cine and *tele* Nucleophilic Substitutions in (η^6-Arene)tricarbonylchromium and Tricarbonyl(η^5-cyclohexadienyl)manganese Complexes

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Addition of a nucleophile to an (η^6-arene)tricarbonylchromium or a tricarbonyl(η^5-cyclohexadienyl)manganese complex substituted with a leaving group X (X = F, Cl, OMe, OPh, NR_2) affords (after treatment with acid) new complexes with the same η^6 or η^5 hapticity. The overall reaction involves addition of the nucleophile *ortho*, *meta*, or *para* with respect to the leaving group and HX elimination.

I. Introduction

Coordination of a transition metal atom to the π-system of an arene **1** and a cyclohexadienyl ring **3** activates the ring towards addition of nucleophiles to give (η^5-cyclohexadienyl)- and (η^4-cyclohexadiene)metal complexes **2** and **4**, respectively (Scheme 1). The (η^6-arene)tricarbonylchromium complexes **1** [M = $Cr(CO)_3$] undergo a number of very useful reactions, and have found significant applications in organic and organometallic syntheses.[1−4] Moreover, their preparation is very easy and they are usually air-stable, crystalline solids and, furthermore, the free arene may readily be released from complexation by mild oxidation of the metal atom. The neutral (η^5-cyclohexadienyl)manganese complexes **3** [M = $Mn(CO)_3$] are beginning to receive more and more attention because they are easily handled in nonpolar solvents and so may be purified very conveniently by silica gel chromatography. They are also easily obtained from the corresponding, highly electrophilic, cationic manganese complexes **1** [M = $Mn^+(CO)_3$] by addition of a wide range of nucleophiles. It has been shown that these neutral manganese complexes **3** display reactivity similar to some extent to that of the (η^6-arene)chromium complexes; thus *cine* and *tele* nucleophilic substitutions and − recently − Pd-mediated reactions[5] have been reported to occur under mild conditions.

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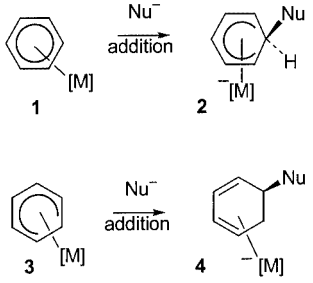
MICROREVIEWS: This feature introduces the readers to the authors' research through a concise overview of the selected topic. Reference to important work from others in the field is included.



Scheme 1

In this review we focus on recent work investigating nucleophilic substitutions on (η^6-ligand)chromium complexes and (η^5-ligand)manganese complexes. After a brief description of the preparation of these complexes (Cr, Mn), some general reactivity patterns mostly related to the nucleophilic substitutions of (arene)$Cr(CO)_3$ are outlined. Later sections concern *cine* and *tele* nucleophilic substitution in chromium and manganese complexes, with up-to-date examples from current literature.

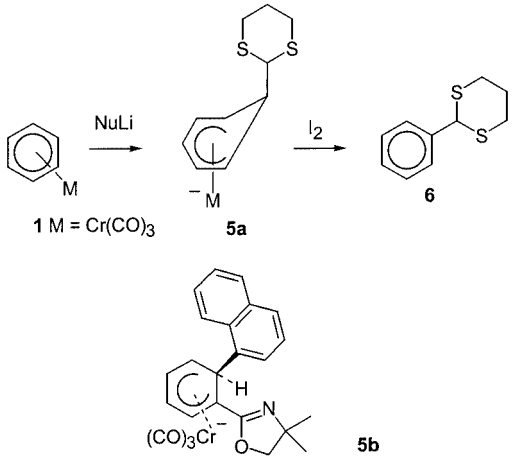
II. Complexation Methods

(Arene)tricarbonylchromium complexes[6] are usually prepared in good yields by heating the free arene with $Cr(CO)_6$ in a high-boiling solvent. The most popular method, described by Mahaffy and Pauson, uses a mixture of di-*n*-butyl ether and THF in a 9:1 ratio.[6c] These complexes are usually yellow, but can be orange or even dark red if the arene is conjugated to an aldehyde, a ketone, or a withdrawing group. They may also be prepared by use of $Cr(CO)_3L_3$,[6b,6e] where L is a two-electron ligand (L = NH_3, CH_3CN, pyridine) or L_3 = naphthalene.[6d] These complexes are decoordinated easily under mild conditions by treatment with I_2, CAN, CO, PPh_3, or Py,[6d] or simply by exposure to air or light.[1c−1e] (Arene)tricarbonylmanganese complexes can be prepared in good yield by treatment of the free arene with $BrMn(CO)_5$ [7a−7c] and $AgBF_4$ in CH_2Cl_2.[7d] Similarly, arene complexes are accessible by treatment of the arene with $Mn(CO)_5ClO_4$, $(acetone)_3Mn(CO)_3^+$ in CH_2Cl_2,[7e] $BrMn(CO)_5$ in the presence of $AlCl_3$,[7f] or $Mn_2(CO)_{10}$, or by transferring $Mn(CO)_3^+$ from cationic (polyarene)$Mn(CO)_3^+$ complexes.[7b,7c] A recent preparation involves a two-step methodology, starting from (η^5-1-halocyclohexadienyl)-$Mn(CO)_3^+$ and involving a Pd-catalyzed carbonylation followed by an easy η^5/η^6 rearomatization with Ph_3CBF_4. This gives a route to the previously unknown (η^6-RCO-arene)$Mn(CO)_3^+$ derivatives (RCO = ester, ketone, amide).[5a]

III. General Reactivity Patterns of (η^6-Arene)tricarbonylchromium Complexes

(Arene)tricarbonylchromium complexes are known to have unprecedented reactivities. It is now well established that η^6-coordinated arenes are susceptible to many manipulations thanks to the electron-withdrawing properties of the $Cr(CO)_3$ entity, which have been compared to the electron removal of a nitro group of nitrobenzene.[1c] It has been reported by Semmelhack et al.[8b] and by Card and Trahanowsky[8c] that carbanion addition occurs under very mild conditions.[8] It has been shown that benzylic and, in certain cases, homobenzylic carbanions are easily formed by deprotonation,[1,9] that benzylic carbocations are stabilized,[1d,9b,10a−10h] and recently that benzylic radicals are interesting intermediates.[11] The $Cr(CO)_3$ residue is also known to play a "stereodirecting" effect in reactions occurring at the periphery of the ring.[1c] The ring hydrogen atoms have increased acidity and are easily deprotonated with organolithium reagents.[1d,10a] In the context of this microreview, we focus, as mentioned, only on the nucleophilic addition reactions on the ring. Thus, before description of *cine* and *tele* S_N reactions, some general information on the reactivity of addition of a nucleophile to an (arene)$Cr(CO)_3$ complex is presented.

2-Lithio-1,3-dithiane reacts with (benzene)tricarbonylchromium [**1**, M = $Cr(CO)_3$] to give an anionic η^5-cyclohexadienyl complex **5a** (Scheme 2). This air-sensitive intermediate can be observed spectroscopically and has been characterized by X-ray diffraction analysis by Semmelhack et al.[8a] Another study of a similar η^5-structure (**5b**) has recently been reported.[8a] Oxidation of **5a** at −78 °C with at least 2.5 mol-equiv. of I_2 gives the substituted arene **6**, together with HI, Cr^{III} and CO.



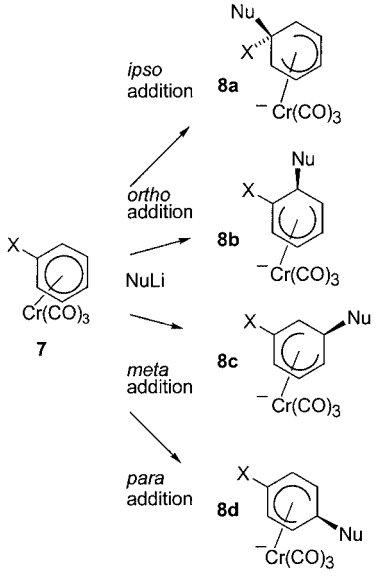
Scheme 2

This reaction has been generalized to other nucleophiles. Table 1 provides a representative sample of the carbanions tested.[8b,8c,12] The regioselectivity of carbon nucleophile addition to a substituted complex **7** is of interest because there are four possible ways to functionalize the ring. The nucleophile can react at the *ipso* carbon atom, bearing the X group, or at the positions *ortho*, *meta*, or *para* to the X group, to yield anionic intermediates **8a**, **8b**, **8c**, or **8d** (Scheme 3).

Table 1. Representative sample of carbanions tested with benzene tricarbonyl chromium

Unreactive carbanions	Successful carbanions	Other reaction[a]
	$LiCH_2CO_2tBu$[b]	
$LiCH_2CO_2tBu$	$LiCH_2CN$[b]	*n*BuLi
MeMgBr	$LiCH_2SPh$[b]	MeLi
Me_2CuLi	2-Li-1,3-dithiane[b]	*s*BuLi
	LiCH=CHR[b]	
	LiPh[b]	
	$LiCMe_3$ [c]	

[a] Metallation of the ring occurs. [b] Ref.[8b] [c] First addition of a carbanion to a (non-halogenated arene)$Cr(CO)_3$ unit.[8c]



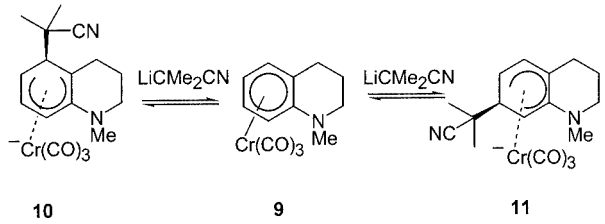
Scheme 3

Table 2. Regioselectivity of the addition of a carbon nucleophile to $C_6H_5XCr(CO)_3$, [8b]

Entry	X	LiNu	*m*/*p* ratio	Yield (%)
1	OMe	$LiCMe_2CN$	3:97:0	93
2	OMe	$LiCMe_2CO_2tBu$	0:100:0	76
3	NMe_2	$LiCMe_2CN$	1:99:0:	92
4	Me	$LiCMe_2CN$	1:97:2	95
5	Me	$LiCMe_2CO_2tBu$	3:97:0	96
6	Cl	$LiCMe_2CO_2tBu$	5:95:0	84
7	Cl	$LiCMe_2CN$	10:89:1	84
8	Me	$LiCH_2CN$	35:63:2	88
9	Cl	$LiCH_2CO_2tBu$	28:72:0	89

Addition of these carbanions can be reversible, but it is not so simple to know whether the addition occurs under kinetic or thermodynamic control.[12,13] In fact, the difference between the kinetic and thermodynamic selectivity is small in most cases, even if some exceptions are known. Thus, it is well precedented that arenes substituted with a donor substituent (**7**, X = OR, NR_2, Scheme 3) are attacked by the nucleophile at a *meta* position (Table 2, Entries 1, 3). The selectivity is also excellent with toluene or chlorobenzene complex in the case of tertiary stabilized carbanions (Table 2, Entries 4−7), but is not so high with primary carbanions (Table 2, Entries 8, 9).

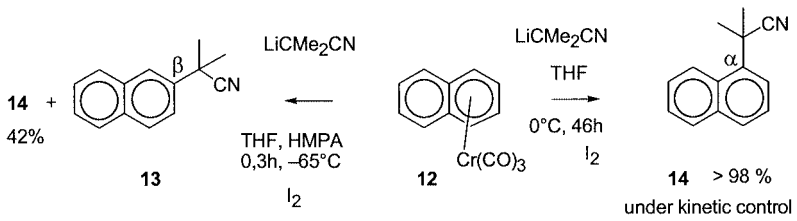
Ullenius et al. presented an interesting example in which the kinetic and the thermodynamic products are not the same, in the particular case of tricarbonyl(*N*-methyltetrahydroquinoline)chromium (**9**, Scheme 4).[13c] Indeed, the ratio of **11/10** changes from 2:1 at −78 °C after 1 min reaction time to 96:4 after 8.6 h at −78 °C, changes being observed with time, temperature, and solvent (THF or THF and 4 equiv. HMPA).



Scheme 4

Kündig et al. also reported interesting results in the case of the tricarbonyl(naphthalene)chromium complex **12**. On addition of $LiCMe_2CN$, a mixture of C_α and C_β complexes **14** and **13** was obtained in the ratio 42:58. Equilibration was avoided because a mixture of THF and HMPA was used. In THF, however, the only product was the α-substituted naphthalene **14** (Scheme 5).[13a] The same study has been undertaken with 1,4-dimethoxynaphthalene, the authors elegantly showing that the rate of equilibration could be slowed down by a factor of 50.000 by an appropriate choice of solvent mixture: THF, THF/HMPT (3:1).[13a] Replacement of lithium with the potassium counterion can slow the reaction down by a factor of 500.

The selectivity of the addition of a carbanion in polar solvents has been discussed in terms of charge control and orbital control. Thus, analysis of orbital control has been proposed by determination of the interaction of the frontier molecular orbitals [HOMO for the nucleophile and LUMO for the (arene)tricarbonylchromium complex].[12,13b] This picture does not explain the differences in selectivity between toluene and anisole complexes, because the LUMOs of these two arenes show the same pattern. Thus, charge control could be very important. This is the reason why the conformation of the complex should be considered. Indeed, in the case of the anisole complex, for example, it is well precedented that the methoxy group is eclipsed by a chromium−carbonyl bond. It is also well known that, in the case of the free anisole, the carbon atom bearing the OMe group is more electrophilic. There is therefore a synergic effect between the role of the methoxy group and that of the conformation of the $Cr(CO)_3$ entity. In solution, in fact, the percentage of the conformer eclipsing the methoxy group of (anisole)tricarbonylchromium should be higher than that of the conformer eclipsing the methyl group of (toluene)tricarbonylchromium. Thus, it might be predicted



Scheme 5

that *meta* selectivity should be better with anisole than with toluene. The percentage of the major conformer takes into account the nature of the substituents attached to the arene ring. Indeed, it has been reported that in solution a substituted arene complex can be considered to be in equilibrium between two conformations: the *syn*-eclipsed conformation SE and the *anti*-eclipsed conformation AE (Figure 1).[3a,14] Thus, if D is an electron donor substituent, the major conformer is the SE one, and if X is an electron-withdrawing group, the major conformer is AE.

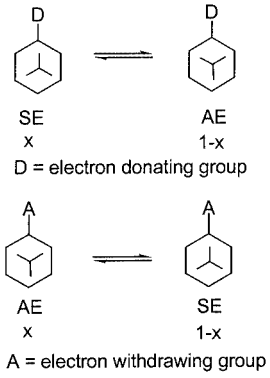
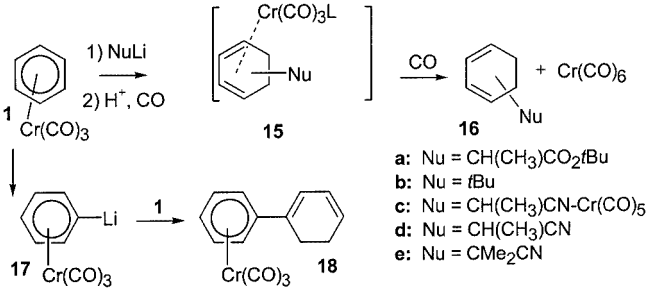


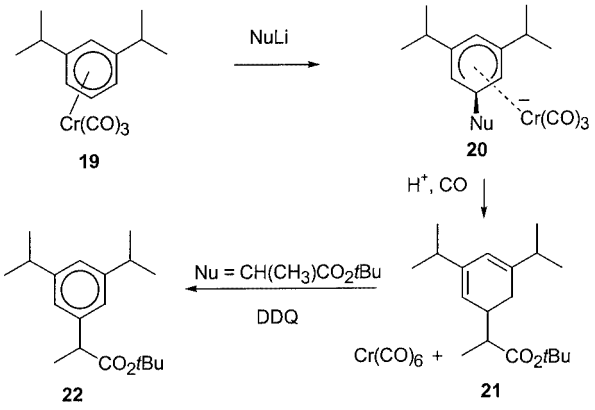
Figure 1. Conformation of the $Cr(CO)_3$ tripod

Addition of different nucleophiles to (benzene)tricarbonylchromium under carbon monoxide (the reaction medium being treated with CF_3CO_2H at −78 °C) has also been reported to give firstly the η^4 complexes **15a** and then the free substituted cyclohexadienes **16a** in 83% yield and $Cr(CO)_6$ in 75% yield [**16b** in 72% yield and $Cr(CO)_6$ in 78% yield] (Scheme 6). With the propionitrile carbanion, under CO, the cyclohexadiene **16c** is recovered and a 30 atm pressure of CO is necessary to obtain the decoordinated cyclohexadiene **16d** in 85% yield and $Cr(CO)_6$ in 85% yield.[15] Determination of the proportion of the cyclohexadienes **16e** (Nu = CMe_2CN) showed that the major isomer is the 1-substituted 1,3-cyclohexadiene (78%). The 2- and 5-sustituted 1,3-cyclohexadienes are obtained in 9 and 13% yields, respectively (Nu = CMe_2CN). A minor complex $[C_6H_5Cr(CO)_3(C_6H_7)]$ has been isolated as a single isomer; it is (1-η^6-phenyl)$Cr(CO)_3$(1,3-cyclohexadiene) (**18**), the formation of which can easily be interpreted in terms of addition of (phenyllithium)$Cr(CO)_3$ (**17**) to (benzene)$Cr(CO)_3$, followed by acid treatment and decoordination of the $Cr(CO)_3$ unit attached to the cyclohexadiene.



Scheme 6

Addition of the nucleophile to tricarbonyl(*meta*-diisopropylbenzene)chromium (**19**) occurs *meta* with respect to the isopropyl groups and, on treatment of the anionic complex **20** with acid under CO, the cyclohexadienes **21** are obtained in 83% yield, together with $Cr(CO)_6$ in 78% yield. The product can be aromatized by treatment with DDQ, giving the free 1,3,5-trisubstituted arene **22** (Scheme 7).[15]



Scheme 7

An examination of the regioselectivity of the addition of a stabilized carbanion LiCHMeCN to a tricarbonyl(spiroindane)chromium complex **23**, giving complex **24** after I_2 oxidation, is interesting. We observed an 81% selectivity at the C-5 carbon atom (Scheme 8).[3c] In the solid state, the C-5 carbon atom is eclipsed by a chromium−carbon bond, and in solution the conformer with the major population (x = 72%) is the one eclipsing the C-5 carbon atom (Figure 2). Thus, the $Cr(CO)_3$ unit adopts a preferred conformation for steric reasons. The regioselectivity of the addition of $LiCH(CH_3)CN$ is the same at −78 °C and at 0

°C, both with THF and with a mixture of THF and HMPA, and involves the eclipsed C-5 carbon atom of the major conformer. This is the conclusion that we have reached in many examples using a stabilized carbanion at low temperature.

Scheme 8

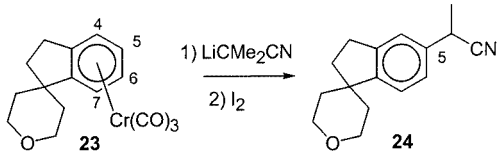
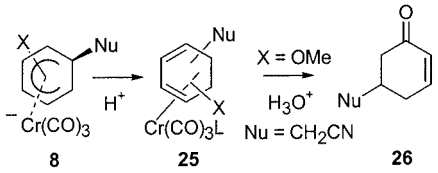


Figure 2. Population of the major conformer

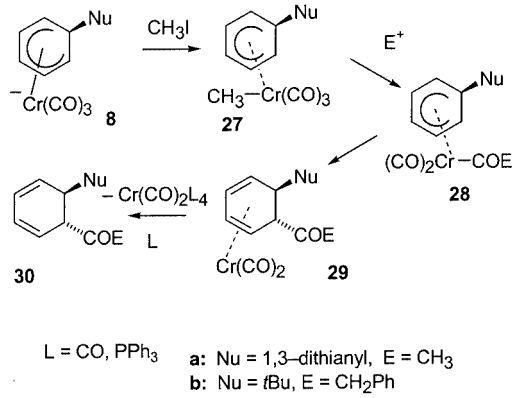
In summary, the regioselectivity of the nucleophilic addition under kinetic control can be explained in terms of charge control and (or) orbital control. The substituents on the arene and the conformation of the $Cr(CO)_3$ tripod play important roles. Under thermodynamic control, the equilibrium can be interpreted in terms of steric and electronic interactions in the intermediate anions, such as **8b**−**d** (Scheme 3).

The anionic η^5-cyclohexadienyl intermediate **8**, obtained by addition of a carbon nucleophile to an arene complex, has been treated with electrophiles. Protonation, for example, occurs at low temperature, giving the η^4-coordinated cyclohexadienes **25** (Scheme 9), with L being (for example) a THF molecule in order to respect the 18-electron rule.[16b] In the case of anisole, the resulting η^4-methoxycyclohexadiene complex **25** has been hydrolyzed to give an enone **26**.[16]



Scheme 9

The anionic intermediate **8** (Nu = 1,3-dithian-2-yl) has also been trapped with a limited set of electrophiles when the nucleophile addition is irreversible. It has been shown that addition of 2-lithio-1,3-dithiane to (η^6-benzene)tricarbonylchromium followed by addition of CH_3I yields a *trans*-disubstituted cyclohexadiene **30a** if the reaction medium is oxidized or treated with a two-electron ligand L (Scheme 10).[17b] CO inserted into the metal−alkyl bond of complex **27** to give the metal−acyl bond of complex **28a**. A reductive elimination can afford the η^4-cyclohexadiene complex **29a** and then the organic compound **30** and $Cr(CO)_2L_4$ through use of a ligand L (L = CO, PPh_3).[1b]



Scheme 10

If *t*BuLi is used as a nucleophile under CO pressure, the anionic intermediate can be trapped in order to recover $Cr(CO)_6$ necessary for the preparation of the starting complex. By addition of *t*BuLi to (benzene)$Cr(CO)_3$ and then benzyl iodide, for example, we obtain the *trans*-cyclohexadiene **30b** (Nu = *t*Bu, E = $CH_2C_6H_5$), but even under 100 atm CO, we recover only a small amount of $Cr(CO)_6$.[18]

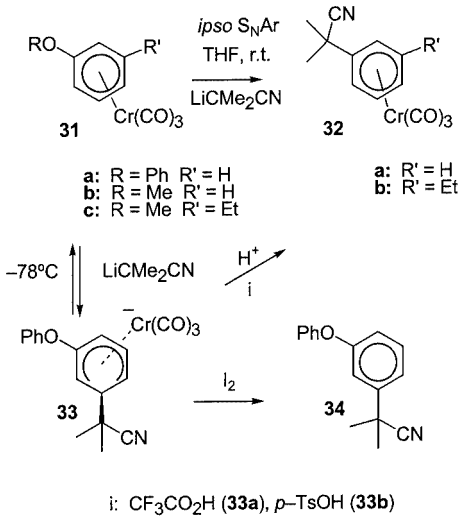
IV. *cine* and *tele* Nucleophilic Aromatic Substitutions: (η^6-Arene)$Cr(CO)_3$ Complexes

IV. a. Organic Carbanions: C−O, C−Cl, C−F Cleavage

One of the first nucleophilic aromatic substitutions described in the literature concerns the addition of sodium methoxide to tricarbonyl(chlorobenzene)chromium (**7**, X = Cl), which gives (anisole)tricarbonylchromium complex (**7**, X = OMe) via the η^5-cyclohexadienyl intermediate **8a** (X = Cl, Nu = OMe). This is the classical *ipso* substitution of the methoxy group at the carbon atom bearing the chloro atom.[19] Usually, however, the kinetic site of addition is at a position bearing a hydrogen substituent, which yields anionic η^5-ligand complexes **8b**, **8c**, and **8d** (Scheme 3).[8b] If equilibration occurs, complexes **8b**−**d** give **8a** and then anisole complex with the irreversible departure of the leaving group X.[1g] It has been shown that the fluorobenzene complex **7** (X = F) is almost 2000 times more reactive than the chlorobenzene complex **7** (X = Cl), in good agreement with a rate-limiting addition of the methoxide anion on the arene ring followed by fast departure of halide. We will not describe these *ipso* reactions in detail − they have been well reported in different reviews[1g] − but will instead consider carbanion addition to carbon atoms *ortho*, *meta*, and *para* with respect to the carbon atom bearing the leaving group.

Whereas direct displacement of oxygen leaving group is not effective, we have shown that treatment of 2-lithio-2-methyl-1,3-dithiane with tricarbonyl(diphenyl ether)chro-

mium (**31a**) at room temperature gives the *ipso*-monosubstituted complex **32a** (Scheme 11).[20]

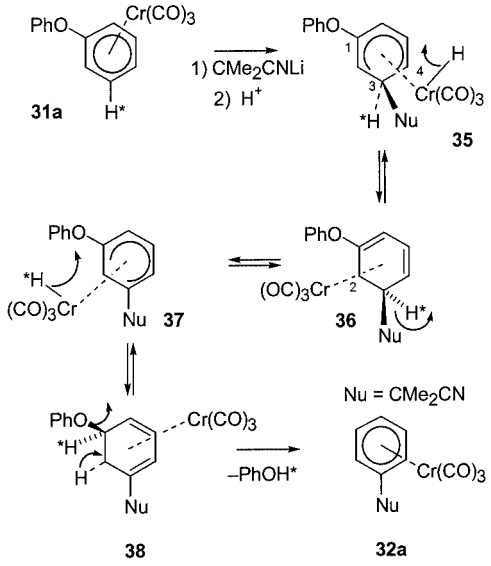


Scheme 11

More interestingly, addition of the same nucleophile at −78 °C affords the anionic intermediate **33**, which is quenched with I_2 at −78 °C to yield the *meta*-disubstituted arene **34** (Scheme 11). Addition occurs *meta* with respect to the PhO group, the overall reaction consisting of a *meta* substitution of a hydrogen atom by the nucleophile.[21]

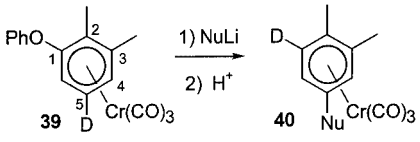
If the anionic intermediate **33** is treated with CF_3CO_2H at −78 °C, complex **32** is again unexpectedly obtained (Scheme 11). The same study with (anisole)$Cr(CO)_3$ (**31b**) and isobutyronitrile carbanion and acid gives phenylisobutyronitrile complex **32a**, but the yield is very low. With *p*TsOH, elimination of MeOH is easier, and complex **32a** is formed in 62% yield. Similarly, treatment of (*meta*-ethylanisole)$Cr(CO)_3$ (**31c**) with $LiCMe_2CN$ and *p*-TsOH affords complex **32b** in 62% yield.[22b]

Taking into account that *ipso* reaction does not occur at −78 °C, we have to consider a new mechanism to explain these unusual results. Addition of $LiCMe_2CN$ to diphenyl ether complex **31a** (Scheme 12) gives (after CF_3CO_2H treatment) the chromium hydride **35**, which can undergo a reductive elimination on the C-4 and C-2 carbon atoms. The new η^4 intermediate **36**, for example, which is a dienol ether, cannot be hydrolyzed in the absence of water. An oxidative addition of the allylic hydrogen atom can give another η^5-cyclohexadienyl complex **37**. Again, a reductive elimination can give the η^4-cyclohexadiene **38**. By elimination of the *anti*-parallel hydrogen atom and the PhO group, a new η^6-arene **32a** is formed. The driving force of the reaction is the rearomatization of the ring, which corresponds to a 1,5-hydrogen shift of the proton located at the C-3 carbon atom (Scheme 12).[21] The nucleophiles that have been tested are the carbanions of CH_3CO_2Me (pK_a = 24.5), $CH_3CH_2CO_2Me$, $(CH_3)_2CHCO_2Me$, CH_3CN (pK_a = 25), CH_3CH_2CN, $(CH_3)_2CHCN$, and 2-phenyl-1,3-dithiane.



Scheme 12

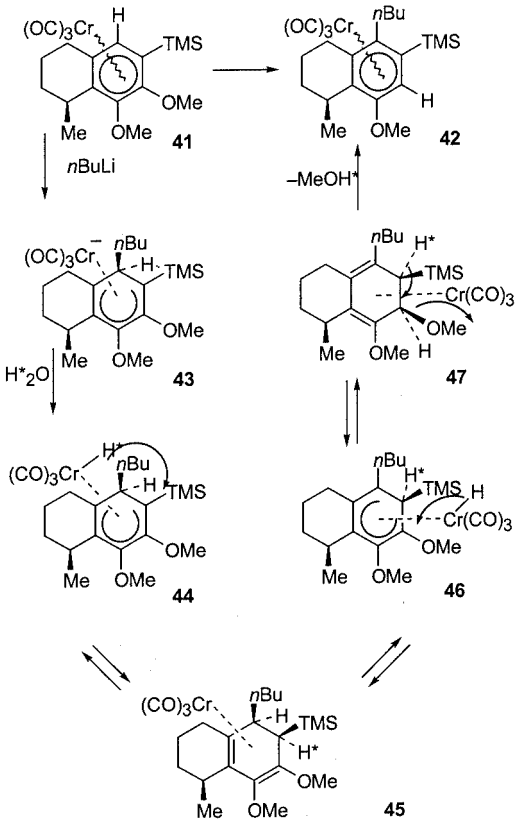
In order to understand the mechanism of this reaction, we undertook the same experiment starting from the labeled tricarbonyl(5-deuterio-2,3-dimethylphenyl phenyl ether)chromium (**39**). We obtained the deuterated complex **40** after treatment with a nucleophile NuLi (Nu = CMe_2CN, CMe_2CO_2tBu, ...) and CF_3CO_2H or CF_3CO_2D (Scheme 13).[21a] This reaction involves a 1,5-deuteride migration from the C-5 carbon atom to the C-1 carbon atom.[21,22] With CF_3CO_2D, we recovered PhOD, showing that the deuterium of the acid is not incorporated into the arene ring. For precision, we called this reaction a *tele-meta* nucleophilic aromatic substitution, in accordance with IUPAC naming schemes. The term *tele* is used to denote reactions in which the entering group takes up a position further than one atom away from the atom to which the leaving group is attached.[23]



Scheme 13

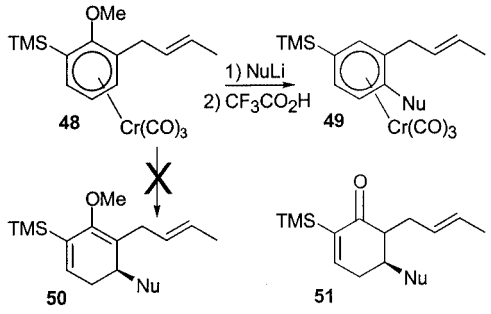
Schmalz et al.[24] reported that addition of *n*BuLi to tetralin derivative complex **41** in THF/HMPA gives a high yield of complex **42**.[24f] This reaction is a *tele* substitution with methoxide as the leaving group. To be more precise, it is a *tele-meta* S_NAr reaction, detailed in Scheme 14. The mechanism should not involve incorporation of deuterium in the ring if the anionic species **43** is trapped with a deuterium source. It is worth noting the ease with which *n*BuLi adds to a carbon atom of the arene ring under conditions that should result in smooth benzylic deprotonation, which according to the authors is disfavored for stereoelectronic reasons. The selective formation of complex **42** is remark-

able because the methoxide expulsion is regioselective: no *tele-para* substitution is observed.



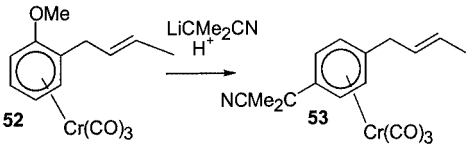
Scheme 14

The same group showed that *tele* substitution is the major pathway in S_NAr reactions of (*ortho*-alkylated η^6-anisole)$Cr(CO)_3$ derivatives such as **48** (Scheme 15).[24c,24e] Treatment of **48** with NuLi (Nu = 2-lithio-1,3-dithiane or *n*BuLi) followed by protonation with CF_3CO_2H does not give the expected enones **51** after hydrolysis of the dienol ethers **50** but, rather, complex **49** by way of a *tele-meta* S_NAr substitution of the MeO group by the nucleophile.



Scheme 15

In close analogy, desilylated complex **52**, when treated with 2-lithioisobutyronitrile and then with CF_3CO_2H, affords the *tele-meta* complex **53** as the major product (Scheme 16).[24e]



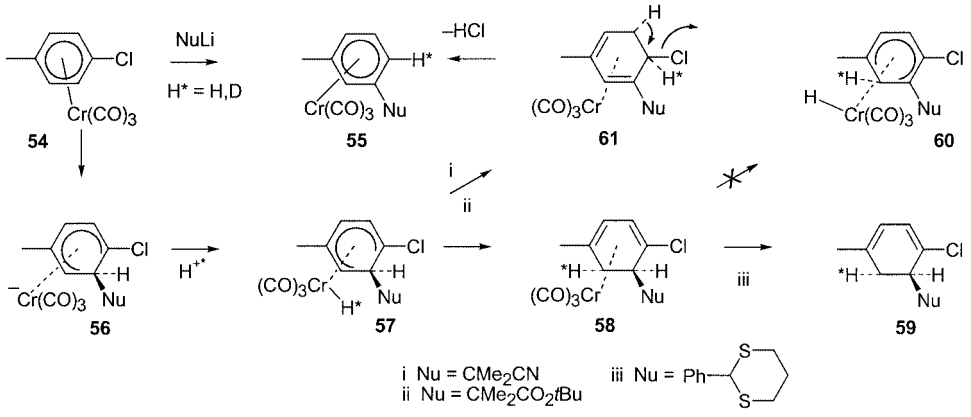
Scheme 16

The addition of stabilized carbanions to tricarbonyl(*para*-chlorotoluene)chromium complex **54** (NuLi and CF_3CO_2H) gives a *meta*-disubstituted complex **55**[25,26] (Nu = CMe_2CN, CMe_2CO_2tBu, p-$CH_3C_6H_4SO_2CHCH_3$. This is termed a *cine* nucleophilic aromatic substitution in accordance with IUPAC recommendations. Indeed a *cine* S_NAr is a reaction in which the incoming group (Nu) takes up a position at the carbon atom *ortho* to the leaving group.[23] With use of CF_3CO_2D, incorporation of deuterium takes place on the carbon atom that bore the leaving group (Scheme 17). If this reaction is performed with 2-lithio-2-methyl-1,3-dithiane, the η^4-cyclohexadiene **58** is obtained by a reductive elimination of the η^5-cyclohexadienyl complex **57**. It is likely that, the nucleophile being too bulky, the *endo*-hydrogen atom cannot be extracted from the carbon atom bearing this nucleophile and the isomerization process is therefore stopped. Instead, decoordination takes place, giving the cyclohexadiene **59**, X-ray analysis of which confirmed the proposed structure.[26b]

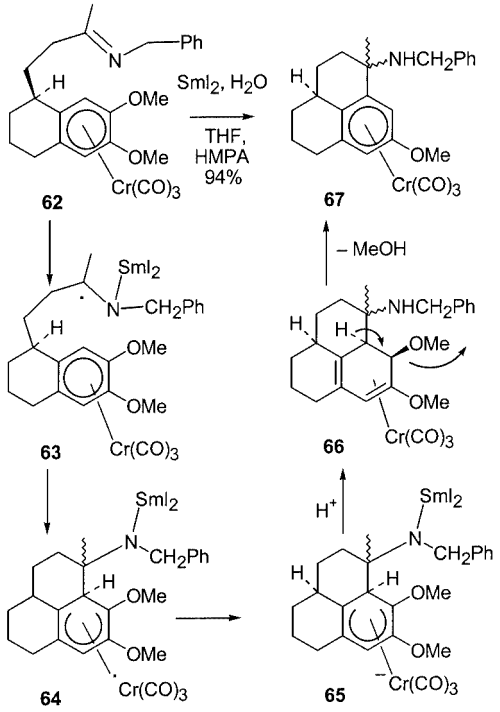
A *cine* S_NAr has been observed by Schmalz et al. in the case of an SmI_2-mediated radical cyclization of ketimines **62** (Scheme 18).[24a] The cyclization product is obtained from addition of azaketyl-type radical **63** to the complexed arene to form intermediate **64**, converted by a single electron transfer to the corresponding anionic complex **65**. Addition of acid affords a hydride, which gives rise to the formation of an η^4 intermediate **66**, which in turn yields complex **67** after a reductive elimination of MeOH. Another *cine* S_NAr with methoxide as a leaving group has been described for the synthesis of hydrophenalene complex **69**, starting from complex **68** (Scheme 19).[24d]

Another impressive example has been found in the case of tricarbonyl(1-chloro-2,6-dimethylbenzene)chromium complex **70** (Scheme 20).[27] In order to avoid addition *ortho* to the chloro atom, we protected the two positions *ortho* and *ortho'* of tricarbonyl(η^6-chlorobenzene)chromium. We thus forced the addition of the nucleophile *para* to the leaving chloride ion. By addition of $LiCMe_2CN$ and CF_3CO_2H, we observed the formation of the 1,3,5-trisubstituted complex **71** in 89% yield. This is a *tele-para* nucleophilic aromatic substitution.[28] Use of CF_3CO_2D results in complex **71** being labeled by a deuterium atom at the carbon atom that bore the leaving group. Thus, we completed the discovery of a trilogy: *cine*, *tele-meta*, and *tele-para* S_NAr.

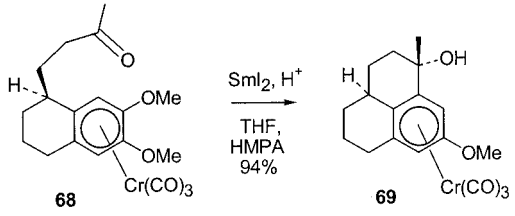
We achieved an analogous reaction with tricarbonyl(η^6-1-fluoro-2,6-dimethylbenzene)chromium complex **72**, by using the reversible addition of $LiCMe_2CN$ in THF at −78 °C and CF_3CO_2H at −78 °C. A mixture of *tele-meta* and *tele-para* substitution products **73** and **74** was isolated in 26



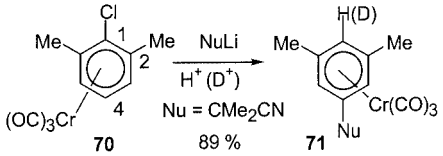
Scheme 17



Scheme 18

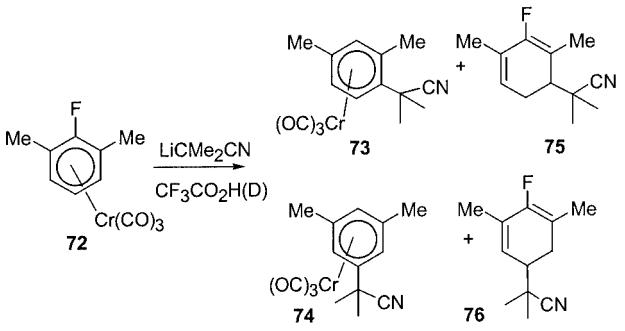


Scheme 19



Scheme 20

and 16% yield, together with a mixture of isomeric cyclohexadienes **75** and **76** in low yield (Scheme 21).[29] In the presence of HMPA, the addition of the nucleophile was irreversible and regioselective, and we recovered mostly the 1,3,5-trisubstituted *tele-meta* complex **74**.

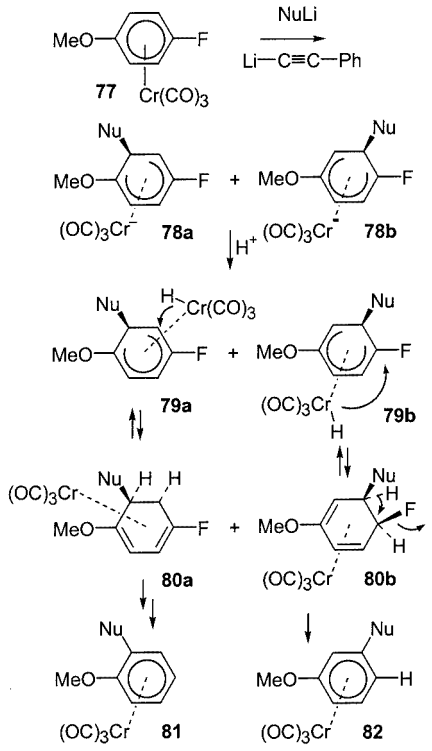


Scheme 21

It is worth noting the difference in the regioselectivities of addition of the nucleophile to the complexes **70** and **72**. In the first case, complex **70**, there is a weak effect from the chloro atom but an important effect from the methyl groups at the C-4 carbon atom. In the second case, that of complex **72**, the directing effect of the fluoro atom (strong *meta* effect) dominates over the effect of the two methyl groups. This study underlines the possibility of controlling the sites of *cine*, *tele-meta*, or *tele-para* substitutions: depending on the nature of the carbanion and on the nature of the leaving group, it is possible to obtain addition of the nucleophile *meta* or *para* to the halogenated atom.

If the *tele-meta* and *cine* substitution mechanisms are applied to the reaction studied by F. E. Hung et al. (Scheme 22), an easy explanation for the formation of the final products may be found. Tricarbonyl(*para*-fluoroanisole)chromium complex **77** was treated with lithium phenylacetylide in THF and HMPA at −78 °C for 1 h and then at −50 °C for 12 h to form two interesting compounds **81** and **82** in a 2:1 ratio and an overall yield of 41% after silica gel column chromatography.[30] We can predict competition between the addition of the nucleophile *meta* to the fluoro atom (strong *meta* effect) and *meta* to the methoxy group (strong mesomeric effect). The following mechanism, invol-

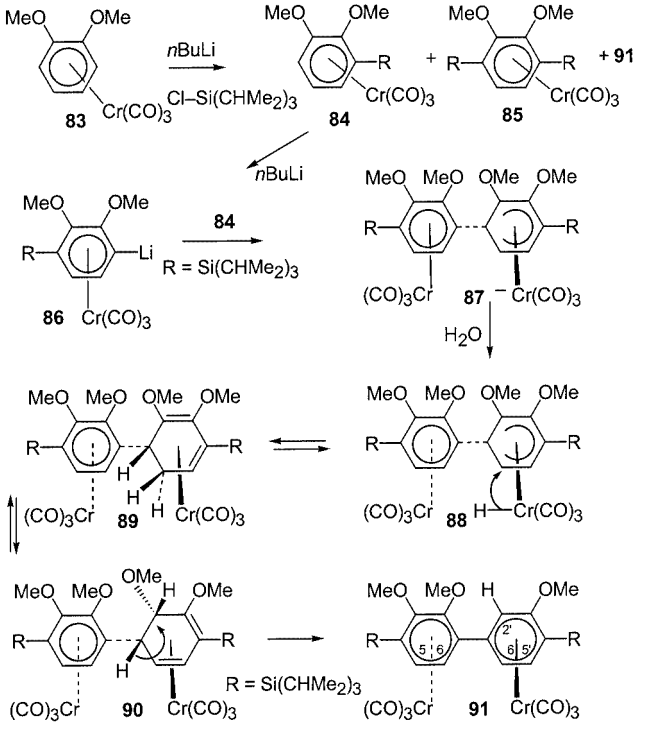
ving an irreversible addition of LiC≡CPh to give anionic intermediates **78a** and **78b**, can be suggested (Scheme 22), with these affording cyclohexadienes **80a** and **80b** on protic workup or on silica gel, via η^5-cyclohexadienyl complexes **79a** and **79b**. After isomerization (for **80a**) and elimination of HF, complexes **81** and **82** are obtained.



Scheme 22

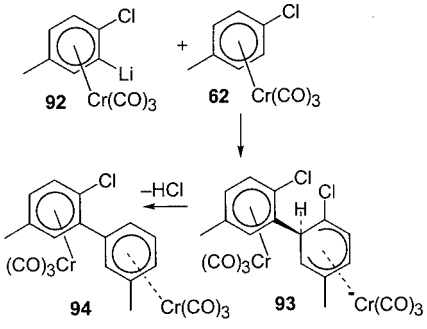
IV. b. Organometallic Carbanions: C−O, C−F, C−Cl Cleavage

When performing the lithiation/silylation of tricarbonyl(-veratrole)chromium (**83**) with *n*BuLi and $ClSi(CHMe_2)_3$, we recovered not only the expected (3-triisopropylsilylveratrole)$Cr(CO)_3$ (**84**) in 17% yield and [3,6-bis(triisopropylsilyl)-veratrole]$Cr(CO)_3$ **85** in 14% yield, but also an unexpected dinuclear complex **91**.[31] Its formation is interpreted as a *cine* S_NAr substitution of one methoxy group of **84** by the lithiated derivative **86**, as depicted in Scheme 23. It is noteworthy that the formation of **91** does not require acid treatment. Thus, the irreversibly formed anionic complex **87** can deliver a chromium hydride **88** on protic workup. Migration of the hydride ion can afford the cyclohexadiene **89**, which is in equilibrium with another cyclohexadiene **90**. Elimination of MeOH finally yields complex **91** in 16% yield. The X-ray structure of this complex shows, as should be expected, the conformations of the two $Cr(CO)_3$ units *anti*-eclipsed with respect to the bulky triisopropylsilyl groups.



Scheme 23

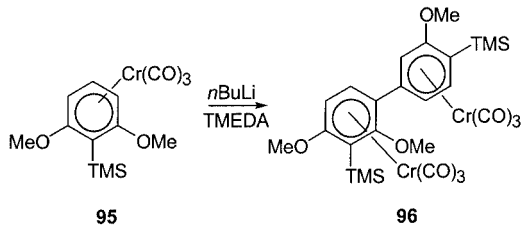
We extended this reaction to (*para*-chlorotoluene)$Cr(CO)_3$ (**62**) (1 equiv.) and treatment with *n*BuLi (0.5 equiv.). Again, without any acid treatment, the dinuclear complex **94** is formed anyway, through a *cine* S_NAr reaction (Scheme 24). The mechanism of this reaction involves lithiation of *para*-chlorotoluene complex **62**, *ortho* to the chloro atom, and then addition of this aryllithium compound **92** *ortho* to the chloro atom of another molecule of **62**. After protonation and rearrangement of the hydride intermediate, elimination of HCl affords the dinuclear complex **94**.[32]



Scheme 24

Another dimetallic compound has been described to be formed by treatment of complex **95** with *n*BuLi and TMEDA at −20 °C followed by addition of TMSCl at 0 °C. The expected silylated complexes are not formed, but the dinuclear complex **96** is obtained instead in high yield

by a *tele-meta* substitution of one of the methoxy groups (Scheme 25).[24b]

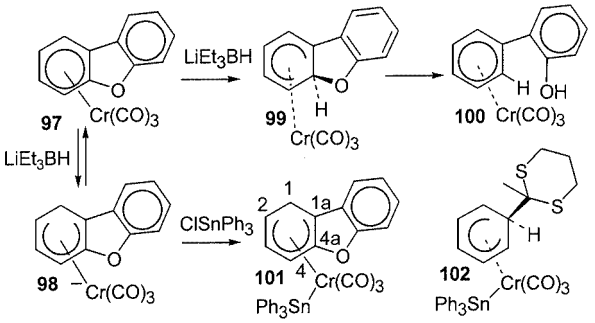


95 96

Scheme 25

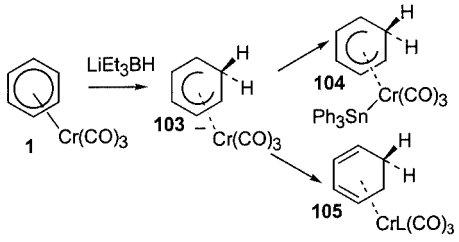
IV. c. Hydrides as Nucleophiles: C−F, C−Cl, C−O, C−N Cleavage

We then investigated the regioselectivity and the reversibility of hydride addition such as that of $LiEt_3BH$ to dibenzofuran complex **97** (Scheme 26).[33,34a] If the reaction is performed at room temperature in a sealed NMR tube in $[D_8]$THF, an unstable anionic complex **98** is obtained. This is pyrophoric under air! If, however, the reaction is performed at 67 °C, complex **100** is isolated in 55% yield as a yellow powder. Many attempts to isolate the anionic intermediate failed, the starting dibenzofuran complex **97** being recovered. However, triphenyltin chloride reacts at the metal center to give the binuclear red complex **101**, the X-ray structure of which definitively corroborates not only the regioselectivity of the addition of the hydride ion but also the η^5-cyclohexadienyl structure, which looks more or less like an unprecedented η^4-cyclohexadiene complex. Indeed, the Cr−C-1a bond was unexpectedly longer (2.41 Å) than the other Cr−C_{ar} bonds: Cr−C-2 2.228 Å, Cr−C-3 2.19 Å, Cr−C-4 2.19 Å, Cr−C-4a 2.25 Å. Another structure **102** has been obtained treating triphenyltin chloride with the anionic adduct of the reaction between (benzene)tricarbonylchromium and 2-lithio-2-methyl-1,3-dithiane.[35] In this case, the bond lengths of the chromium atom to the η^5-cyclohexadienyl framework are not so different, at 2.28, 2.19, 2.18, 2.20, and 2.30 Å.



Scheme 26

We successfully performed an analogous reaction with (benzene)tricarbonylchromium (**1**) and obtained a new binuclear Sn−Cr complex **104** by addition of $LiEt_3BH$ and $ClSnPh_3$. The X-ray structure confirms the η^5 structure (Scheme 27).[34] In solution, the NMR spectra of these η^5 complexes are characteristic, and their data are listed in Table 3. The hydrogen atom 1-H_{exo} in all cases resonates at the highest field as a doublet resulting (for **98**) from a ^1J (11 Hz) geminal coupling with 1-H_{endo}. The latter appears as a doublet of triplets from combined ^1J (11 Hz) and ^3J (6 Hz) coupling of 1-H_{endo} with 1-H_{exo} and 2- ,6-H, respectively. It is noteworthy that treatment of the anionic complex **103** with CF_3CO_2H in $[D_8]$THF in a sealed NMR tube at −78 °C affords a deep red solution, which turns orange-yellow at room temp. The ^{1}H NMR spectrum indicates the formation of an unstable η^4-cyclohexadiene complex **105**, the ^{1}H NMR spectroscopic data of which show peaks at δ = 5.80, 3.80, and 2.10, in good agreement with the spectra of carbonyl(1,3-cyclohexadiene)chromium derivatives.[36]



Scheme 27

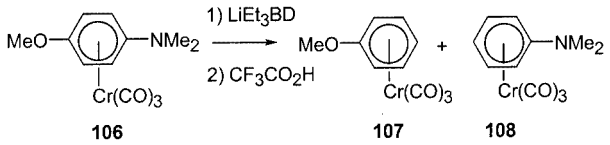
Table 3. Selected ^{1}H and ^{13}C NMR spectroscopic data of (η^5-cyclohexadienyl)$Cr(CO)_3$

Complex	1-H_{exo}	1-H_{endo}	2-H	3-H	4-H
98[a]	2.76	3.59	2.63	4.57	5.63
101[a]	2.80	4.06	3.42	3.88	6.71
103[a]	2.58	2;85	2.53	4.74	5.43
104[a]	1.60	2.43	2.60	3.72	6.06
5a[a] [8b]	–	[b]	[b]	4.35	4.82
5b[c] [8a]	–	3.37	–	5.64	4.99[d]
102[e] [35]	–	3.57	3.80	4.32	6.00
Complex	C-1	C-2	C-3	C-4	
101[e]	28	61	90	67	
103[a]	27	46	98	76	
104[c]	26	60	95	85	

[a] $[D_8]$THF. [b] Under a multiplet at δ = 1.4−3.1. [c] C_6D_6. [d] Signal of 5-H at δ = 4.41, of 6-H at δ = 4.76.[e] $CDCl_3$.

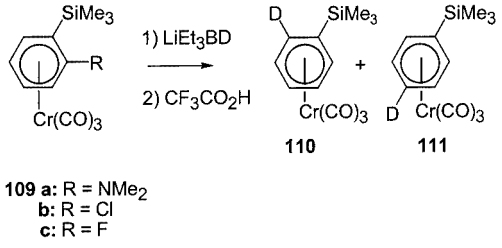
We then investigated the cleavage of a carbon−nitrogen bond. Addition of $LiEt_3BH$ to *para*-methoxydimethylaniline complex **106** at room temp., followed by treatment with CF_3CO_2H, affords two complexes, the anisole and aniline complexes **107** and **108** in 34% and 24% yields, respectively, showing competition between carbon−oxygen cleavage and carbon−nitrogen cleavage (Scheme 28).[34,37] Addition of an excess of $LiEt_3BH$ to **108** is necessary to obtain (after CF_3CO_2H treatment at room temp.) a red solution (which

rapidly becomes yellow) of (benzene)$Cr(CO)_3$ and the starting material.



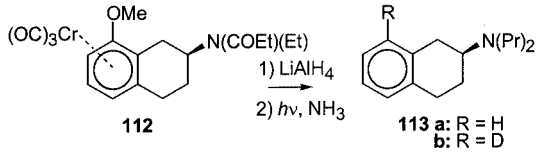
Scheme 28

We carried out a similar experiment with a complex possessing a well-defined $Cr(CO)_3$ conformation. We chose an [η^6-1-(dimethylamino)-2-(trimethylsilyl)benzene]$Cr(CO)_3$ (**109a**), which gave a mixture of 2- and 4-deuterio derivatives of [η^6-2-(trimethylsilyl)benzene]$Cr(CO)_3$ **110** and **111** in 56% yield in the ratio 84:16 (Scheme 29) after treatment with $LiEt_3BD$ and CF_3CO_2H. With *ortho*-chloro and *ortho*-fluoro(trimethylsilyl)benzene complexes **109b** and **109c**, however, we observed the almost quantitative formation of a single compound **111** through a *tele-meta* S_NAr.[34b]



Scheme 29

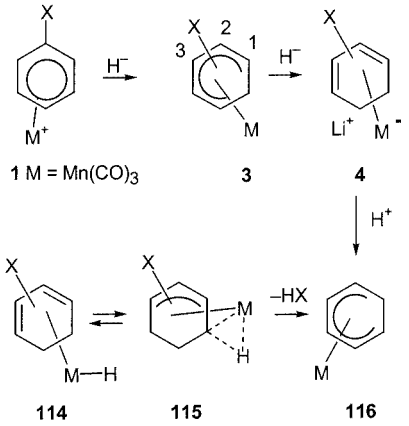
Another example of C−O cleavage by a hydride ion is described by Hacksel et al., who obtained an interesting arene **113a**, with loss of an OMe group, after addition of $LiAlH_4$ to tetrahydronaphthalene complex **112**, and decoordination of $Cr(CO)_3$[38] (Scheme 30). Two kinds of substitution − a *tele-meta* S_NAr or an *ipso* substitution − seem likely at this stage and could explain the formation of the observed product. However, the authors, when performing the reaction with $LiAlD_4$, obtained the compound **113b**, deuterated at the carbon atom that bore the methoxy group, in good agreement with an *ipso* S_NAr. If a *tele-meta* S_NAr had occurred, a deuterio complex labeled at the position *meta* to the carbon atom that bore the methoxy group should have been obtained.



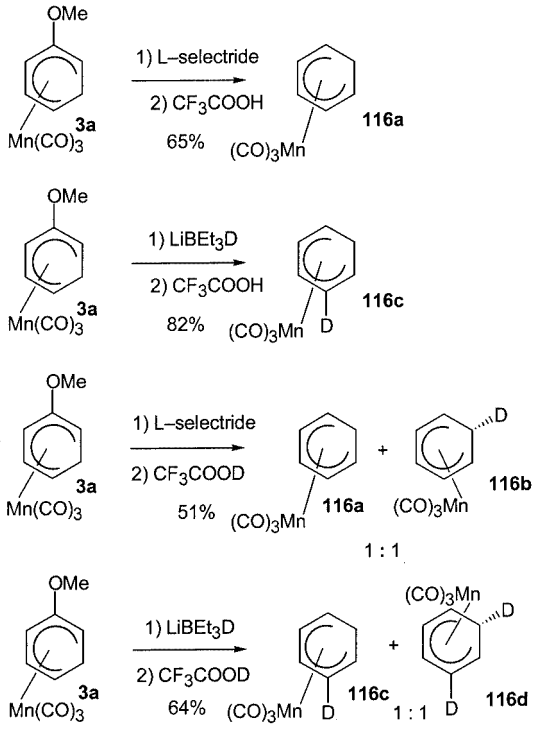
Scheme 30

V. *cine* and *tele* Nucleophilic Substitutions: (η^5-Cyclohexadienyl)$Mn(CO)_3$ Complexes

It is now well established that tricarbonyl[phenoxy-, methoxy-, chloro-, fluoro-, (dimethylamino)-substituted η^6-arene]chromium complexes undergo cleavage of aromatic C−O, C−Cl, C−F, C−NMe_2 bonds upon treatment first with a nucleophile or a hydride ion and then with acids. The first step of these reactions is the formation of anionic η^5 intermediates, which can undergo different isomerizations once protonated. We were interested in transposing this study to manganese complexes, encouraged by the convincing demonstration by Brookhart et al. of the facile isomerization of cyclohexenyl isomers **115** involving manganese−hydrogen−carbon agostic bonds (Scheme 31).[39] Indeed, these authors reported that treatment of the neutral complexes **3**, obtained by hydride addition to cationic tricarbonyl(X-substituted η^6-arene)manganese complexes **1**, resulted in the formation of anionic complexes **4** and, on addition of water, a stable complex **115**



Scheme 31



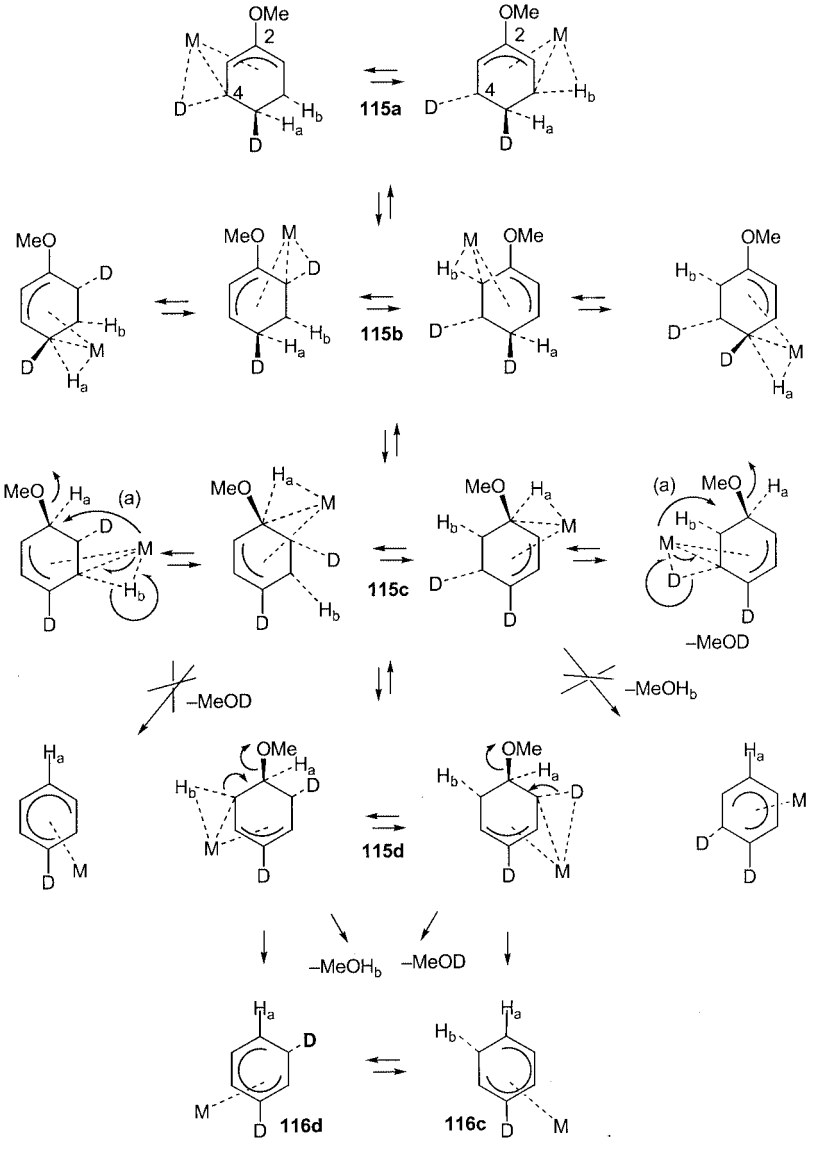
Scheme 32

with a three-center Mn−H−C agostic bond (X = OMe, for example) (Scheme 31). We therefore repeated this reaction, starting from various (η^5-cyclohexadienyl)manganese complexes substituted with a leaving group X, in order to eliminate HX after H^-, H^+ treatment. We obtained a new complex **116**, again with an η^5 structure.

V. a. C−O Cleavage

Addition of L-selectride to the η^5 complex **3a**, followed by protonation with MeOH or CF_3CO_2H, gives the known η^5-cyclohexadienyl complex **116a** in 65% yield if the reaction mixture is heated in THF for 3 h. With $LiEt_3BD$ and CF_3CO_2H, complex **116c** is recovered in 82% yield (Scheme 32). If $LiEt_3BH$ and CF_3CO_2D are used, a mixture of complexes **116a** and **116b**, deuterated at the *endo* position, is recovered in a ratio of 1:1 and in 51% yield. When complex **3a** is treated with $LiEt_3BD$ and MeOH, a single deuterated complex **116c** is obtained in 82% yield. Similarly, treatment of complex **3a** with $LiEt_3BD$ and CF_3CO_2D results in a mixture of complexes **116c** and **116d** being recovered in a 1:1 ratio and in 64% yield. These data are consistent with a four-step mechanism involving hydride addition, protonation, isomerization, and elimination. We will focus only on the last step. The formation of the various labeled products obtained has been explained in terms of the easy isomerization of different η^3-cyclohexenyl intermediates such as **115** in an acidic medium. We thus considered all the possible hydrogen migrations giving the mono- and the dideuterated complexes **116c** and **116d** in order to understand the elimination of MeOH(D) (Scheme 33).

The exact mechanism of this reaction is not yet known precisely, because the π-allyl complexes **115a**, **115b**, **115c**, and **115d**, which are in equilibrium, can be represented by two different agostic bonds in the cases of the symmetrical derivatives **115a** and **115d** and by four different agostic bonds in the cases of the unsymmetrical derivatives **115b** and **115c**. Thus, in the last elimination step, complex **115d**



Scheme 33

could eliminate either $MeOH_b$ or MeOD, giving complexes **116c** and **116d**. In fact, we arrived at the conclusion that 1,5-elimination could occur between the OMe group and an agostic hydrogen atom, and we never observed a 1,2-elimination of OMe and a non-agostic hydrogen atom. Thus, the hydrido-demethoxylation of complex **3a** occurred by hydride ion addition at the C-5 carbon atom and elimination of the methoxy group at the C-2 carbon atom (Figure 3). By analogy with the chromium complexes, this is a *tele-para* nucleophilic substitution.[40]

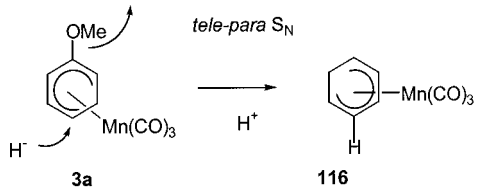
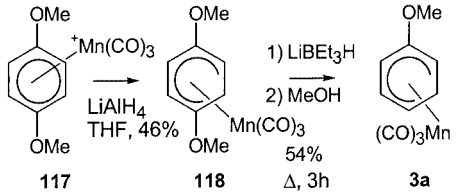


Figure 3. *tele-para* S_N

In the case of the tricarbonyl(*para*-dimethoxybenzene)manganese complex **117**, addition of $LiAlH_4$ in THF at −78 °C affords complex **118** in 46% yield (Scheme 34).



Scheme 34

The addition of L-selectride (4 equiv.) to complex **118**, followed by protonation with MeOH (6 equiv.) and heating of the solution for 3 h, resulted in the formation of a single isomer tricarbonyl(η^5-2-methoxycyclohexadienyl)manganese complex **3a** in 54% yield. The formation of this can be interpreted in terms of a *cine* or a *tele-meta* nucleophilic substitution (Figure 4). We extended these reactions to other examples showing the possibility of C−N, C−Cl and C−S bond cleavage.

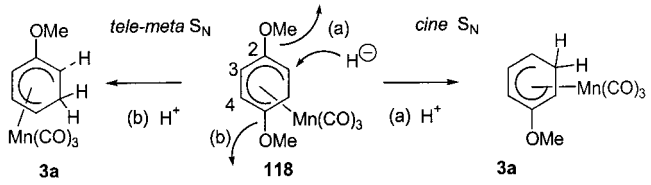
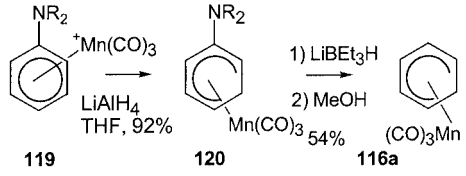


Figure 4. *cine* or *tele-meta* S_N

V.b. C−N Cleavage

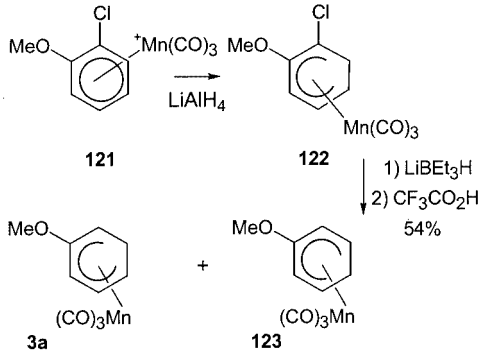
Addition of $LiAlH_4$ to [(diethylamino)benzene]-$Mn^+(CO)_3$ (**119**) exclusively yields the expected *meta*-addition product **120** in 92% yield. Addition of L-selectride followed by protonation with CF_3CO_2H at −78 °C gives, after warming to room temp., the η^5-cyclohexadienyl complex **116a** in 54% yield (Scheme 35).[40]



Scheme 35

V. c. C−X Cleavage (X = F,Cl)

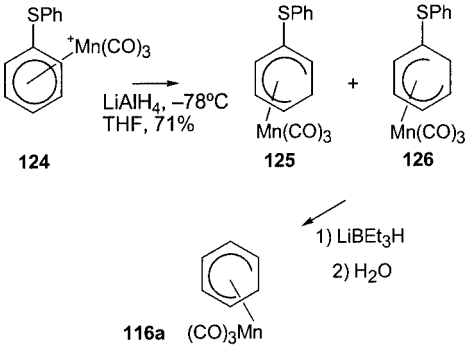
Complex **122** (obtained in 57% yield from addition of $LiAlH_4$ to (*ortho*-chloroanisole)$Mn^+(CO)_3$ complex **121** behaves similarly, reacting with L-selectride and then CF_3CO_2H to afford the 2- and 3-methoxycyclohexadienyl complexes **3a** and **123** in a 45:55 ratio (Scheme 36). Cleavage of the C−Cl bond occurs very quickly even at low temperature, contrary to the C−O bond cleavage, which requires higher temperature.



Scheme 36

V. d. C−S Cleavage

Addition of $LiAlH_4$ to (η^6-phenylthiobenzene)-$Mn^+(CO)_3$ complex **124** gives two neutral complexes **125** and **126** in 71% yield and in a 30:70 ratio. Complex **126**, if treated with L-selectride and water and heated in refluxing THF for 20 h, affords complex **116a** in 38% yield (Scheme 37). We have never succeeded in cleaving the C−S bond in the case of the corresponding (arene)$Cr(CO)_3$ complexes (Scheme 37).[40]



Scheme 37

VI. Concluding Remarks

The reactivity of (arene)tricarbonylchromium and -manganese complexes involved in *cine* and *tele* nucleophilic substitutions has been described. The use of chromium complexes provides rapid routes to compounds that are difficult to obtain in organic chemistry. Thus, addition at low temperature of a stabilized carbanion to an (arene)tricarbonylchromium complex substituted with a leaving group X, followed by addition of CF_3CO_2H, yields new arene complexes and HX through the cleavage of carbon−oxygen, carbon−halogen, and carbon−nitrogen bonds. The addition of the nucleophile occurs *ortho*, *meta*, or *para* to the leaving group, depending mainly on the nature and on the relative positions of the substituents on the arene ring. There is no doubt that development in this area will be extended in our laboratory and also elsewhere, not only in the cases of chromium or manganese complexes such as we have already discovered, but also in the case of other metals. These *cine* and *tele* S_N processes appear to be efficient organometallic reactions and represent a new tool for organic chemists. By taking advantage of the presence of the tripod $Cr(CO)_3$, which remains coordinated to the arene ring of the final product, a further functionalisation is possible and so broadens the scope of potential applications.[41]

Isomerization of η^4-cyclohexadiene intermediates occurs through 1,5-hydrogen shifts. The driving force of these reactions is the elimination of HX, with aromatization of the η^4 complexes into the η^6-arenes in the case of (η^6-ligand)Cr complexes.

In the case of Mn complexes, we extended these reactions and found that carbon−oxygen, carbon−halogen, carbon−nitrogen, and even carbon−sulfur bonds can be cleaved by *cine* and *tele* S_N processes if the starting neutral (substituted η^5-cyclohexadienyl)$Mn(CO)_3$ is treated with a hydride ion and a proton source, yielding (η^5-cyclohexadienyl)$Mn(CO)_3$ complex and HX. The driving force of these reactions is again the elimination of HX, transforming an η^3 complex into an η^5-cyclohexadienyl complex.

VII. Abbreviations

CAN: ceric ammonium nitrate; DDQ: 2,3-dichloro-5,6-dicyanobenzoquinone; HMPA: hexamethylphosphoramide; L: $2e^-$ ligand; LDA: lithium diisopropylamide; S_N: nucleophilic substitution; S_NAr: nucleophilic aromatic substitution; THF: tetrahydrofuran; TMEDA: tetramethylethylenediamine; TMSCl: trimethylsilyl chloride.

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