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# ($\eta^6$-Arene)tricarbonylchromium and ($\eta^5$-cyclohexadienyl) tricarbonylmanganese complexes: indirect nucleophilic substitutions

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**Contents**



**Abstract**

Treatment of X-substituted ($\eta^6$-arene)tricarbonylchromium complexes with a nucleophile and a proton source afforded new arenetricarbonylchromium complexes via chromium hydride intermediates and elimination of HX (*cine* and *tele* nucleophilic aromatic substitutions). Treatment of ($\eta^5$-X-substituted-cyclohexadienyl)tricarbonyl manganese complexes with hydride and a proton source gave $\eta^5$-cyclohexadienyl complexes resulting from a cleavage of the C–X bond: the $\eta^3$-X-substituted cyclohexenyl intermediates underwent elimination of an agostic hydrogen and the X group. 

*Keywords:* Arene; Arene complexes; Aromatic substitution; Benzenetricarbonylchromium; Benzenetricarbonylmanganese; Nucleophilic substitution

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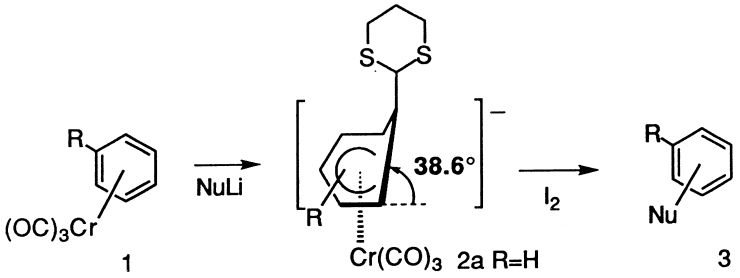



Scheme 1. Addition of a carbanion to an arenetricarbonylchromium complex

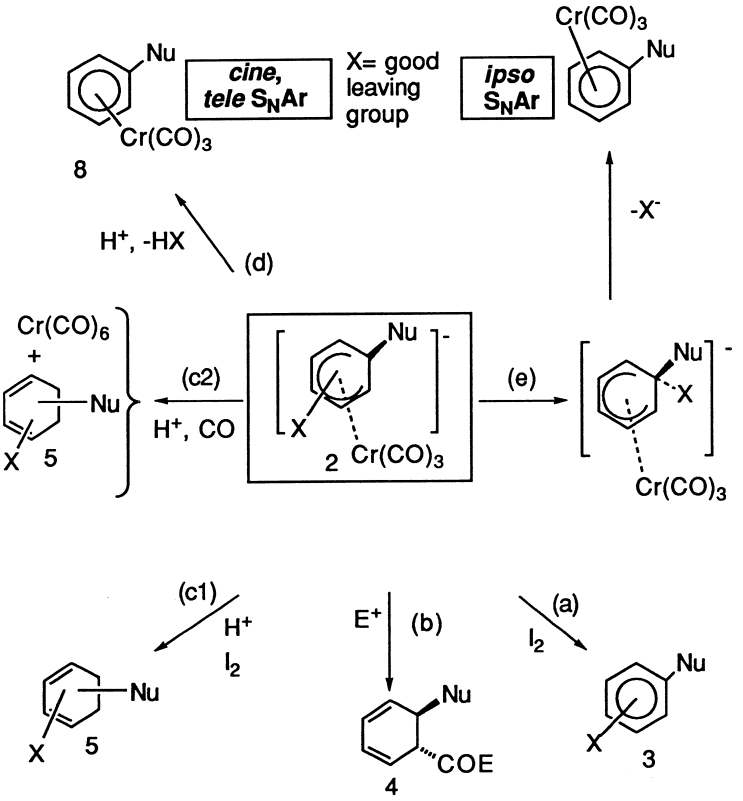
## 1. Introduction

Tricarbonylchromium and manganese π-arene complexes have found significant applications particularly in organic synthesis [1– 36]. They are easily prepared (for Cr-complex preparations see [37–39], for Mn-complex preparations see [40–42]) and the arene group is readily released from complexation in the case of chromium complexes. The arene ligand is a six-electron system occupying three coordination sites and the electron withdrawing power of the $Cr(CO)_3$ entity is similar to that of the nitro group of nitrobenzene. A decreased electon density of the arene ring is confirmed by the ease of addition of a carbanion [1– 36]. This electron density decrease is more significant in the case of cationic tricarbonylmanganese π-complexes. Indeed a large variety of carbanions [43– 68] can be added to these manganese complexes, for example ketone enolates and Grignard reagents (see for example [69,70]).

## 2. Arenetricarbonylchromium complexes

Preparation of arenetricbonylchromium complexes is easily achieved in good yield usually by heating the free arene with $Cr(CO)_6$ in a high boiling solvent [37–42]. Addition of a carbanion, first reported by Card and Trahanovsky in the case of a nonhalogenated arene ($^t$BuLi and ethylbenzenetricarbonylchromium) followed by $Ce^{IV}$ oxidation yielded 2 isomeric $^t$butylethylbenzene [71]. This reaction has been extended in the case of a large variety of nucleophiles. The first step which is the exo addition of the nucleophile to the face opposite to the tricarbonylchromium entity has been definitively proved by the X-ray structure of the anionic intermediate complex. Indeed, adduct of 2-lithio-1,3-dithiane and benzenetricarbonylchromium **1** afforded an anionic complex with an $\eta^5$-cyclohexadienyl structure **2a** (Scheme 1). The deformation of the $sp^2$ carbon from the planarity is 38.6° [72]. We will show the key role of this anionic ($\eta^5$-cyclohexadienyl)tricarbonylchromium complex **2**, the fate of which depends on the experimental conditions used. Some of these reactions are summarised in Scheme 2.

Oxidation of **2** releases the substituted arene **3** and the chromium is oxidized [72], whereas reaction of **2** with particular electrophiles yields *trans* disubstituted cyclohex-




Scheme 2. Reactivity of the anionic complex 2

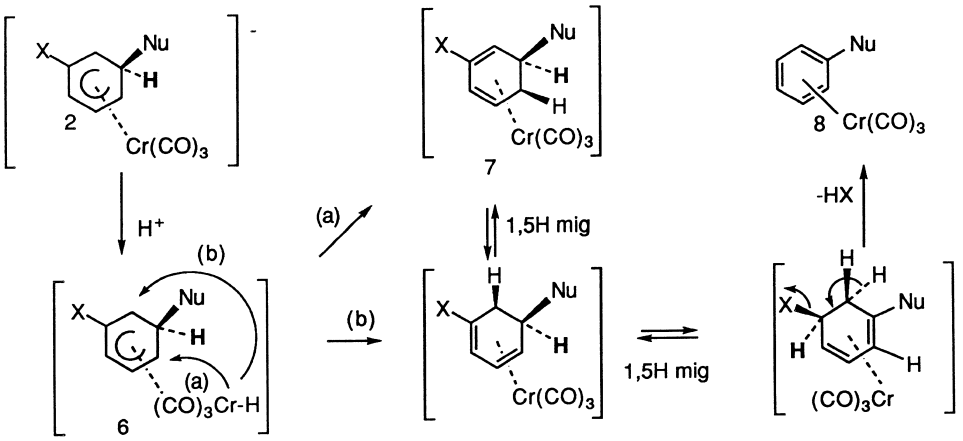
adienes **4** with or without CO insertion (path b, Scheme 2). These reactions have been recently extended into an asymmetric version [73– 84].

Treatment of **2** with acid gives a mixture of isomeric substituted cyclohexadienes **5** after iodine oxidation (path c1, Scheme 2) [72]. Treatment of **2** with acid under CO atmosphere yields also isomeric substituted cyclohexadienes **5** (path c2, Scheme 2) but $Cr(CO)_6$ is recovered and can be used to prepare starting arenetricarbonylchromium complexes [85]. In this case, we have never succeeded in isolating ($\eta^4$-cyclohexadiene)chromium complexes. The formation of compound **5** involves a chromium-hydride after acidic treatment of complex **2** (the presence of an agostic bond is not excluded [79]).

In this review, we focus on the reactivity of anionic complexes such as **2** in acidic medium when they are substituted by good leaving groups (path d, Scheme 2).

### 2.1. *Tele–meta* nucleophilic aromatic substitution

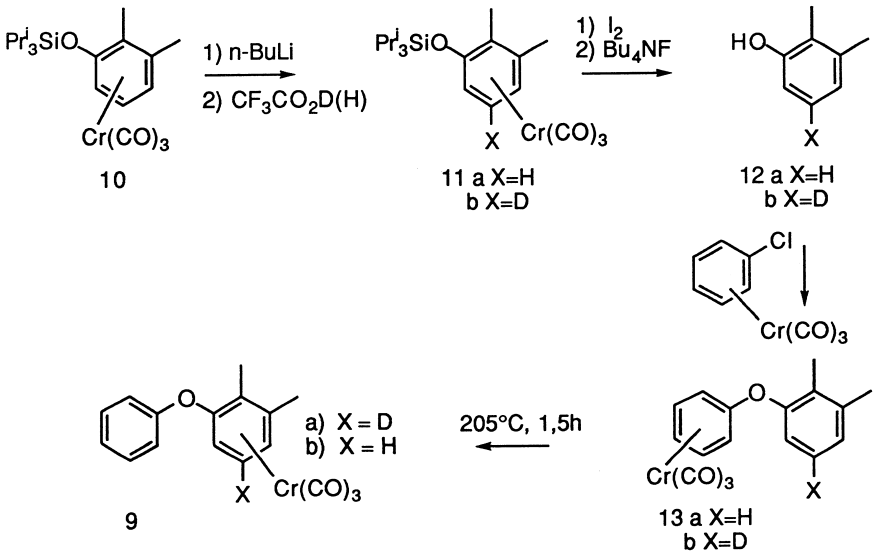
When we started this study, we thought that if complex **2** was substituted by a good leaving group X, we could expect, after a proper treatment, an elimination of HX in order to recover a new arenetricarbonylchromium complex (Scheme 3) [86].




Scheme 3. *Tele–meta* nucleophilic aromatic substitution

Indeed treatment of complex **2** with a strong acid yields complex **8** whose formation can be explained as follows: protonation of the anionic compound **2** affords the chromium–hydride complex **6** (Scheme 3). Hydride migration to the $\eta^5$-cyclohexadienyl ring gives rise to an $\eta^4$-cyclohexadiene complex **7**. Then isomerization of this cyclohexadiene, thanks to 1,5 H-migrations, allows elimination of HX which rearomatizes the ring: this is the driving force of the reaction.

In order to prove this migration, we prepared a labelled diphenylethertricarbonylchromium complex **9a** (Scheme 4) substituted by two methyl groups at the C-2 and C-3 positions in order to avoid addition of the nucleophile to these carbons

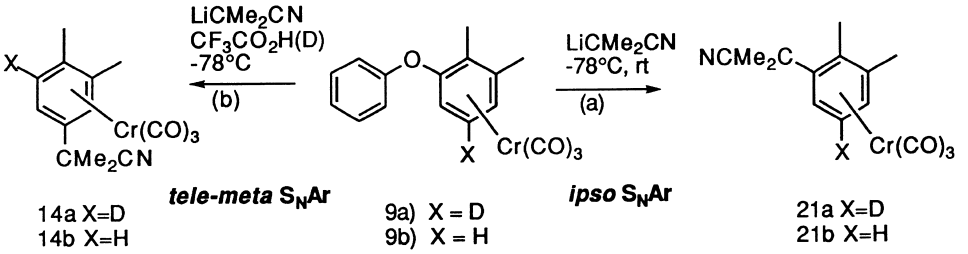



Scheme 4. Preparation of labelled diphenylethertricarbonylchromium complex **9b**

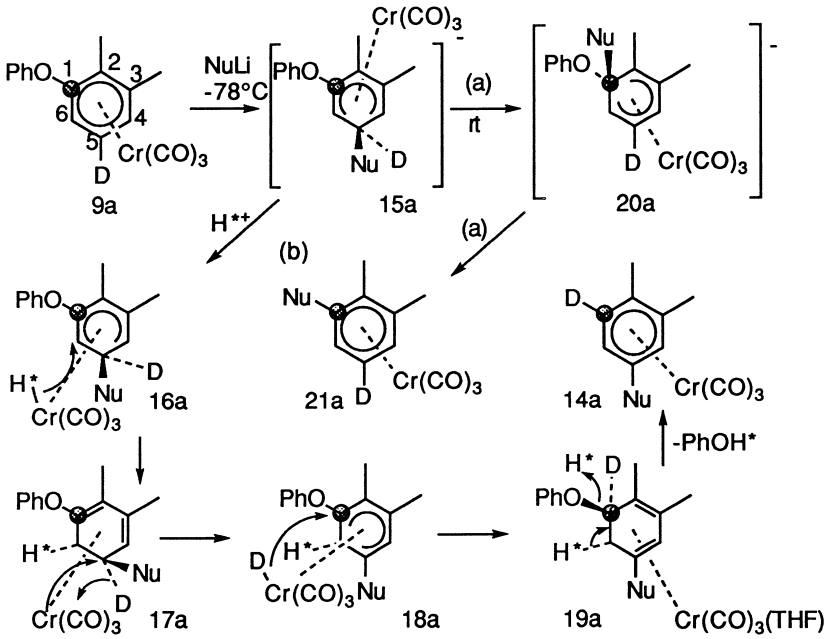
[87]. Treatment of 1-triisopropylsilyloxy-2,3-dimethyl-benzene complex **10**, with *n*-BuLi and $CF_3CO_2D$ gives the 5-deutero complex **11b** (*meta*-lithiation with respect to the silyloxy group). 2,3-Dimethyl-5-deuteriophenol **12b**, obtained by iodine oxidation of complex **11a** followed by $Bu_4NF$ treatment, reacts with chlorobenzenetricarbonylchromium to yield the diphenylether complex **13b**.

Migration of the $Cr(CO)_3$ entity from one cycle to the other one is accomplished by heating crystals of complex **12b** at high temperature. The same experiments with X = H give complex **9b** (Scheme 4). Complexes **9a** and **9b** treated with $Me_2CLiCN$ and $CF_3CO_2H(D)$ generate complexes **14a** and **14b** (Scheme 5).

These results can be easily explained. The first step is the addition of the nucleophile $Nu^-$ to the C5 carbon (Scheme 6). The anionic complex **15a**, trapped with




Scheme 5. *Tele–meta* nucleophilic aromatic substitution




Scheme 6. Tele–meta SnAr: 1.5 deuteride migration

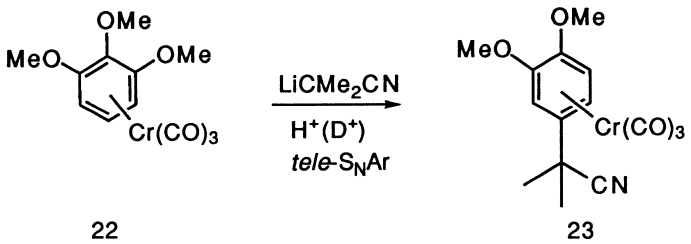
the acid gives a chromium hydride **16a** which migrates on the C-6 carbon. The Cr atom of the resulting $\eta^4$-cyclohexadienyl complex **17a** inserts into the C–D bond yielding a new ($\eta^5$-cyclohexadienyl)chromium hydride **18a**. After migration of the deuterium on the C-1 carbon, the resulting ($\eta^4$-cyclohexadienyl)chromium complex, which is probably an 18 electron complex **19a**, can eliminate a phenol molecule to give rise to the formation of **14a**. This is a *tele* nucleophilic aromatic substitution (*tele* $S_NAr$) according to IuPAC nomenclature. 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 [88]. To be more precise, we called it *tele–meta* $S_NAr$ [87].

It is worthy to note the role of the temperature, indeed treatment of complex **9a** with 2-lithioisobutyronitrile at $-78$ °C followed by warming at 25 °C gives complex **21a** via an *ipso* nucleophilic aromatic substitution (Scheme 5 path a, Scheme 6 path a, see also Scheme 2 path e).

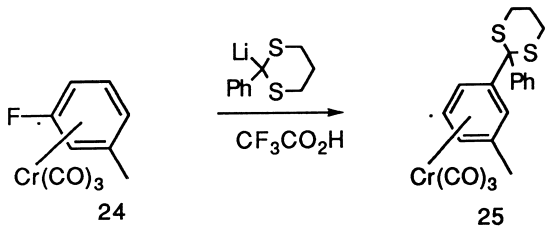
We reported then other examples of *tele* $S_NAr$. Treatment of ($\eta^6$-1 2,3-trimethoxybenzene) **22** with isobutyronitrile carbanion and then with acid affords quantitatively 4-substituted ($\eta^6$-veratrole)tricarbonylchromium complex **23** according to a *tele–meta* nucleophilic aromatic substitution [89,90] (for other examples of departure of methoxy groups also see [91–93]) (Scheme 7).

In the case of *meta*-fluorotoluenetricarbonylchromium complex **24**, addition of 2-lithio-2-phenyl-1,3-dithiane yields, after acid treatment, the *meta*-disubstituted complex **25** via a *tele–meta* $S_NAr$ [94] (Scheme 8).

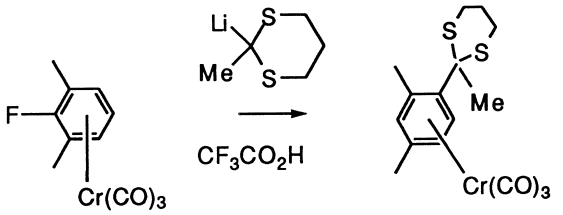
2,6-Dimethylfluorobenzenetricarbonylchromium complex **26** reacts with 2-lithio-2-methyl-1,3-dithiane and $CF_3CO_2H$ and affords the trisubstituted complex **27** via




Scheme 7. Preparation of a4-substituted veratrole complex




Scheme 8. *Tele–meta* SnAr




26 27

Scheme 9. *Tele–para* SnAr

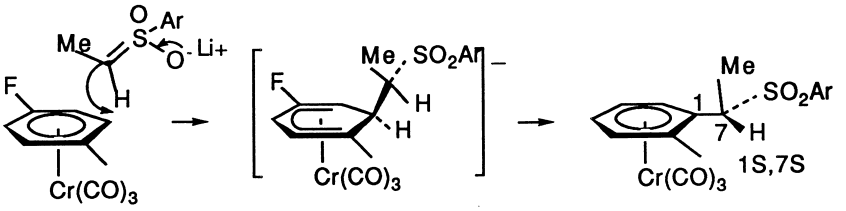
a *tele–meta* $S_NAr$ (Scheme 9) [94]. No formation of 1,3,5 trisubstituted complex is detected.

In the case of *para*-fluoro-toluenetricarbonylchromium complex **28**, addition of α-sulfonyl carbanion followed by acid treatment yields only one diastereoisomer **30** via the anionic complex **29**. This reaction sheds light on some aspects of dynamic stereochemistry. We proposed an approach of the carbanion which minimizes the interactions between the carbanion and the starting complex (Scheme 10). This could explain the formation of the SS/RR complex **30** [95,96] (for nomenclature used see [97,98]).

We next considered the question of the reactivity of a very simple nucleophile: an hydride. So, *ortho*-halogeno-trialkylsilylbenzenetricarbonylchromium complex **31a** or **31b** reacts with deuteride ($Et_3BDLi$) affording, after $CF_3CO_2H$ treatment, deutero-trimethylsilyl-benzenetricarbonylchromium complexes **32a** and **33a** (90/10) via a *tele-meta* nucleophilic aromatic substitution, or deutero-triisopropylsilyl-benzenetricarbonylchromium complex **32b** (Scheme 11) [99].

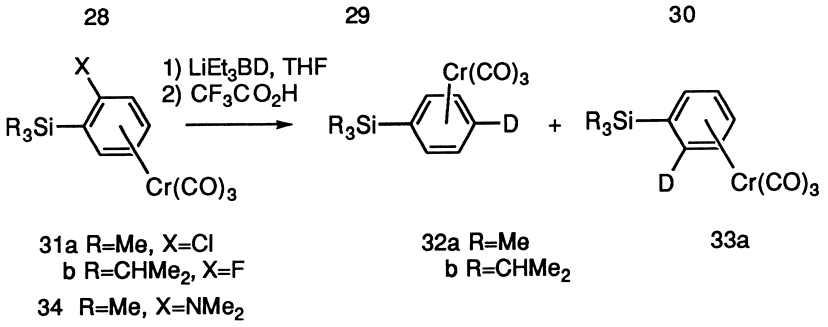
Cleavage of carbon–chloride, carbon–fluoride or carbon–oxygen bonds is well precedented in organic chemistry [100], but cleavage of a carbon–nitrogen bond is much more difficult. Thus we tried reaction of hydrides with aniline complexes. Addition of deuteride ($LiEt_3BD$) to a THF solution of *ortho*-trimethylsilyl-*N*,*N*-dimethylanilinetricarbonylchromium complex **34** yields deuterio-trimethylsilyl benzenetricarbonylchromium complexes **32a** and **33a** (20/80) after $CF_3CO_2H$ treatment, both resulting from *tele–meta* $S_NAr$ (Scheme 11) [101].

In order to shed light on the mechanism of hydride addition to an arenetricarbo-




28 29 30

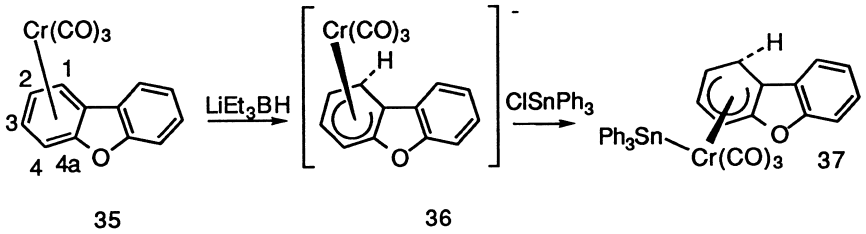
Scheme 10. *Tele–meta* SnAr



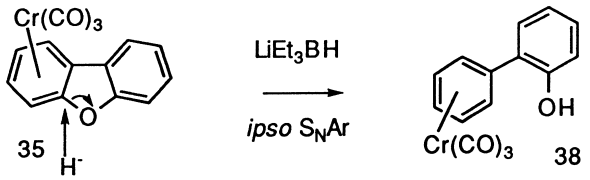

Scheme 11. *Tele–meta* SnAr

nylchromium complex, we undertook different studies with disubstituted complexes. Treatment of dibenzofurantricarbonyl chromium complex **35** with $LiEt_3BH$ yields the anionic compound **36** which can be obtained as a yellow powder [102,103]. Addition of triphenyltinchloride to this anionic intermediate **36** gives the dinuclear complex **37** whose X-ray structure confirms the regioselective addition of hydride to the C-1 carbon at low temperature (Scheme 12). It is worth noting that addition of $LiEt_3BH$ at 67 °C to complex **35** gives, after hydrolysis, the biphenyl derivative **38** (Scheme 13, *ipso* $S_NAr$). This clearly shows that the *meta*-addition occurs under reversible conditions, complex **36** undergoing an isomerization that ultimately leads to C–O bond *ipso* cleavage and liberation of complex **38**.

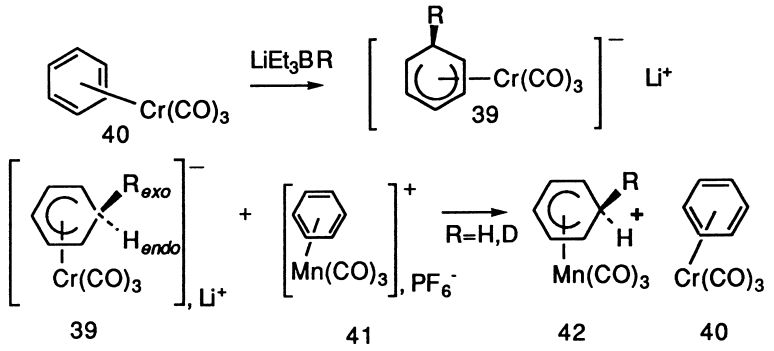
We used an other method to establish the reversible addition of hydride to an arenetricarbonylchromium complex: complex **39**, obtained quantitatively by adding $LiEt_3BH$ to benzenetricarbonylchromium complex **40** reacted with cationic benzenetricarbonylnanganese complex **41** [104] to give a mixture of complexes **40** and




Scheme 12. Trapping of the anionic complex by $ClSnPh_3$




Scheme 13. Addition of hydride to dibenzofurane complex




Scheme 14. Reversible addition of hydride to **40**

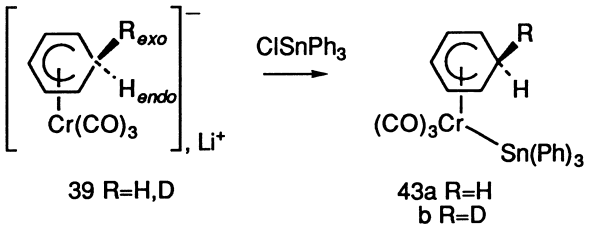
neutral $\eta^5$-cyclohexadienylmanganesetricarbonyl **42**. This is the result of an hydride transfer from **39** toward the electrophilic complex **41** (Scheme 14) [102,103].

Anionic complexes **39** whose $^1$H NMR spectrum can be achieved in THF-*d*8 in a sealed tube, (R = H, D) can also be trapped by triphenyltin chloride giving the Sn–Cr complex **43a** (R = H) (Scheme 15) or **43b** [102,103].

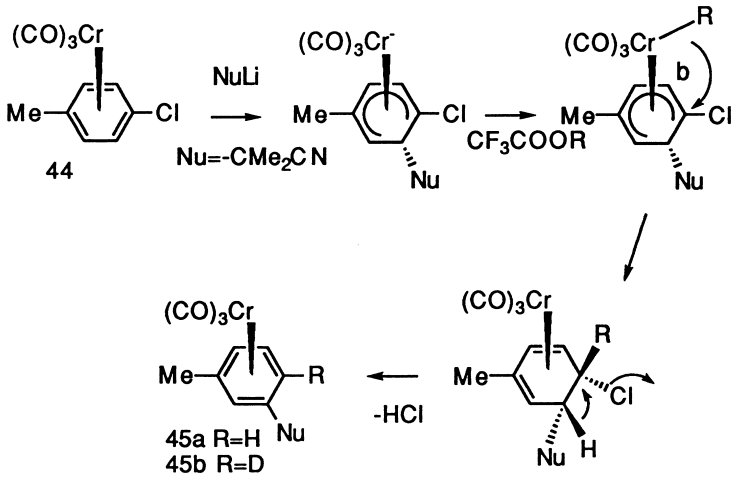
## 2.2. *Cine* nucleophilic aromatic substitution

We next considered the question of another $S_NAr$ in which the entering group Nu might take up a position ortho to the leaving group (a chloride atom or a methoxy group for example) [105,93] (a few examples of *cine* substitutions have been recently described [106]). We studied the addition of 2-lithioisobutyronitrile to **44** followed by $CF_3CO_2H$ treatment. Complex **45a** is obtained as the major product (Scheme 16). This reaction clearly shows that the carbanion addition occurs *ortho* to the leaving group and *meta* to the methyl group. When $CF_3CO_2D$ is used, the deuterio complex **45b** is obtained in a good agreement with a mechanism, involving hydride migration, then HCl elimination as depicted in Scheme 16.

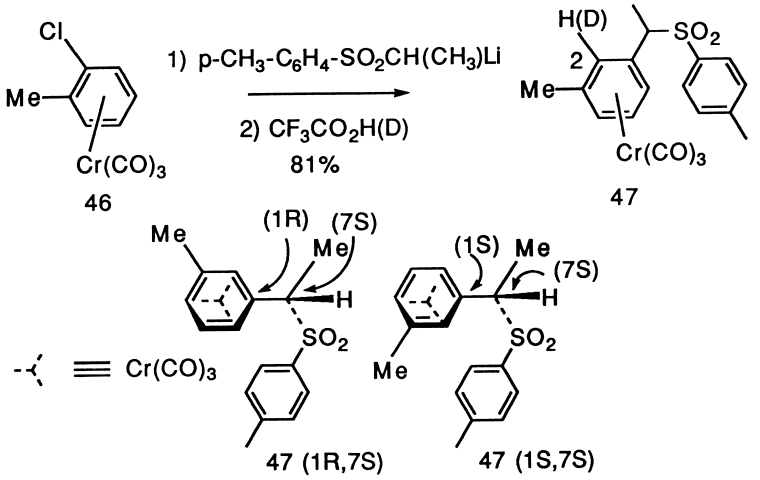
In the case of complex **46**, addition of the anion of ethyl-*para*-tolylsulfone affords, after acid treatment, one regioisomer constituted by only one diastereoisomer **47** (Scheme 17). If $CH_3CO_2D$ is used, complex **47** is deuterated at the C-2 carbon in a good agreement with a *cine* $S_NAr$. But we were not able to obtain an X-ray structure




Scheme 15. Formation of a dinuclear Cr–Sn($\eta^5$-cyclohexadienyl) complex




Scheme 16. *Cine* SnAr

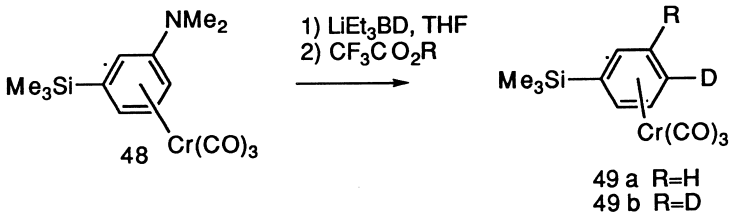



Scheme 17. *Cine* SnAr

in order to know which one of the two diastereoisomers: 1*R*, 7*S*, (1*S*, 7*R*) or 1*S*, 7*S* (1*R*, 7*R*) was obtained (Scheme 17) [95–98]. In the case of *meta*-trimethylsilyl, *N*,*N*-dimethylanilinetricarbonylchromium complex **48**, complex **49a** (or **49b**) is obtained under the same experimental conditions (Scheme 18) [101].

### 2.3. *Tele–para* nucleophilic aromatic substitution

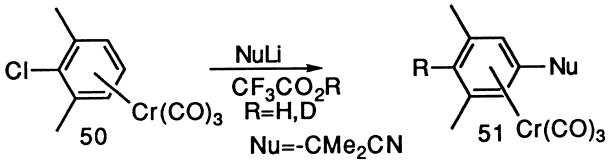
A third new substitution, namely a *tele–para* $S_NAr$, was discovered in the case of 2,6-dimethyl,chlorobenzenetricarbonylchromium complex **50**. Reaction of 2-lithio,



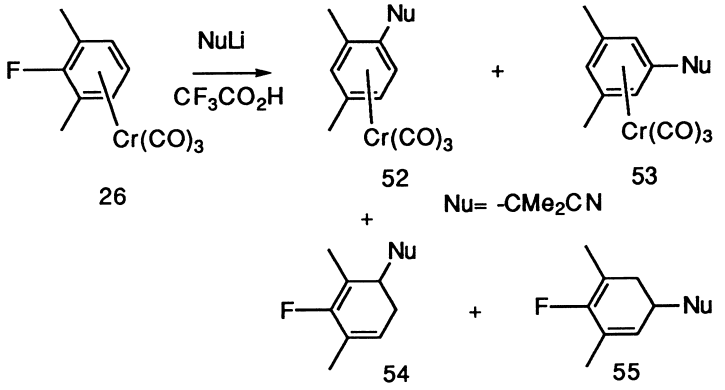

Scheme 18. *Cine* SnAr

2-methylpropionitrile with complex **50** affords after quenching with $CF_3CO_2H(D)$ a single arenetricarbonylchromium complex **51** via a *tele–para* nucleophilic aromatic substitution (Scheme 19) [107].

Reaction of 2-lithio-2-methylpropionitrile with 2,6-dmethylfluorobenzene **26** gives rise to the formation of complexes **52**, **53** and cyclohexadienes **54**, **55**. The same reaction is more regioselective in the presence of HMPA, indeed it yields cyclohexadienes **54** and **55** (1/3) and only complex **53** (Scheme 20) meaning probably that **53** and **55** are formed under kinetic control [108–111]. Thus, thanks to these last examples, we concluded that the entering groups could take up a position two atoms away from the atom to which the leaving group was attached.




Scheme 19. *Para–tele* SnAr




Scheme 20. *Tele–meta* and *tele–para* SnAr

## 3. Cationic arenetricarbonylmanganese complexes

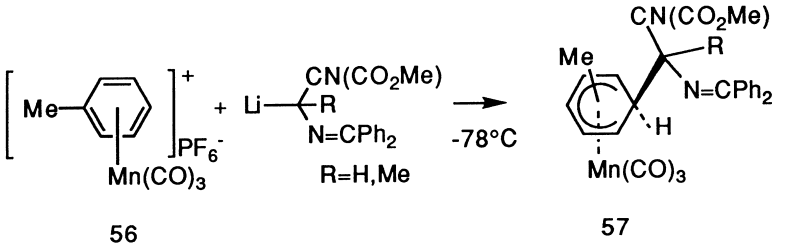
The activation of arenes by coordination to transition metals provides a synthetic route to functionalized arenes in the case of Cr. The manganese mediated functionalization of arenes is also attractive because of the high electrophilicity of the corresponding compounds. A wide variety of nucleophiles can be added to the arene ring [43– 68]. We decided to study not only the reactivity of cationic ($\eta^6$-arene)tricarbonylmanganese complexes, but also of neutral substituted ($\eta^5$-cyclohexadienyl) tricarbonyl manganese complexes.

### *3.1. Reactivity of cationic arenetricarbonylmanganese complexes.*

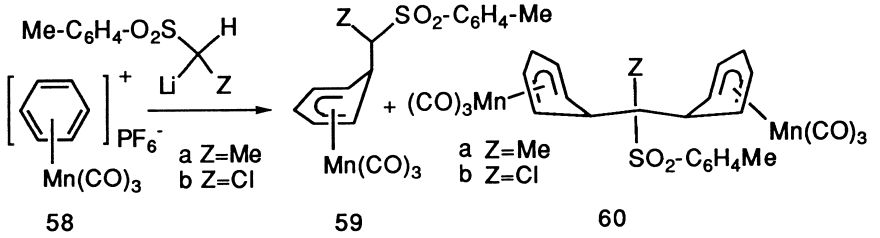
Nucleophilic aromatic addition of stabilized carbanions give almost quantitatively corresponding stable $\eta^5$-neutral cyclohexadienyl manganese complexes. α-Iminoesters or iminonitriles carbanions react with toluenetricarbonylmanganese **56** and give the $\eta^5$-cyclohexadienyl complexes **57** (Scheme 21). Two regioisomers are obtained (*meta*:*ortho* = 70:30) [112,113].

α-Sulfonyl or α-chloro-sulfonyl carbanions react with the cationic benzene complex **58** to yield as the major product an unexpected bimetallic compound **60** whose formation can be explained by the addition of the benzylic carbanion obtained from the neutral complex **59** with the starting compound **58** (Scheme 22) [112,113]. α-Nitro carbanions react with *para*-chlorotoluenetricarbonylmanganese **61** and give neutral complexes **62** and **63** (Scheme 23).

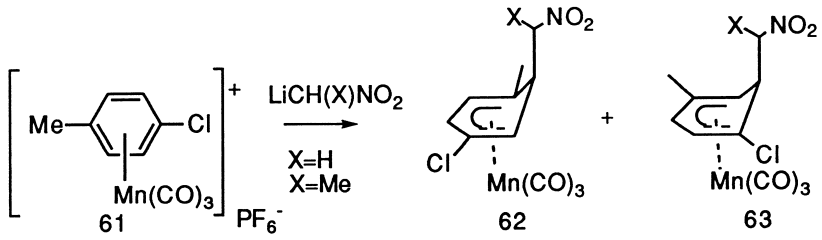
α-Chloroester, α-bromoester, α-isocyanoester, nitrile carbanions react nearly quan-




Scheme 21. Addition of imino-nitrile and ester carbanions




Scheme 22. Addition of x-sulfonyl carbanions

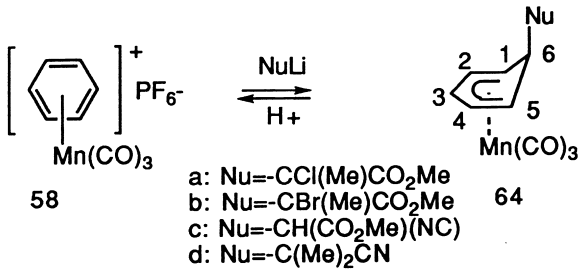



Scheme 23. Addition of x-nitro carbanions

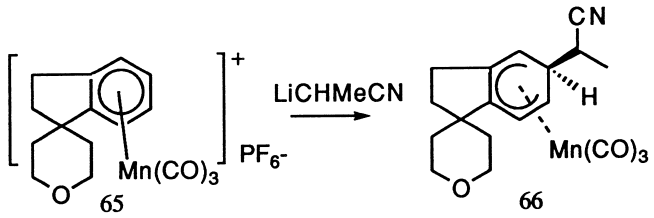
titatively with the hexafluorophosphate of benzenetricarbonylmanganese **58** to give the corresponding neutral $\eta^5$-cyclohexadienylmanganese complex **64** (Scheme 24) [114,115]. The X-ray structure of complex **64a** showed an ($\eta^5$-cyclohexadienyl) structure. The cyclohexadienyl ring is nearly planar and folded about $C_1C_6C_5$ with an angle of 35°. The $sp^3$ $C_6$ carbon of the ring is eclipsed by a Mn–CO bond in agreement with other ($\eta^5$-cyclohexadienyl) complex structures [115].

More sophisticated cationic ($\eta^6$-arene) complex such as spiroindane derivative **65** has been synthesized and was reacted with 2-lithio-2-methylpropionitrile. We obtained, as the major product, the regioisomer **66** (Scheme 25) [114]. This regioselective reaction could be of interest if applied to the synthesis of 2-aryl propionic acids which are known to have anti-inflammatory properties.

Knowing that ketone enolates and anionic Fischer type carbenes have similar reactivity, we added Fischer type carbene carbanions **67** to the cationic arene complex



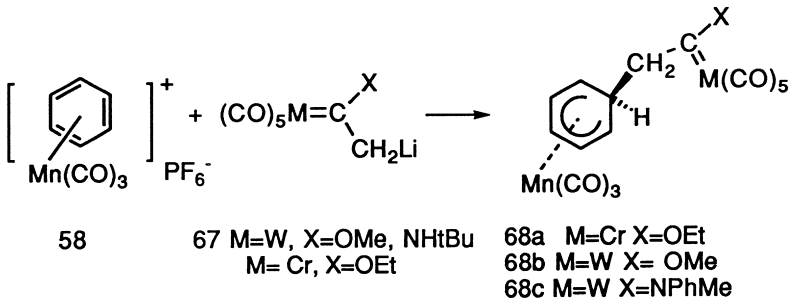

Scheme 24. Addition of carbanions



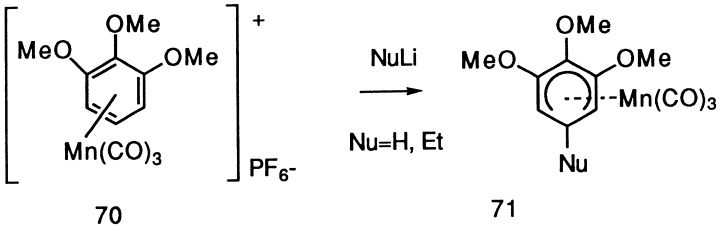

Scheme 25. Addition of propionitrile carbanion to **65**

**58** and we prepared the bimetallic complexes **68** (Scheme 26). The X-ray structure of the *Z* isomer of bimetallic complex **68c** was determined [116].

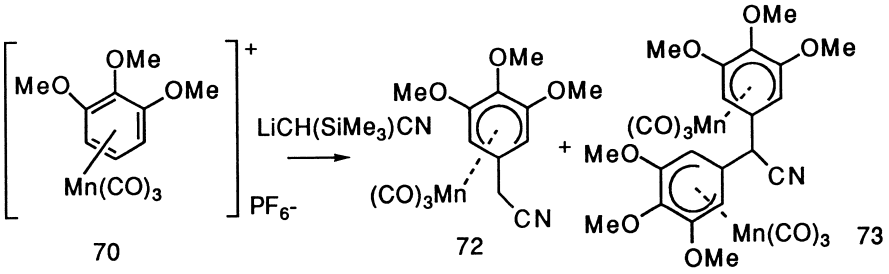
We then focused our attention on preparation of 5-substituted 1, 2, 3-trimethoxy benzene derivatives, the structures of which are found in natural products or in pharmacologically active compounds. Our investigations in this field showed that nucleophiles react with ($\eta^6$-1,2,3-trimethoxybenzene)tricarbonylmanganese **70** to give addition products mainly at the C. carbon (Scheme 27). In the case of addition of $LiCH(SiMe_3)CN$, mononuclear complex **72** and dinuclear complex **73** are obtained after desilylation on chromatography column [117] (Scheme 28).




Scheme 26. Addition of Fischer type carbene carbanions




Scheme 27. Addition of a nucleophile to **70**

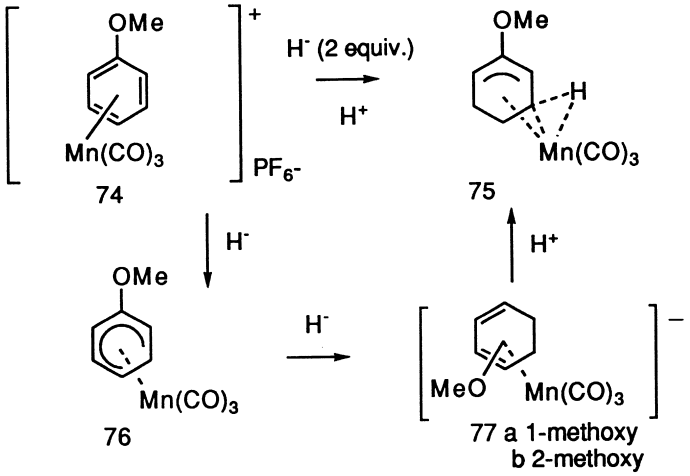



Scheme 28. Preparation of mono and dinuclear complexes

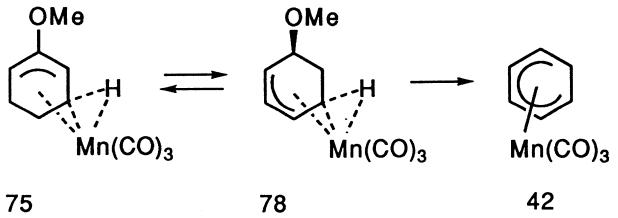
### 3.2. Reactivity of neutral ($\eta^5$-cyclohexadienyl) tricarbonylmanganese complexes

Facile isomerization of ($\eta^3$-cyclohexenyl)tricarbonylmanganese complexes involving Mn–H–C agostic bond (two electron, three-center Mn–H–C bond) has been described by Brookhart et al. [118]. These compounds can be prepared from $\eta^6$ or $\eta^5$ complexes. Thus complex **75** is obtained by treating the cationic anisoletricarbonylmanganese complex **74** with hydride and then with acid (Scheme 29). The first equivalent of hydride affords the neutral $\eta^5$-2-methoxy-cyclohexadienyl complex **76**. Addition of a second equivalent of hydride ($KB(O\text{–}i\text{-}Pr)_3H$) to this complex generates 1-methoxy and 2-methoxycyclohexa-1,3-diene anions 77. Using L-selectride as hydride source, we obtained only the 2-methoxy isomer **77b** [119]. Addition of acid gives as the sole isomer the 2-methoxy-($\eta^3$-cyclohexenyl)manganesetricarbonyl complex **75** via protonation of the anionic complex **77** followed by migration of the hydrogen to the proximal face of the ring.

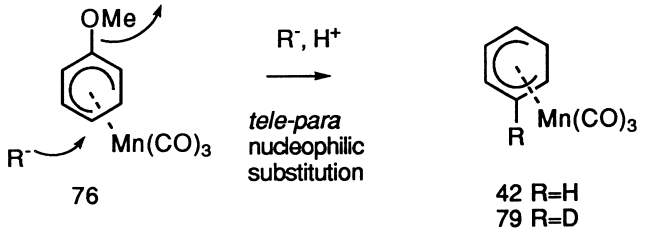
We wanted to obtain the isomerization of complex **75** in such a way that MeOH elimination would be possible to give rise to the formation of an other $\eta^5$-cyclohexadienyl complex. We showed that isomerization of complex **75** could occur after heating it in THF-*d*8 at 70 °C in a sealed NMR tube. In the absence of acid or base, no MeOH elimination is observed. In the presence of MeOH or $CF_3CO_2H$ for example, heating complex **75** in THF for 3 h results in the formation of ($\eta^5$-cyclohexadienyl)tricarbonylmanganese complex **42** via a new complex **78**. This postulated ($\eta^3$-methoxycyclohexenyl)tricarbonylmanganese intermediate **78** could undergo elimination of an agostic hydrogen and the methoxy group with formation of the $\eta^5$ compound **42** (Scheme 30). In other words, complex **42** could be synthesized from compound **76** via substitution of the methoxy group by an hydride (Scheme 31). Because of the position of the entering group ($H^-$) relative to that of the leaving group ($MeO^-$), we called this reaction a *tele–para* nucleophilic




Scheme 29. *Tele–para* nucleophilic substitution




Scheme 30. Elimination of methanol




Scheme 31. Addition of hydride and acid to an ($\eta^5$-cyclohexadienyl)manganese complex

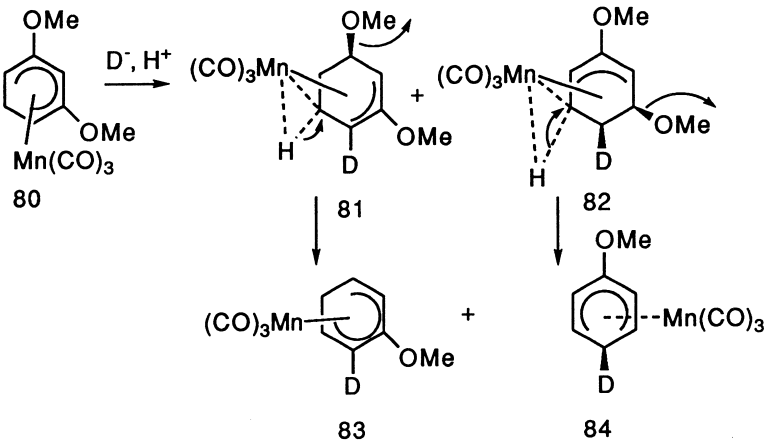
substitution by analogy with the $S_NAr$ in ($\eta^6$-arene)chromium complex series. Using deuteride and (or) labeled acid, we studied the mechanism of this reaction: for example, addition of deuteride to complex **76** gives exclusively deuterated complex **79** after acid treatment and heating (Scheme 31).

We extended this reaction to other ($\eta^5$-X-substituted-cyclohexadienyl) tricarbonylmanganese complexes (X = OR, Cl, $NMe_2$, SPh) which gave, under the same conditions, ($\eta^5$-cyclohexadienyl) complexes resulting from a cleavage of the C–O, C–Cl, C–N and C–S bonds after hydride and a proton source treatment.

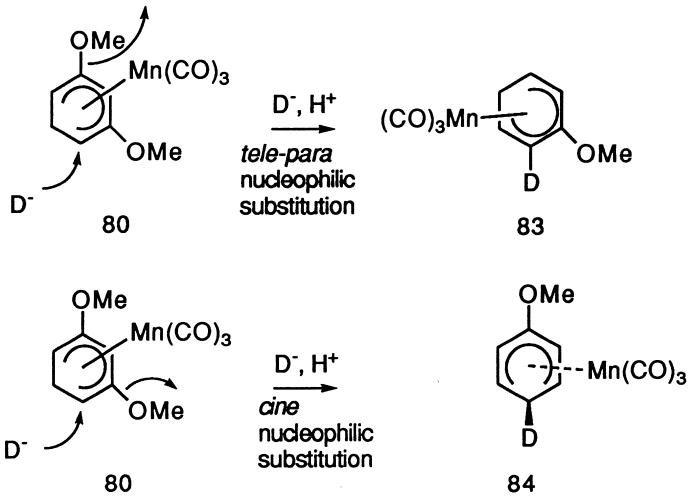
For example complex **80** affords complexes **81** and **82** after deuteride and acid treatment (Scheme 32). By heating these $\eta^3$-cyclohexadienyl compounds, elimination of MeOH occurs and gives rise to the formation of the labeled complexes **83** and **84**, the formation of which can be explained by an overall *tele–para* substitution for complex **83** and *cine* for complex **84** (Schemes 32 and 33) [119].

These reactions represent the first *cine* and *tele*-substitutions in the case of Mn complexes.

In summary, arenetricarbonylchromium and manganese complexes allow the addition of a wide variety of nucleophiles under mild conditions. In the light of our results, it is clear that the three new nucleophilic substitutions (*cine*, *tele–meta* and *tele–para*) which have been discovered by our group, broaden the scope of the applications of these complexes in organic chemistry. The intermediates involve chromium-hydrogen and manganese–hydrogen (or agostic) bonds. The organometallic entity $Cr(CO)_3$ or $Mn(CO)_3$ remains coordinated either to the arene cycle or to the cyclohexadienyl ring.




Scheme 32. *Tele–para* and *cine* nucleophilic substitutions




Scheme 33. *Tele–para* and *cine* nucleophilic substitutions

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