tele-Substitution† in Arenetricarbonylchromium Complexes involving a Hydrogen Migration

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tele-Substitution of the phenoxy group of diaryloxidetricarbonylchromium complexes by a carbon nucleophile has been shown to involve an overall *meta* hydrogen migration.

Reactions of arenetricarbonylchromium complexes with carbon nucleophiles, $\mathrm{Nu^-}$, have been reported to give anionic complexes (A) which yield substituted cyclohexadienes (B) upon acid treatment (equation 1).[2] However, in the case of diphenylethertricarbonylchromium, acid treatment of the corresponding anion (A), followed a different pathway, namely elimination of phenol to give a substituted arenetricarbonylchromium. For example, a *para*-substituted toluene complex is obtained from the 2-methyldiphenylether derivative (equation 2).[3]

This communication reports the synthesis of the deuterium-labelled arene complex (**5a**) and its reaction with the lithium salt of isobutyronitrile, which provides some information on the mechanism of this unusual transformation. 1-Tri-isopropylsiloxy-2,3-dimethylbenzene, obtained by treatment of 2,3-dimethylphenol with tri-isopropylchlorosilane, was treated with $\mathrm{Cr(CO)_6}$ to yield complex (**1**) (73% yield). Lithiation of (**1**) with $\mathrm{Bu^nLi}$[4] followed by quenching with

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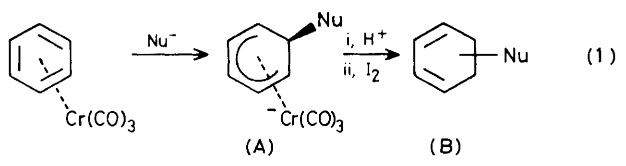
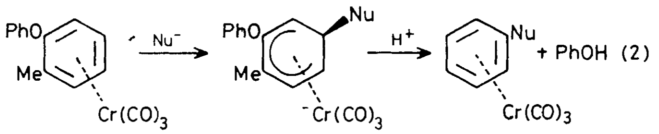
† The term '*tele*-substitution' is used to denote reactions in which the entering group takes up a position more than one atom away from the atom to which the leaving group is attached.[1] *tele*-Substitutions are well precedented in organic synthesis.[8]



(1)



(2)

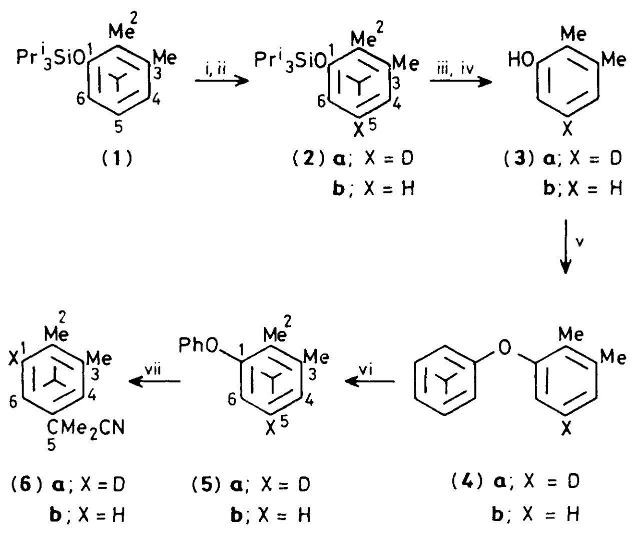
CF_3CO_2D gave the 5-deuterio complex (**2a**) (88% yield).[‡] 2,3-Dimethyl-5-deuteriophenol (**3a**), obtained by iodine oxidation of complex (**2a**) followed by Bu_4NF treatment, reacted with chlorobenzenetricarbonylchromium[6] to yield the diphenyl ether derivative (**4a**). Migration of the tricarbonylchromium entity of complex (**4a**) from one arene ring to the other was accomplished by heating pure (**4a**) at 205 °C. This haptotropic rearrangement[7] gave (**5a**) (60% yield), which when treated with Me_2CLiCN followed by CF_3CO_2H or CF_3CO_2D, generated the tetrasubstituted complex (**6a**). The same series of reactions starting from 2,3-dimethylphenol (**3b**) gave the protio complexes (**4b**), (**5b**), and (**6b**) (Scheme 1). ^1H and ^{13}C n.m.r. spectroscopic data for the complexes (**1**) and (**2**)[§] indicate clearly that lithiation has occurred regioselectively at the C-5 carbon atom which is eclipsed by a chromium carbonyl bond[5] in the more stable conformer, thus confirming the results of Widdowson *et al.*[4] concerning the lithiation of tri-isopropylsiloxybenzenetricarbonylchromium.

^1H and ^{13}C n.m.r. spectroscopic data of the products (**6**)[¶] also clearly show that the deuterium atom migrated from its original C-5 position in complex (**5a**) to the C-1 carbon atom which was originally bearing the phenoxy group.

In conclusion, our results demonstrate that addition of a carbanion to the C-5 carbon of 1-phenoxy-2,3-dimethylbenzenetricarbonylchromium followed by acid treatment gives *tele*-substitution[†] in which there is a hydrogen migration from the C-5 to the C-1 carbon atom.

To our knowledge, this is the first chemical demonstration of an overall *meta* hydrogen migration in an arenetricarbonylchromium complex.[||]

Satisfactory spectral and analytical data have been obtained for all new compounds.



Scheme 1. *Reagents and conditions:* i, Bu^nLi, tetrahydrofuran (THF), −78 °C; ii, CF_3CO_2D (5 equiv.); iii, I_2 (5 equiv.), THF, room temp.; iv, Bu_4NF, THF, room temp., 24 h; v, $PhClCr(CO)_3$ (1 equiv.), dimethylformamide, 50 °C, 22 h; vi, 205 °C, 1.5 h; vii, Me_2CLiCN (1 equiv.), −78 °C, THF, CF_3CO_2H (5 equiv.). The symbol $>\!\!-$ represents the tricarbonylchromium conformation.

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[‡] An excess of n-BuLi was necessary because lithiation also occurred on the methyl *meta* to the tri-isopropylsiloxy group which is eclipsed by a chromiumcarbonyl bond in the more stable conformer.[5]

[§] ^1H N.m.r. $(CD_3)_2CO$ (J in Hz) (**1**) δ 5.08 (4-H, d, J 6.2), 5.64 (5-H, t, J 6.6), 5.33 (6-H, d, J 6.6). In the deuteriated complex (**2a**), the δ 5.64 resonance is absent and the δ 5.08 and 5.33 resonances are singlets. ^{13}C N.m.r. $(CD_3)CO$ (**1**) δ 140.54 (C-1), 90.46 (C-4), 94.95 (C-5), 83.39 (C-6). In the deuteriated complex (**2a**) the δ 94.95 resonance is a triplet.

[¶] A 500 MHz ^1H–^{13}C COSY n.m.r. spectrum ($CDCl_3$) was used to identify the chemical shift of each proton relative to each carbon. ^1H N.m.r. (**6b**) δ 5.49 (4-H, s), 5.41 (6-H, d, J 5.9), 5.25 (1-H, d, J 5·9). The δ 5.25 resonance is absent in the deuteriated complex (**6a**) and the δ 5.41 resonance is a singlet. ^{13}C N.m.r. (**6b**) δ 93.22 (C-1), 93.18 (C-4), 110.84 (C-5), 89.56 (C-6). The 93.22 resonance is a triplet in the deuteriated complex (**6b**).

[||] The results of Jaouen *et al.* who observed racemisation in the substitution of (+)-methyl 2-fluorobenzoic acid tricarbonylchromium complex by $NaNH_2$ can be explained by an analogous mechanism.[2,9] We thank one of the referees for bringing this work to our attention.