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**).

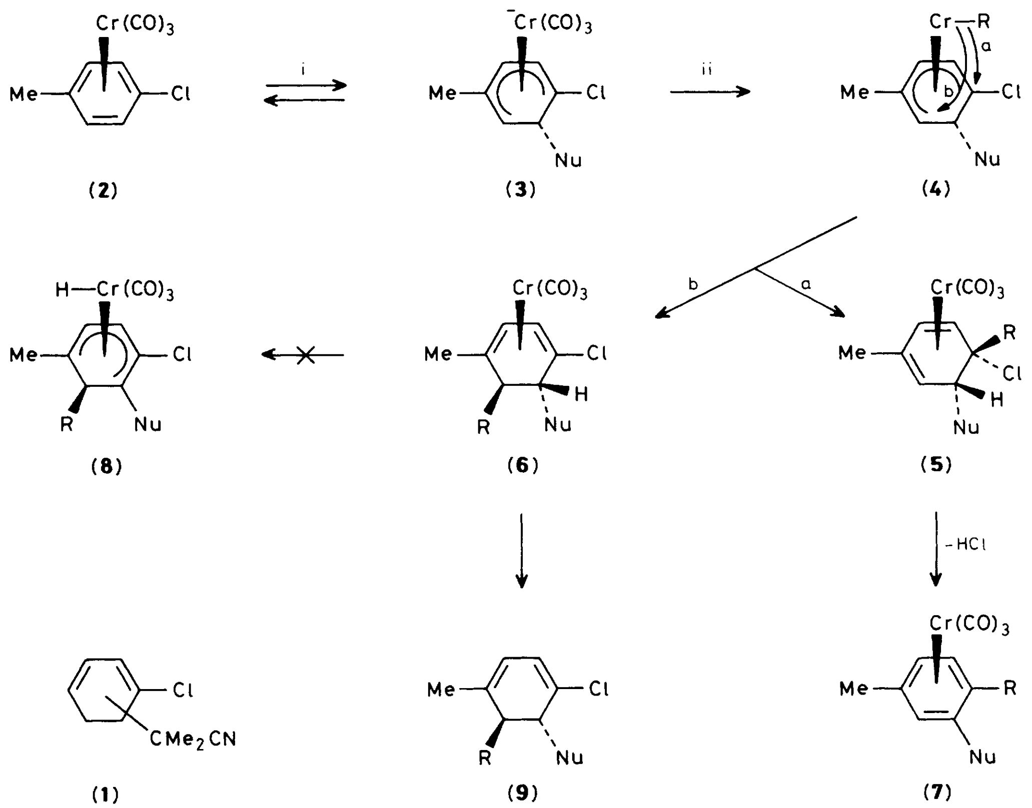
Several features of these reactions are noteworthy. When the hydride of complex (**4d**) migrates to the carbon which is *ortho* to the methyl group and *meta* to the chloro group, the reaction stops at this stage,[3] affording complex (**6d**). Apparently, hydrogen abstraction does not occur to give 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**).[¶]

[†] 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$_2$CN, R = H
b; Nu = –CMe$_2$CN, 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$_3$CO$_2$H or CF$_3$CO$_2$D.

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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‖ 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.