tele-Substitution[†] in Halogenobenzenetricarbonylchromium Complexes

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tele-Substitution of the chloro group of 1-chloro-2,6-dimethylbenzenetricarbonylchromium by a carbon nucleophile readily occurs at the position *para* to the leaving group.

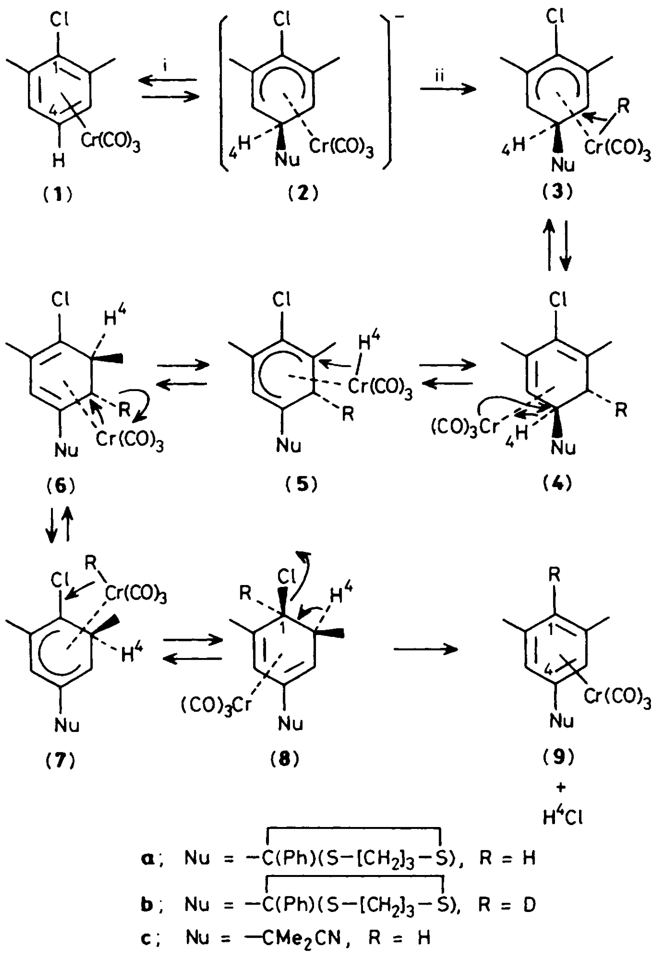
We recently reported that a *cine*-substitution reaction occurs when *para*-chlorotoluenetricarbonylchromium reacts with a carbanion which is then treated with CF_3CO_2H[2] and that a *meta*-*tele*-substitution occurs when (η^6-1-phenoxy-2,3-dimethylbenzene)tricarbonylchromium reacts with a nucleophile, followed by CF_3CO_2H treatment.[3] In other words, nucleophilic attack occurred in these two reactions *ortho* and *meta*, respectively, to the leaving halogeno or phenoxy group. We extend herein our results to the addition of a nucleophile at a carbon *para* to a halogeno leaving group.

1-Chloro-2,6-dimethylbenzenetricarbonylchromium (**1**) (obtained by lithiation of 1-chloro-2-methylchlorobenzenetricarbonylchromium followed by methylation with MeI, 93% yield) gave upon treatment with 2-lithio-2-phenyl-1,3-dithianyl at −78 °C and then with CF_3CO_2H, the trisubstituted complex (**9a**)[‡] (79% yield). When CF_3CO_2D is used, the deuteriated complex (**9b**)[‡] is obtained (79% yield).

Complex (**1**), upon treatment with 2-lithio-isobutyronitrile at −78 °C and then with CF_3CO_2H yielded the complex (**9c**)[‡] (89% yield).

[†] The term '*tele*-substitution' is used in accordance with IUPAC recommendations to denote reactions in which the entering group takes up a position more than one atom away from the atom to which the leaving group is attacked.[1]

[‡] Satisfactory spectral and analytical data have been obtained for all new compounds. ^{1}H N.m.r. $(CD_3)_2CO$ for clarity, the same numbering has been retained for complexes (**1**) and (**9**). (**9a**): δ 8.20, (ArH *ortho*, 2H, m), 7.51 (ArH *meta* + *para*, 3H, m), 5.50 (1-H, 1H, s), 5.30 (3-H and 5-H, 2H, s), 2.78 (S-CH_2, 4H, m), 2.12 (Me, 6H, s), 2.00 (S–CH_2–C*H*$_2$, 2H, m). (**9b**): the 5.50 resonance is absent. (**9c**): 5.50 (3-H and 5-H, 2H, s), 5.41 (1-H, 1H, s), 2.27 (Ar-*Me*, 6H, s), 1.77 (Me, 6H, s). (**1**): δ 2.38 (Me, 6H, s), 5.56 (Ar-H, 3H, s). ^{13}C N.m.r. $(CD_3)_2CO$ (**9a**): 234.32 (CO), 138.60 (free Ar-H), 131.75, 129.69 (free ArH *ortho* + *meta*), 128.94 (free Ar-H, *para*), 118.82 (C-4), 107.95 (C-6, C-2), 97.55 (C-1), 94.96 (C-3,C-5), 62.03 (S–C–S), 30.64 (SCH_2), 24.88 (SCH_2–C*H*$_2$), 20.64 (Me). (**9c**): 234.26 (CO), 123.18 (CN), 116.92 (C-4), 111.56 (C-2,C-6), 95.15 (C-1), 89.88 (C-3,C-5), 37.46 (*C*Me$_2$), 28.92 (Me), 20.67 (Ar-*Me*). (**1**): 233.86 (CO), 112.66 (C-1), 109.64 (C-2,C-6), 94.29 (C-4), 93.66 (C-3,C-5), 20.26 (Me).



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

These unusual, highly regioselective, *tele*-nucleophilic aromatic substitutions at a position *para* to the leaving group prove that the isomerization of the double bonds occurs during this process contrary to the situation with *para*-chlorotoluenetricarbonylchromium.[2] The mechanism described in Scheme 1 accounts for these results. Thus, the 4-H proton is lost from (**8**) by elimination of HCl. Deuterium is incorporated into the complex (**9b**) at the C-1 carbon using CF_3CO_2D.

In conclusion, our results show that *para-tele*-substitution which is well precedented in organic chemistry[4] occurs upon treatment of 1-chloro-2,6-dimethylbenzenetricarbonylchromium with a carbanion followed by acid treatment. This reaction represents to our knowledge the first *para-tele*-substitution reaction of halogenobenzenetricarbonylchromium complexes. The proposed mechanism implies stereospecific hydrogen migrations and HX elimination which have already been demonstrated in a previous communication.[3a]

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