{2,3}$ 5.77, $J_{2,Me}$ 1.61).

¶ Indeed, minor products [(**9c**)–$Cr(CO)_5$] and [(**9d**)–$Cr(CO)_5$] on which the $Cr(CO)_5$ moiety is co-ordinated to one sulphur atom, were isolated. These complexes gave the corresponding free cyclohexadienes (**9c**) and (**9d**) in solution.



a; Nu = $-CMe_2CN$, R = H
b; Nu = $-CMe_2CN$, R = D
c; Nu = $-C(Ph)(S-[CH_2]_3-S)$, R = H
d; Nu = $-C(Ph)(S-[CH_2]_3-S)$, R = D

Scheme 1. i: LiNu; ii: CF_3CO_2H or CF_3CO_2D.

On the other hand, when the hydride of complex (**4d**) migrates to the carbon bearing the chloride atom yielding the cyclohexadiene (**5d**), this complex readily eliminates HCl to rearomatize to the *cine*-substitution complex (**7d**)§

In conclusion, our results show that *cine*-substitution occurs upon treatment of *p*-chlorotoluenetricarbonylchromium with a carbanion followed by acid treatment. This reaction represents to our knowledge the first *cine*-substitution[4] of arenetricarbonylchromium complexes. In one case, the isolation of the cyclohexadienes (**9c**) demonstrates clearly that this reaction proceeds *via* reductive elimination in a chromium hydride intermediate (**4**). This provides a better understanding of the details of the mechanism of this reaction.||

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References

1 M. F. Semmelhack and H. T. Hall, *J. Am. Chem. Soc.*, 1974, **96**, 7091 and 7092; S. G. Davies, 'Organotransition Metal Chemistry, Application to Organic Synthesis,' Pergamon Press, Oxford, 1982.
2 M. F. Semmelhack, *J. Organomet. Chemistry Library*, 1976, **1**, 361; J. P. Collman and L. H. Hegedus, 'Principles and Applications of Organotransition Metal Chemistry,' Mill Valley, California, 1980.
3 F. Rose-Munch, E. Rose and A. Semra, *J. Chem. Soc., Chem. Commun.*, 1986, 1108; J. C. Boutonnet, F. Rose-Munch, and E. Rose, *Tetrahedron Lett.*, 1985, **26**, 3989; J. C. Boutonnet, J. Levisalles, J. M. Normant, and E. Rose, *J. Organomet. Chem.*, 1983, **255**, C21.
4 R. E. Markwell, *J. Chem. Soc., Chem. Commun.*, 1979, 428; D. P. Self, D. E. West, and M. R. Stillings, *J. Chem. Soc., Chem. Commun.*, 1980, 281.
5 J. C. Boutonnet, L. Mordenti, E. Rose, O. Le Martret, and G. Precigoux, *J. Organomet. Chem.*, 1981, **221**, 147; J. C. Boutonnet, J. Levisalles, F. Rose-Munch, E. Rose, G. Precigoux, and F. Leroy, *ibid.*, 1985, **290**, 153.

|| Preliminary results showed that *ipso*-, *cine*-, and *tele*-substitution occurred in the case of *o*- and *m*-chlorotoluenetricarbonylchromium complexes showing the importance of the conformation of the $Cr(CO)_3$ group of the complexes relative to the regioselectivity of carbanion addition,[5] the nature of the carbanion, and the experimental conditions.