

HIGHLY REGIOSELECTIVE AROMATIC SUBSTITUTION  
ON A DIARYLOXIDETRICARBONYLCHROMIUM COMPLEX

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*Summary* : Ortho-substituted diaryloxydicarbonylchromium (0) complexes  $\text{PhOAr-Cr(CO)}_3$ , treated with carbanions  $\text{Nu}^-$ , give, after acid quenching, paradisubstituted complexes  $\text{NuAr-Cr(CO)}_3$  via a 1,3-hydride migration followed by elimination of phenol : the overall sequence of the reaction consists in a regioselective *meta* substitution of the phenoxy group by the nucleophile.

Reactions of arene-tricarbonylchromium (0) complexes with nucleophiles show interesting applications (1-6). We report now our recent finding that diaryloxydicarbonylchromium(0) complexes act differently according to reaction conditions.

$\text{PhOPh-Cr(CO)}_3$  1 (7) (95% yield from  $\text{Ph}_2\text{O}$  and  $\text{Cr(CO)}_6$ ) reacts with nucleophiles such as  $\alpha$ -cyano and  $\alpha$ -alkoxycarbonyl carbanions to afford, after iodine oxidation of the anionic complexes 2, the *meta* substituted diphenyloxides 3 (yields = 43-88%). Whether the anionic complexes 2 at  $-78^\circ\text{C}$  are treated with  $\text{CF}_3\text{CO}_2\text{H}^\S$  (5 equivalents) at the same temperature, or warmed up to room temperature, the same monosubstituted complexes 4 are obtained (yields = 50-88%, scheme 1).

These experiments suggest that complex 4 may be formed by two different mechanisms. To shed light on these mechanisms, we undertook the same reactions with an *ortho* substituted diaryloxydicarbonylchromium complex :  $\text{PhO-}o\text{-MeC}_6\text{H}_4\text{-Cr(CO)}_3$  5 (63% yield from 1 by treatment with  $n\text{-BuLi}$  and  $\text{MeI}$ ).

1) Complex 5 reacts with isobutyronitrile anion to yield the anionic complex 6,  $\text{CF}_3\text{CO}_2\text{D}$  quenching of which at  $-78^\circ\text{C}$  leads to complex 11 containing no deuterium (Yield=79%). We suggest the following sequences in order to interpret the formation of product 11 : treatment of complex 5 with a nucleophile and with  $\text{CF}_3\text{CO}_2\text{D}$  would give the  $\eta^5$ -cyclohexadienyl chromium deuteride 7. An intramolecular reductive elimination would give the endo-6-deutero,

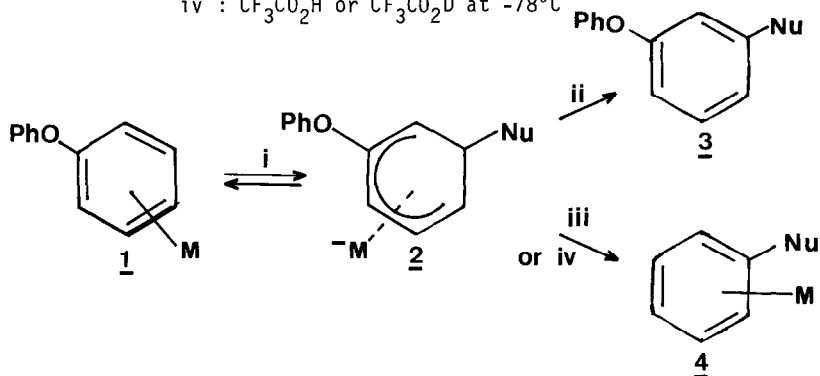
§ An analogous reaction with anisole- $\text{Cr(CO)}_3$  has been reported without explanation (3c)

Scheme 1 : Nu =  $-\text{CH}_2\text{CN}$ ,  $-\text{CH}(\text{CH}_3)\text{CN}$ ,  $-\text{C}(\text{CH}_3)_2\text{CN}$ ,  $-\text{CH}(\text{CH}_3)\text{CO}_2\text{tBu}$  ;

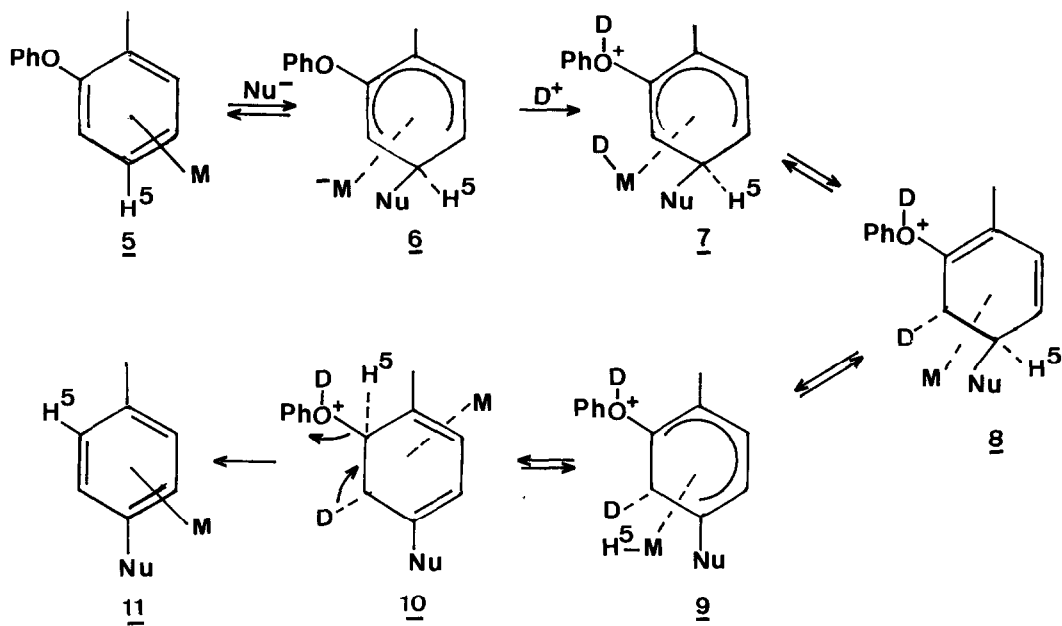
$-\text{C}(\text{Ph})-\text{S}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{S}$  except the reaction iii.

i : NuLi,  $-78^\circ\text{C}$  ; ii :  $\text{I}_2$  ; iii : warmed up to r.t. :

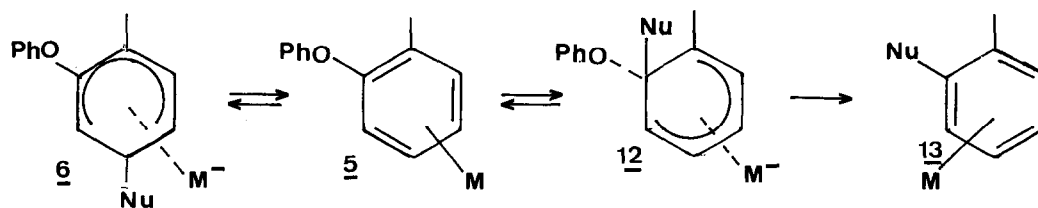
iv :  $\text{CF}_3\text{CO}_2\text{H}$  or  $\text{CF}_3\text{CO}_2\text{D}$  at  $-78^\circ\text{C}$



Scheme 2 : M =  $\text{Cr}(\text{CO})_3$



Scheme 3 : M =  $\text{Cr}(\text{CO})_3$



$\eta^4$ -cyclohexadienyl complex 8. The  $\eta^4$ -cyclohexadienyl complex 10 would be then obtained after the H5 proton migration on the chromium atom of complex 8 giving chromium-hydride 9 followed by migration of the hydride on the C1 carbon bearing the phenoxy group. The elimination of the protonated phenoxy group on the C1 carbon and the deuterium on the C6 carbon would create a new double bond. This elimination, followed by the complexation of the free double bond formed would give the stable complex 11. It represents the driving force of the reaction and it is at our knowledge unprecedented in the literature. The overall sequence of the reaction consists on a meta substitution of the phenoxy group of diarylether-Cr (CO)<sub>3</sub> by a nucleophile.

In the case of benzene or anisole-Cr (CO)<sub>3</sub> treated with a nucleophile and CF<sub>3</sub>CO<sub>2</sub>H, formation of  $\eta^4$ -cyclohexadienes-Cr (CO)<sub>3</sub> or cationic  $\eta^4$ -cyclohexadienes tricarbonylchromium hydrides complexes have been postulated (3a-d). SEMMELHACK proposed that the mixture of cyclohexadienes isomers obtained after iodine oxidation may result from isomerization of the olefin units while attached to the metal (3a-d).

2) Complex 5 reacts with the same carbanion at -78°C and if the reaction mixture is warmed up to room temperature, the ortho disubstituted complex 13 is obtained. An ipso attack of the nucleophile on the arene carbon bearing the phenoxy group could explain the formation of the complex 13. Ipso addition has been reported for chloro and fluorobenzene-Cr (CO)<sub>3</sub> complexes (3a, 8-9) and more recently on xanthene-cyclopentadienyl iron cations complexes (10). In the case of chloro or fluorobenzene-Cr(CO)<sub>3</sub> complexes, only tertiary anions, for example, tertiary  $\alpha$ -cyano or  $\alpha$ -alkoxycarbonyl carbanions, substitute the halogen. However in the case of diaryloxy-Cr (CO)<sub>3</sub> complexes, primary, secondary and tertiary  $\alpha$ -alkoxycarbonyl carbanions substitute the phenoxy group. (Scheme 3)

In conclusion, depending on the experimental conditions, it is possible to synthesize a para 11 or an ortho disubstituted toluene-Cr (CO)<sub>3</sub> 13 starting from ortho methyl-diphenyl-ether-Cr (CO)<sub>3</sub> 5. These highly regioselective reactions are promising in the synthesis of polysubstituted arenes because the chromium is not lost during the procedure and because these reactions can be generalized to arene-Cr (CO)<sub>3</sub> complexes bearing a methoxy group §.

The new compounds have spectral properties in agreement with the proposed structure (11)

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§ For example, anisole-Cr (CO)<sub>3</sub> gives with a good yield 2-methyl 2-phenyl propionitrile-Cr (CO)<sub>3</sub> when treated with isobutyronitrile anion and pTsOH (work in progress).

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- 11) Complex 11 (Nu = CMe<sub>2</sub>CN, Y = 74%, F dec = 109 - 111°C. (<sup>1</sup>H) NMR (Me<sub>2</sub>CO.d<sub>6</sub>) : 6H (Me<sub>2</sub>CCN) 1,73 s ; 3H (Me Ar) 2,24 s ; 2H (H-3 and H-5) 5,46 d, J = 6,8 ; (H-2 and H-6) 5,97 d, J = 6,8. (<sup>1</sup>H) NMR of the crude reaction showed that complex 13 is a minor product : Y = 7%. Complex 13 (Nu = CMe<sub>2</sub>CN, not optimized yield = 28% and 49% recovered starting material. (<sup>1</sup>H) NMR (Me<sub>2</sub>CO.d<sub>6</sub>) : 3H (Me anti) 1,76 s ; 3H (Me syn) 1,88 s ; 3H (MeAr) 2,60 s ; 1H (H5) 5,40 t, J = 8,2 ; 1H (H3) 5,45 d, J = 7,0 ; 1H (H4) 5,83 t, J = 6,3 ; 1H (H6) 5,96 d, J = 6,8.

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