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Metalated (η^6-arene)tricarbonylchromium complexes in organometallic chemistry

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Contents

Abstract

(η^6-Arene)$Cr(CO)_3$ complexes differ from their chromium-free analogs in that they undergo a variety of new transformations as a result of the electron withdrawing effect and the stereocontrol effected by the $Cr(CO)_3$ moiety. Two classes of application are apparent: (1) those that use the $Cr(CO)_3$ group as an auxiliary which may eventually be removed upon completion of a sequence of reactions; and (2) those that aim at designing novel molecules incorporating a $Cr(CO)_3$ moiety and possessing specific stereochemical properties. We present a detailed review of the extensive chemistry of metalated (η^6-arene)$Cr(CO)_3$ complexes developed in the past 30 years and illustrate the main methods of preparation as well as the most important structural, physical and chemical properties of this family of compounds. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Chromium–arene complexes; Polynuclear transition metal complexes; Organometallics; Syntheses

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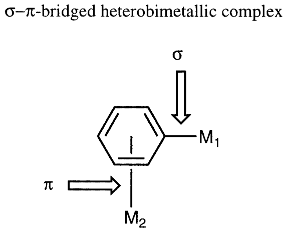
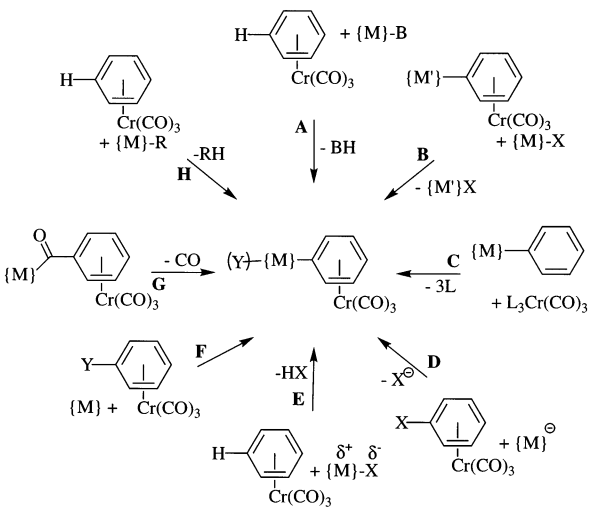
1. Introduction

(η^6-Arene)tricarbonylchromium complexes are widely used in metal-mediated organic synthesis. Numerous reviews have already addressed the advantages of this family of complexes [1]. The peculiar stereochemical control effected by the $Cr(CO)_3$ moiety, which influences the reactions taking place in the vicinity of the arene ring, is exploited in many synthetic applications. Among those known, the lithiation of the arene ligand is one synthetic application that has been extensively investigated owing to the mild conditions required for this reaction to occur with classical organolithium-bases. Comprehensive monographs have been published dealing with the applications of in situ-generated (η^6-lithioarene)tricarbonylchromium complexes in metallo-organic synthesis (Scheme 1, $M_1 = Li$, $M_2 = Cr(CO)_3$) [1a,k]. At present there is a growing interest in the palladium-catalyzed cross-coupling reactions involving (η^6-arene)tricarbonylchromium complexes.

Here, we would like to present a detailed review of the extensive chemistry of metalated (η^6-arene)$Cr(CO)_3$ complexes developed over the past 30 years. We will describe the main preparation methods as well as the most significant structural, physical and chemical properties of this family of compounds (Scheme 1, M_2=$Cr(CO)_3$). Several reports have emphasized the potential of chiral planar (η^6-arene)$Cr(CO)_3$ complexes [2] as auxiliaries in organic synthesis [3] or as ligands in homogenous catalysis [4]. These planar chiral chromium complexes can be prepared from the corresponding planar chiral metalated (η^6-arene)$Cr(CO)_3$ complexes. The intention of this review is to outline those peculiarities of metalated (η^6-arene)$Cr(CO)_3$ that distinguish them from their chromium-free analogs. The review is divided into three sections that address the main synthetic methods, the structural properties and the stoichiometric reactivity of the title compounds. In one of the following sections, we draw attention to the chemistry of (η^6-lithioarene)$Cr(CO)_3$ complexes that have frequently been used as intermediates in metal-mediated organic syntheses as well as in the preparation of various σ–π-bridged heteropolymetallic complexes. The palladium-catalyzed cross-coupling reactions, in which the transient Cr(0), Pd(II) σ–π arene-bridged species are thought to play a central role, are also mentioned with particular emphasis on the behavior of the $Cr(CO)_3$ moiety under catalytic conditions. We mention all the cases of metalated (η^6-arene)tricarbonylchromium complexes and pay particular attention to those bearing a σ-bonded transition metal or a metalloid (Sn) center, also referred to as the arene σ–π bridged heterobimetallic complexes (Scheme 1) [5].



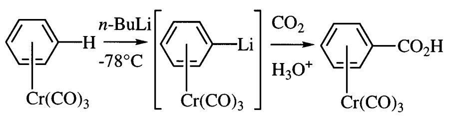
Scheme 1.



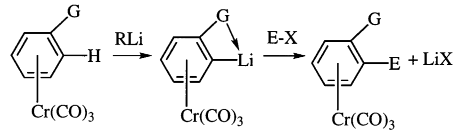
Scheme 2.

2. The main methods for the synthesis of heterobimetallic complexes derived from (η^6-arene)tricarbonylchromium complexes

Bimetallic complexes derived from (η^6-arene)$Cr(CO)_3$ complexes have been synthesized on a preparative scale by at least six different methods. Scheme 2 summarizes these synthetic routes, which range from the classical reactions of deprotonation–lithiation (Scheme 2, path A), transmetalation (Scheme 2, path B) and ligand exchange (Scheme 2, path C) to the more (η^6-arene)tricarbonylchromium-specific aromatic nucleophilic (Scheme 2, path D) and electrophilic (Scheme 2, path E) additions of anionic and cationic metal complexes, respectively. Less frequently reported are the reactions involving an interaction between a metal and an aromatic carbon–halogen bond (oxidative addition in cross-coupling reactions, Grignard-like procedures) (Scheme 2, path F) and the extrusion of CO ligand from acylmetal-substituted (η^6-arene)$Cr(CO)_3$ complexes (Scheme 2, path G) or the cleavage, in neutral conditions, of a C_{Ar}–H bond (*ortho*-manganation and 1,2-polymetalation) (Scheme 2, path H).

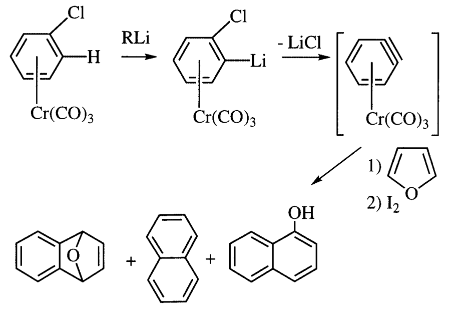


Scheme 3.



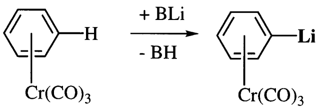
G: -F > -C(O)NHR > -NHC(O)R > -CH$_2$NR$_2$ = -OMe >> -CH$_2$OMe > -NR$_2$ = -SR

Scheme 4.



Scheme 5.

2.1. Deprotonation–lithiation of (η^6-arene)Cr(CO)$_3$ complexes; main landmarks



(1)

This report is not intended to cover the immensely wide-ranging work performed on the deprotonation–lithiation of (η^6-arene)Cr(CO)$_3$ complexes. Our aim is to focus on the issues related to the deprotonation step (Eq. (1)). For the reader interested in further applications of these lithiated species in organic synthesis, the information is available in the literature given below.

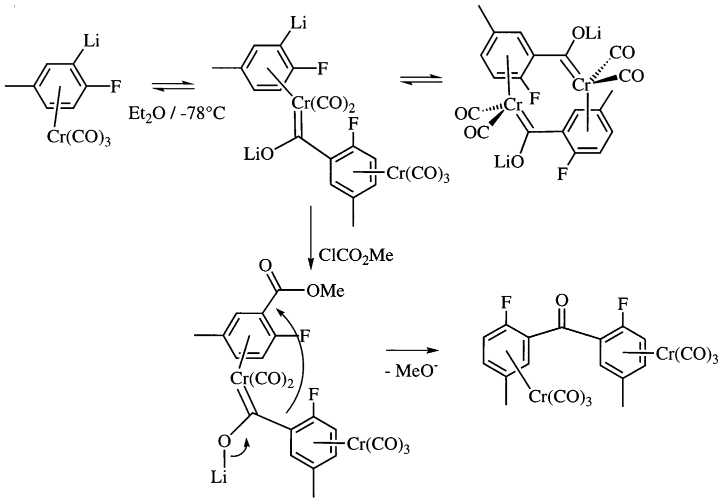
2.1.1. General considerations concerning the deprotonation reaction

The first report of a lithiation of (η^6-benzene)-Cr(CO)$_3$ on reaction with RLi was published in the late 1960s by Nesmeyanov et al. [6]. The deprotonation of a coordinated arene ligand was readily carried out at a low temperature, in a polar coordinating solvent; the in situ-formed lithio reagent was trapped with CO$_2$ to afford the corresponding benzoic acid complex in low yield (Scheme 3). This preliminary study triggered all the subsequent physico-chemical studies and synthetic applications.

The enhancement of the acidity of the aromatic protons upon coordination of the arene functionality to the Cr(CO)$_3$ moiety is one of the most important properties of this class of organometallic compound. The acidity of (η^6-arene)Cr(CO)$_3$ complexes is about 7 pK_a units less than that of the uncoordinated ligand, which in the case of benzene is 41.2 [7]. It has been further shown that the presence of substituents containing heteroelements facilitates *ortho*-metalations by chelation or the inductive effect, an observation which is commonly made with uncoordinated aromatic compounds [8] (Scheme 4). The presence of bulky alkoxy or alkylamino substituents, however, has shown to prevent *ortho*-lithiation and favor deprotonation at *meta* and *para* positions [9]. Further, it has been shown that the order of priority in the regiocontrol of lithiation reactions at positions *ortho* to an 'assisting' substituent is somewhat different from those of the chromium-free aromatic substrates [10]. The following order was established for (η^6-arene)Cr(CO)$_3$ complexes by Widdowson's group: –F > –C(O)NHR > –NHC(O)R > –CH$_2$-NR$_2$ = –OMe ≫ –CH$_2$OMe > –NR$_2$ = –SR (Scheme 4).

In a particular case of the chromium complex of *N*,*N*-dimethylaniline, complexation was shown to make the *ortho*-lithiation reaction less regio-selective than it is with the uncoordinated substrate [11]. It has also been demonstrated that the deprotonation of a benzylic position can compete with the deprotonation of an aromatic position since both sites have similar pK_a values and because the kinetic acidity of the benzylic positions is expected to be much higher than that of the aromatic ones [12].

(η^6-Lithioarene)Cr(CO)$_3$ species are extremely reactive, which precludes their isolation and their subsequent structural study. Until now, no X-ray diffraction study pertaining to such species exists. Card and Trahanovski have studied the behavior of (η^6-benzene)Cr(CO)$_3$ in the presence of *n*-BuLi in THF at various temperatures [13]. The authors observed that the reaction of the benzene complex with *n*-BuLi at − 20 °C afforded the corresponding lithiated species, which was characterized by ^{1}H-NMR. On warming the reaction mixture to 0 °C, they reported that the lithiated species evolved to give (η^6-*n*-butylbenzene)-Cr(CO)$_3$. Although the exact mechanism of this reaction has not been established clearly, several proposals were made. Semmelhack and Ullenius pointed out that the decomposition of (η^6-2-lithio-chlorobenzene)-Cr(CO)$_3$ proceeded at 273 K according to a first-order kinetic law with the proposed intermediacy of a (η^6-benzyne)Cr(CO)$_3$ species [14] (Scheme 5). Experiments devised to trap this intermediate were carried out in the presence of furane and afforded, albeit with low conversion, a mixture of products, some of which appeared to originate from a reaction with a benzyne-type species (Scheme 5).



Scheme 6.

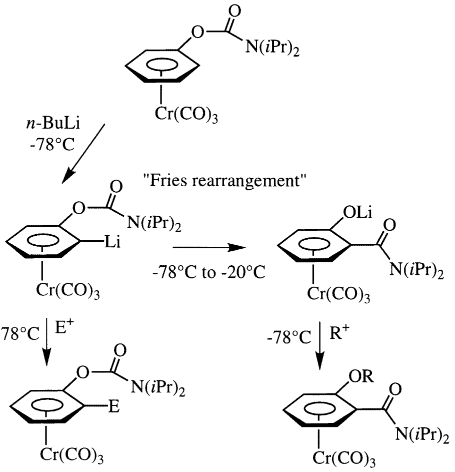
Another study clarified the decomposition process, demonstrating that even at 195 K a lithio intermediate can attack the carbonyl ligand of the $Cr(CO)_3$ group of a second lithiated species generating a binuclear acylchromate intermediate: this was subsequently trapped by reaction with chloroformates [15] (Scheme 6).

Kündig et al. demonstrated that, depending on the nature of the organolithium reagent, a reversible deprotonation of the coordinated arene ring is possible, leading to interconverting products [16]. In their study, the authors subjected a complex of naphthalene to the action of *n*-BuLi at − 78 °C. It was demonstrated that the lithiation is kinetically controlled and that the reaction leads exclusively to the formation of a product lithiated at the 2 position. The addition of a secondary amine to the medium resulted in the equilibration of the two lithiated isomers, among which the thermodynamic product lithiated at the 1 position is favored.

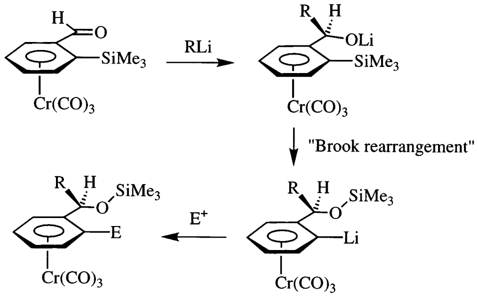
It has been shown that *ortho* lithiated (η^6-acyloxy or carbamoyl-arene)$Cr(CO)_3$ complexes are prone to undergo the Fries rearrangement [9,17] in which the lithiated position of the arene attacks the acyl group attached to the oxygen atom (Scheme 7). This usually undesired side-reaction was recently optimized and elegantly used by Kündig and co-workers [17b].

Evidence for the Brook rearrangement was found in chromium complexes of benzylic alkolates and has been proposed as a mild route toward *ortho* lithiated (η^6-arene)$Cr(CO)_3$ complexes. An elegant example of the Brook rearrangement is the addition of a nucleophile to an *ortho*-silylated benzaldehyde complex, affording an alkolate intermediate, which then attacks the adjacent trialkylsilyl group in an intramolecular reaction, yielding the corresponding *ortho* lithiated product (Scheme 8) [18].

Complexes of benzyl alcohol and benzylamine behave peculiarly when treated with *t*-BuLi. In both compounds, the expected deprotonation of the aromatic ring is supplanted by a complex nucleophilic attack, affording after protonation a novel (η^4;η^2-cyclohexadienyl)benzylidene complex [19]. Chiral α-methyl *N*,*N*-dimethylbenzylamine complexes react selectively with both *n*-BuLi and *t*-BuLi; with both bases the lithiation occurs at an *ortho* site, implying a



Scheme 7.



Scheme 8.

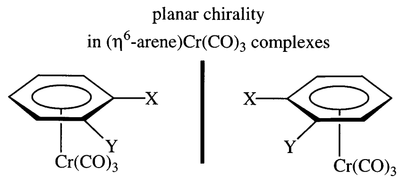
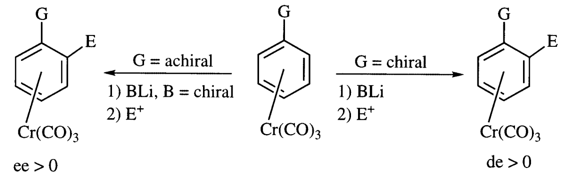
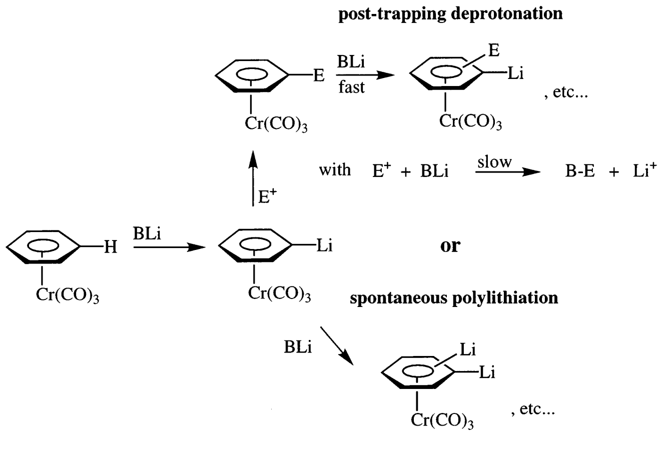


Fig. 1. Planar chirality in (η^6-arene)Cr(CO)$_3$ complexes.



Scheme 9.



Scheme 10.

reaction pathway in which the steric interaction between the methyl group attached to the benzylic carbon and the Cr(CO)$_3$ moiety is minimized [20]. This selectivity, which stems from the stereocontrol caused by the Cr(CO)$_3$ moiety, has been fruitfully extended both to the derivatives of ephedrine and pseudoephedrine [21] and the synthesis of chiral bi- and tri-dentate ligands [22] and other asymmetric organometallic compounds [23].

2.1.2. *(η^6-Lithioarene)Cr(CO)$_3$ complexes and planar asymmetry*

In recent years, a great deal of work has focused on the exploration of routes leading to planar chiral (η^6-arene)Cr(CO)$_3$ [24] complexes with the mediation of lithiated species (Fig. 1). Notably, Uemura and Koide took advantage of the planar chirality of a derivative of (η^6-benzaldehyde)Cr(CO)$_3$ to generate a series of chromium-free axially chiral benzamides [25].

This field may be split into two major directions that differ in the means used for the generation of enantiomerically/diastereomerically enriched planar chiral complexes (Scheme 9). The first method is based on the use of a starting chiral mono-substituted (η^6-arene)Cr(CO)$_3$ complex in which the chiral part is introduced either by reacting a benzaldehyde derivative with a chiral auxiliary belonging to the family of diols [26], sugars [27], aminoetheroxides [28], amides [29], diamines [30] or alternatively by using chiral derivatives of phenol [31] or pyrrolidines [32] (Scheme 9). The second methodology is based on the use of a chiral base that generates, with the induction of asymmetry, the corresponding transient planar chiral *ortho*-lithio product starting from achiral mono-substituted complexes [33] (Scheme 9). The latter route towards enantiomerically enriched planar asymmetric (η^6-arene)-Cr(CO)$_3$ derivatives is frequently implemented using lithium amides that have pK_a constants similar in value to those of the arene complexes. One of the most commonly employed bases is the chiral C_2-symmetric lithium dibenzylamide [(Ph)(Me)CH]$_2$NLi [34]. An alternative way of inducing an enantioselective lithiation of an achiral (η^6-arene)Cr(CO)$_3$ substrate is the association of an achiral alkyllithium base with a chelating chiral tertiary diamine [35].

2.1.3. *'Poly-lithiation' of (η^6-arene)Cr(CO)$_3$ complexes*

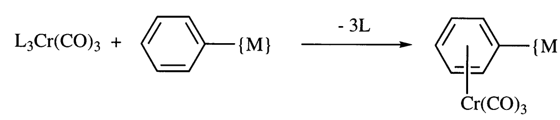
Numerous reports of one-pot polylithiation reactions of (η^6-arene)Cr(CO)$_3$ complexes have been published [17b, 34c, 36]; however, it is only recently that Gibson et al. have addressed this issue systematically [37]. Semmelhack and co-workers made the first mention of such a reaction, observing that the lithiation of an anisole complex and its subsequent electrophilic trapping yielded a tri-substituted product resulting from an apparent double deprotonation reaction [8a]. Although no conclusive mechanistic study has been published so far, two mechanisms can be considered as reasonably accounting for such apparent polylithiation (Scheme 10).

The first mechanism entails the spontaneous mono-, di-, or polylithiation of the substrate upon proton-abstraction by the base BLi. The second requires a 'post-trapping deprotonation', or in other words successive deprotonation–trapping–deprotonation processes enabled by the unreacted BLi or even by the lithiated (η^6-arene)Cr(CO)$_3$ species acting as a base.

The first alternative implies that the mono-lithiated arene ring is sufficiently acidic to allow a second deprotonation or that the second deprotonation is faster than the first one (Scheme 10). As stated above, there is no reliable structural and spectroscopic information on lithiated (η^6-arene)Cr(CO)$_3$ complexes which would make it possible to determine whether the electronic effect of Li as a substituent does or does not de-activate the aromatic ring towards further H-abstractions.

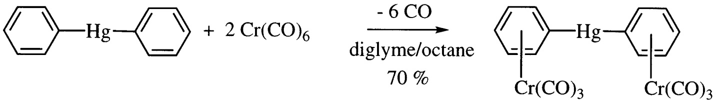
The second alternative implies that the electrophilic trapping of the base BLi itself is rather slower than the deprotonation of the arene complex, which is probable with sterically encumbered amides, such as TMP-Li [36b] (TMP: 2,2,6,6-tetramethylpiperidine), or/and sterically demanding electrophiles such as R_3M^+ (M: Si [34a,c], Sn [34e]).

2.2. Ligand exchange reactions



(2)

The main method for the preparation of (η^6-arene)$Cr(CO)_3$ complexes entails the thermolysis of a mixture of $Cr(CO)_6$ and the aromatic ligand [38] in a coordinating solvent of high boiling point. Variations on this procedure allow the preparation of complexes under milder conditions, at lower temperatures by using more labile chromium substrates of the general formula $L_3Cr(CO)_3$ (L = Py, NH_3, CH_3CN, L_3=C_6H_6, $C_{10}H_8$) [39](Eq. (2)). The compound $[(\eta^6\text{-}C_6H_5)Cr(CO)_3]_2Hg$ [40] was synthesized by the former method. It was prepared in 70% yield by reacting diphenylmercury(II) with $Cr(CO)_6$ in a boiling mixture of diglyme and octane (Eq. (3)). Raush and Gloth synthesized the same trinuclear complex in 61% yield by reacting (η^6-benzene)$Cr(CO)_3$ with diphenylmercury(II) in dioxane [41]. The compound $[(\eta^6\text{-}C_6H_5)Cr(CO)_3]_2Hg$ decomposes at temperatures higher than 200 °C [42] to afford metallic mercury as well as various products including $[(\eta^6\text{-}C_6H_5)Cr(CO)_3]_2$ that may be the product of the recombination of a hypothesized $[(\eta^6\text{-}C_6H_5)Cr(CO)_3]^\bullet$ radical.



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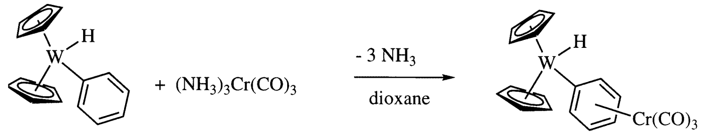
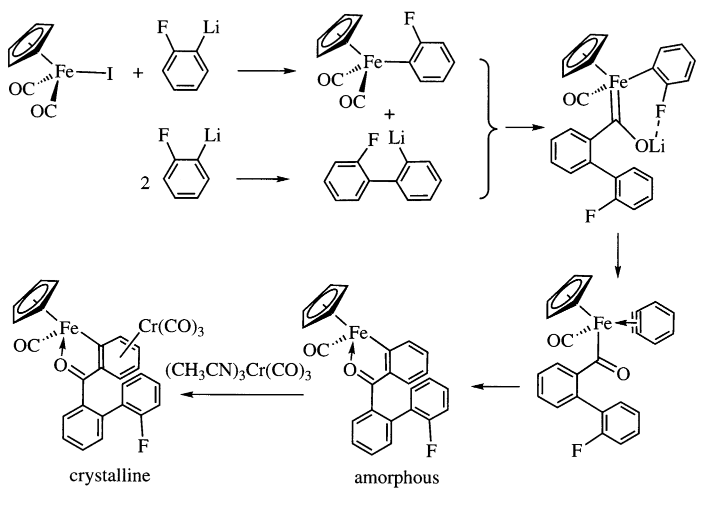
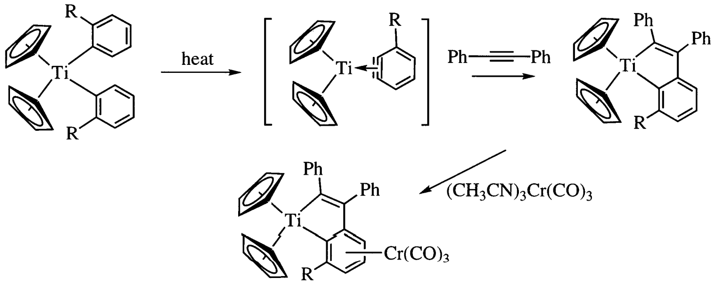


(4)

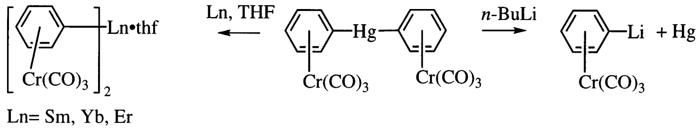
Similarly, a heterobimetallic complex containing a σ-bonded tungsten(IV) center was reported to form upon reacting $Cp_2W(H)(Ph)$ and $(NH_3)_3Cr(CO)_3$ in refluxing dioxane [43] (Eq. (4)). The resulting complex was obtained in 76% yield. The first example of a Fe(II), Cr(0) dinuclear complex was prepared by Nesmeyanov et al. by reacting $Cp(CO)_2Fe\text{–}Ph$ with $Cr(CO)_6$ in a mixture of diglyme and pentane at 139 °C [44]. The product, in which the $Cr(CO)_3$ moiety is coordinated to the phenyl group, was obtained in 68% yield after purification. Another series of biphenyl and naphthalene derivatives substituted by at least one Fp-group (Fp– = $Cp(CO)_2Fe$–) was synthesized following the same procedure [45]. In a similar fashion, an iron(II)-cyclometalated compound was reacted with $(CH_3CN)_3Cr(CO)_3$ to prepare the corresponding $Cr(CO)_3$ complex and characterize it by X-ray diffraction analysis (Scheme 11). The reaction afforded a single product in which the $Cr(CO)_3$ group was found to be bonded to the more electron-rich aromatic ring [46]. Similarly, the reaction of $(CH_3CN)_3Cr(CO)_3$ with the product of pyrolysis of $Cp_2Ti(2\text{-}F\text{–}C_6H_4)_2$ and Ph–C≡C–Ph afforded a new cyclotitanated (η^6-



Scheme 11.



Scheme 12.

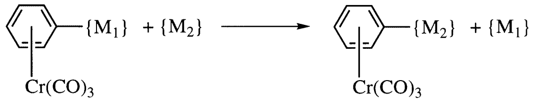


Scheme 13.

arene)Cr(CO)$_3$ complex in 60–70% yield [47], which was subsequently characterized by X-ray diffraction analysis (Scheme 12).

Trialkylstannane derivatives [48] were synthesized by ligand exchange methods as early as 1963. Seyferth and Alleston synthesized (η^6-Me$_3$Sn–C$_6$H$_5$)Cr(CO)$_3$ by the thermolysis of Cr(CO)$_6$ in the presence of the corresponding arene in 34% yield with ethylene glycol–dimethyl ether as the solvent [48a]. Various analogous organostannanes, such as (η^6-1,4-(Me$_3$Sn)$_2$–C$_6$H$_4$)-Cr(CO)$_3$ and [(η^6-C$_6$H$_5$)Cr(CO)$_3$]$_2$SnMe$_2$, were also prepared by Poeth et al. using this thermolytic method in yields of about 40–15% [48b]. Following Öffele's procedure, Ustynyuk and co-workers synthesized α- and β-trimethylstannylnaphtalene complexes in respective yields of 38 and 12% by a Lewis-acid-catalyzed ligand exchange reaction between the aromatic substrate and *fac*-(C$_5$H$_5$N)$_3$Cr(CO)$_3$ [48c,d]. Wright synthesized *para*- and *meta*-substituted (η^6-[(*n*-Bu)$_3$Sn]$_2$C$_6$H$_4$)Cr(CO)$_3$ in 91 and 75% yield, respectively, by reacting the arene ligand with (MeCN)$_3$Cr(CO)$_3$ in THF [48e].

2.3. Transmetalation

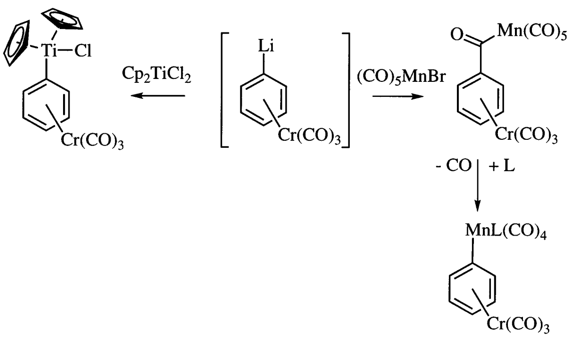


(5)

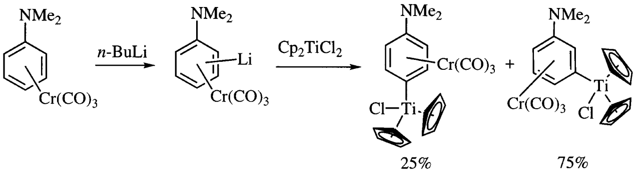
The reaction of [(η^6-C$_6$H$_5$)Cr(CO)$_3$]$_2$Hg with *n*-BuLi allows the efficient formation of the corresponding (η^6-phenyllithium)Cr(CO)$_3$ (Scheme 13) [41]. Starting from the same diphenylmercury(II) complex, a series of σ–π complexes containing a lanthanide ion in the + II oxidation state was also prepared in satisfactory yields via a transmetalation reaction [49] (Eq. (5)). The exchange of Hg(II) for Sm(II), Yb(II) or Er(II) was carried out in THF by reacting the mercury(II) substrate with solid metallic lanthanide (Scheme 13). The Cr–Ln ratio of 2:1 was determined by X-ray fluorescence analysis. The resulting product proved to be highly air-sensitive on the removal of the solvating molecule of THF.

Wright used bisorganostannyl derivatives of (η^6-arene)Cr(CO)$_3$ complexes to generate *meta* and *para*-bislithiated complexes which were used subsequently for the synthesis of various *meta* and *para* bishalogeno and phosphino complexes [48e].

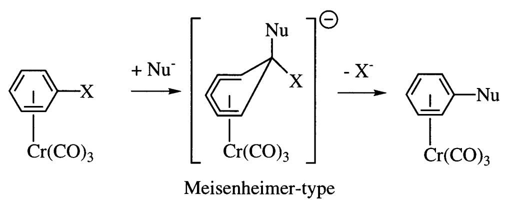
Lithiated (η^6-arene)Cr(CO)$_3$ species are often employed in metal exchange reactions with complexes of Mn(I) [50], Ti(IV) [51] (Scheme 14) and Au(I). The reaction between (η^6-1-Li,2-R–C$_6$H$_4$)Cr(CO)$_3$ (R = H, F) and (CO)$_5$MnBr affords a benzoyl manganese(I) complex (31% yield). This complex could be converted into a Mn(I), Cr(0) σ–π complex by expulsion of carbon monoxide (Scheme 14), which was achieved by adding either a 2-electron ligand such as a phosphine or even a 4-electron di-phosphine ligand to the reaction medium. The authors did not propose a mechanistic scheme that could rationalize the formation of the first benzoyl–metal product. However, it is reasonable to assume that the initial addition of the lithiated agent to



Scheme 14.



Scheme 15.



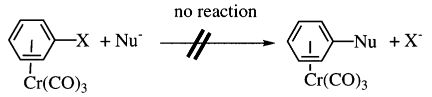
Scheme 16.

$(CO)_5MnBr$ occurs at a carbonyl ligand [52] rather than directly at the Mn(I) center. The benzoylbromomanganate thus formed would then eliminate Br^- and coordinate an exogenous CO ligand provided by the decomposition of electronically unsaturated organometallic species. The reaction of one equivalent of $(\eta^6\text{-1-Li,R–}C_6H_4)Cr(CO)_3$ (R = H, 2-F, 4-CH_3) with Cp_2TiCl_2 affords the corresponding Ti(IV), Cr(0) heterobimetallic complexes with yields ranging from 52 to 69% (Scheme 14) [51a]. Reaction of two equivalents of $(\eta^6\text{-Li–}C_6H_5)Cr(CO)_3$ and $(\eta^6\text{-1-Li,4-}CH_3\text{–}C_6H_4)$-$Cr(CO)_3$ with Cp_2TiCl_2 affords the corresponding heterotrinuclear products with respective yields of 37 and 29%. The in situ lithiation of $(\eta^6\text{-}(CH_3)_2N\text{–}C_6H_5)$-$Cr(CO)_3$ affords a mixture of lithiated species that yields essentially two isomeric heterobimetallic Ti(IV), Cr(0) complexes (64% conversion) upon stoichiometric reaction with Cp_2TiCl_2 [51c] (Scheme 15). The two isomers were titanated at the *meta* (75%) and *para* (25%) positions, respectively, relative to the *N*,*N*-dimethylamino group. Heterobimetallic σ–π complexes containing gold(I) were synthesized similarly by the stoichiometric reaction of $(\eta^6\text{-1-Li,R–}C_6H_4)Cr(CO)_3$ (R = H, 2-F) with the electrophilic $(PPh_3)Au$–Cl and were isolated in 48% (R = H) and 62% (R = 2-F) yields, respectively [51a].

Ustynyuk and co-workers developed a method for the selective introduction of substituents into either the coordinated or non-coordinated ring in $(\eta^6$-naphthalene$)Cr(CO)_3$ [48c,d]. In their procedure, the naphthalene complex was deprotonated at low temperature by *n*-BuLi, and the resulting α- and β-lithiated derivatives were converted into the corresponding trimethylstannyl products with an overall conversion of 74% and a ratio of α- over β-substituted organostannyl complex, α/β of 0.44.

2.4. Aromatic nucleophilic substitution

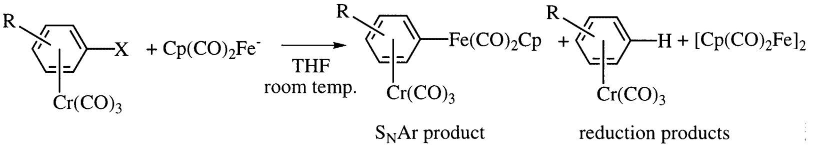
Aromatic nucleophilic substitution reactions that involve $(\eta^6$-arene$)Cr(CO)_3$ complexes in which the arene ligand bears a potentially good leaving group (principally fluoro and chloro substituents [53], but in some cases alkoxy groups [54]) have been extensively studied with a wide variety of organic nucleophiles. The mechanism of this reaction consists of two elementary steps (Scheme 16): (1) the formation of a transient anionic Meisenheimer-like $(\eta^5$-cyclohexadienyl)tricarbonylchromate intermediate [55] upon nucleophilic attack at the *ipso* position bearing the leaving group –X; and (2) the elimination of X^- and regeneration of a neutral $(\eta^6$-arene$)Cr(CO)_3$ complex.



(6)

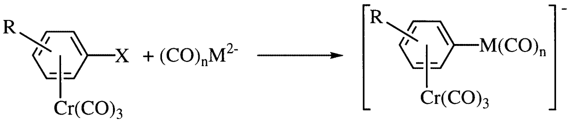
$Nu^- = (CO)_4Co^-, (CO)_5Mn^-, Cp(CO)_3Mo^-, Cp(CO)Ni^-$

When organometallic anionic nucleophiles were first applied to arene chromium complexes by Heppert et al. [56] the authors reported that anions such as $Na[Co(CO)_4]$, $Na[Mn(CO)_5]$, $Na[CpMo(CO)_3]$ and $Na[CpNi(CO)]$ would not react with halogeno–arene complexes (Eq. (6)). In good agreement with King's scale of nucleophilicity [57], only the most nucleophilic organometallic monoanions such as $CpFe(CO)_2^-$ and $Cp^*Fe(CO)_2^-$ displayed any reactivity with fluoro- and chloro-substituted arene complexes. For instance, $K[CpFe(CO)_2]$ could be made to react with $(\eta^6\text{-}FC_6H_5)Cr(CO)_3$ at 22 °C in THF to afford $[\eta^6\text{-}\{Cp(CO)_2Fe\}\text{–}C_6H_5]Cr(CO)_3$ in 10% yield (Eq. (7)). An analogous reaction using the chlorobenzene substrate did not yield a bimetallic product but rather $(\eta^6$-benzene$)Cr(CO)_3$ and $[Cp(CO)_2Fe]_2$ as a consequence of a reduction reaction. A whole series of substituted complexes of chlorobenzene, i.e. $(\eta^6\text{-1-Cl,R–}C_6H_4)Cr(CO)_3$ (R = 4-CF_3, 3-CF_3, 4-MeO(O)C, 4-F, 4-Cl, 3-Cl, 3-CH_3O, H, 3-CH_3, 4-CH_3), was reacted with $M[Cp(CO)_2Fe]$ (M = Na, Et_4N). The corresponding Fe(II), Cr(0) bimetallic complexes were isolated with yields ranging from 15 to 63%. In addition to these heterobimetallic species, reduction reaction products were also isolated in proportions that were shown to depend directly on: (1) the reducing power of the anion ($Cp^*(CO)_2Fe \gg Cp(CO)_2Fe$); (2) the electron donating ability of the R-group (electron donor $\gg$ electron acceptor); (3) the substitution pattern of the arene ligand (*ortho* $\gg$ *meta* $\cong$ *para*); and (4) the identity of the leaving group ($I \gg Cl > F$). Subsequently, Hunter and coworkers reported the synthesis of various complexes with the general formula $(\eta^6\text{-1,4-}C_6H_4XFp)Cr(CO)_3$ (X = H, Me, Cl, OMe, Fp = $Cp(CO)_2Fe$) (32–80% yield) [58] by applying a similar method. The chloro-substituted bimetallic complex was synthesized by the stoichiometric reaction of $Cp(CO)_2Fe^-$ with (η^6-1,4-dichlorobenzene)$Cr(CO)_3$ whereas the other three heterobimetallic compounds were synthesized starting from the corresponding fluoro-substituted arene complexes. (η^6-Fluorobenzene)$Cr(CO)_3$ reacted efficiently with (η^5-MeC_5H_4)$(CO)_2Fe^-$ and (η^5-indenyl)$(CO)_2Fe^-$. The corresponding heterobimetallic products were recovered with 57 and 42% yield, respectively [59].



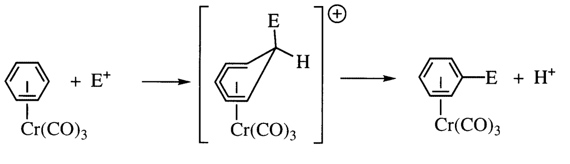
(7)

Dianionic metalcarbonyl nucleophiles are highly reactive towards halogenoarene complexes (Eq. (8)). The 'Collman reagent' $Na_2[Fe(CO)_4]$ was reported to react with (η^6-chlorobenzene)$Cr(CO)_3$ at 22 °C in a mixture of THF and NMP to afford the mono-anionic heterobimetallic $\sigma-\pi$ compound $Na[(\eta^6\text{-}C_6H_5\{Fe(CO)_4\})Cr(CO)_3]$ in 45% yield [60]. The latter was efficiently isolated by extraction into degassed water followed by precipitation with aqueous tetra-alkylammonium halides. The dianionic Collman salt displayed a tendency to displace a $Cp(CO)_2Fe$– group from (η^6-$\{Cp(CO)_2Fe\}$–C_6H_5)$Cr(CO)_3$ according to a nucleophilic substitution-like mechanism, which yielded the corresponding mono-anionic complex $[(\eta^6\text{-}\{(CO)_4Fe\}C_6H_5)Cr(CO)_3]^-$ [61]. Other dianionic nucleophiles of the formula $M(CO)_5^{2-}$ ($M = Cr, W$) were reported to react poorly with (η^6-fluorobenzene)$Cr(CO)_3$ and the resulting mono-anionic heterobimetallic products $[(\eta^6\text{-}\{(CO)_5M\text{–}C_6H_5\})Cr(CO)_3]^-$ were recovered in low yields ($M = Cr$, 33%; $M = W$, 11%).

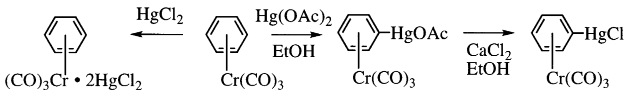


M = Fe, n = 4, 45 %
M = Cr, n = 5, 33 %
M = W, n = 5, 11 %

(8)



Scheme 17.

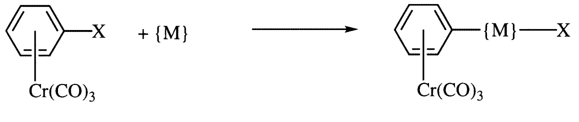


Scheme 18.

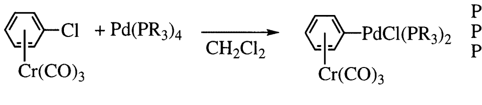
2.5. Aromatic electrophilic substitution

It is well established that the electrophilic $Cr(CO)_3$ moiety in (η^6-arene)$Cr(CO)_3$ complexes deactivates the arene ligand towards aromatic electrophilic substitution reactions (Scheme 17). In the literature, few examples of Friedel–Crafts acetylation reactions with arene–chromium complexes can be found [62]. The lack of regioselectivity of the reported transformations discouraged further investigation. The mercuration of aromatics by the reaction of an arene with $Hg(OAc)_2$ in a polar protic solvent is known to proceed via a typical S_EAr mechanism [63] (Scheme 18). In many cases a competing process involving the transfer of electrons appears to predominate [64]. Magomedov and co-workers originally prepared (η^6-C_6H_5–HgCl)$Cr(CO)_3$ in 43% yield by the sequential reaction of the benzene complex with mercury(II) diacetate in refluxing ethanol followed by the treatment of the reaction mixture with a saturated ethanol solution of $CaCl_2$ [65]. Recently, several new examples of *ortho*-mercuration reactions of (η^6-arene)$Cr(CO)_3$ complexes possessing endogenous ligands have been reported [65c]. It is important to note that the arene mercuration reaction occurs only if $Hg(OAc)_2$ is used. Mercury dichloride reacts with (η^6-arene)$Cr(CO)_3$ substrates at the metal center to yield a new neutral adduct with the formula (η^6-arene)$Cr(CO)_3 \cdot 2HgCl_2$ [66] (Scheme 18). The chloromercurio–arene complexes are generally stable and moderately air sensitive.

2.6. 'Insertion' of a metal into a C_{Ar}–X bond



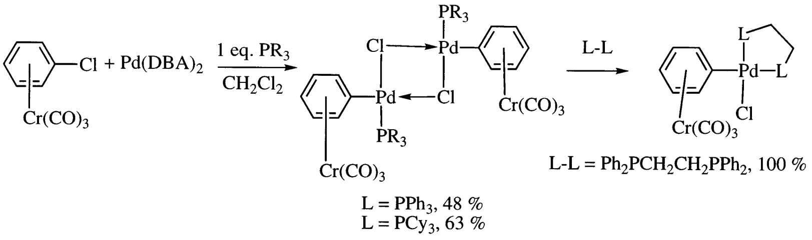
(9)



$PR_3 = PPh_3$, 94 %
$PR_3 = PEt_2Ph$, 81 %
$PR_3 = PEtPh_2$, 100 %

(10)

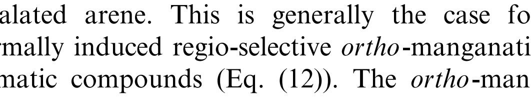
Ten years ago, the synthesis of a series of palladated (η^6-arene)$Cr(CO)_3$ complexes was reported by Basset and co-workers [67]. The preparation of the Pd(II), Cr(0) heterobimetallic complexes was achieved via the oxidative-addition (Eq. (9)) of Pd(0) substrates to the C_{Ar}–Cl bond of (η^6-chlorobenzene)$Cr(CO)_3$ at room



Scheme 19.

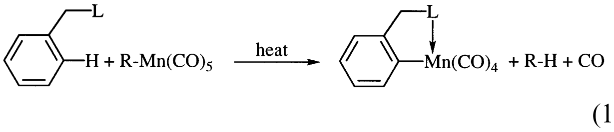
temperature (r.t.). The particular mildness of the conditions required for the 'nucleophilic' insertion of the palladium into the C_{Ar}–Cl bond were attributed to the coordination of the adjacent arene ligand by the $Cr(CO)_3$ moiety which greatly enhances the rate of the oxidative-addition as compared with the other reactions involving uncoordinated halogenobenzene derivatives [68]. Two Pd(0) sources were used in these investigations: $Pd(PPh_3)_4$ and $Pd(dba)_2$ (dba: dibenzylideneacetone). With the phosphine–palladium substrate, binuclear complexes were synthesized in yields ranging from 81 to 100% (Eq. (10)) while reactions of the dibenzylideneacetone complex gave chloro-μ-bridged tetranuclear species in yields ranging from 48 to 63% (Scheme 19). The Pd(II), Cr(0) heterometallic species are moderately air-sensitive and were further investigated as models of the intermediates thought to be involved in the Pd(0)-catalyzed carbonylation of halogen-substituted (η^6-arene)$Cr(CO)_3$ complexes (vide infra Section 2.9) (Scheme 19).

2.7. Metalation via C_{Ar}–H bond cleavage in neutral conditions

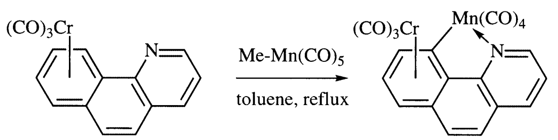


(11)

By *aromatic carbon–hydrogen bond cleavage in neutral conditions* (Eq. (11)) we mean a process in which no ionic substrate or intermediate is involved in the overall chemical transformation leading to the formation of a metalated arene. This is generally the case for the thermally induced regio-selective *ortho*-manganation of aromatic compounds (Eq. (12)). The *ortho*-manganation reaction occurs when an alkylmanganesepentacarbonyl complex R–$Mn(CO)_5$ and an aromatic substrate bearing an endogenous ligand are heated to reflux in an aliphatic solvent. A C_{Ar}–H bond activation step leads to the elimination of R–H and the formation of a stable chelated *cis*-$L_2Mn(CO)_4$ species where L_2 is the chelating arene ligand. The exact mechanism of this reaction has not yet been elucidated fully. Since the late 1960s, an enormous variety of cyclomanganated complexes have been synthesized from the derivatives of 2-phenylpyridine, azobenzene, aromatic ketones and aldehydes, aromatic phosphines and phosphites, aromatic imines and benzylthioethers [69].

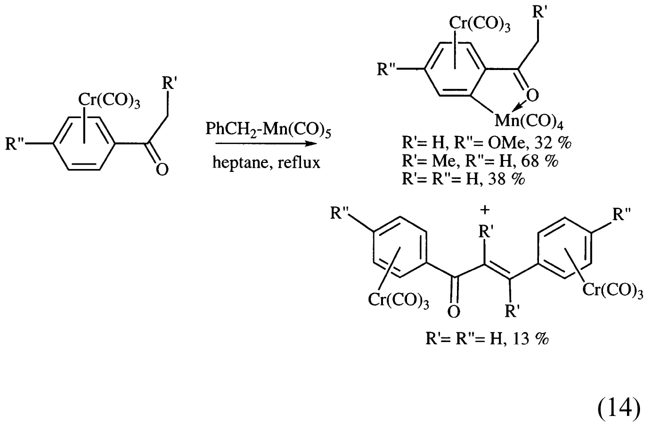


(12)

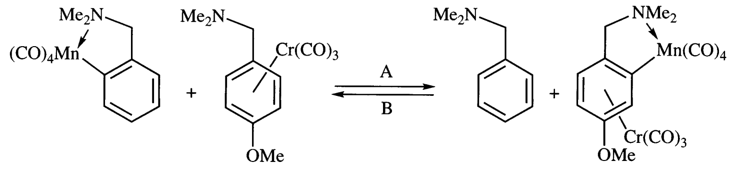


(13)

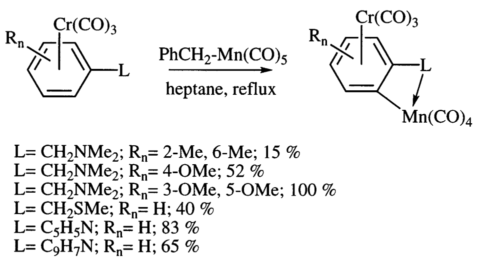
The first example of a cyclomanganated (η^6-arene)$Cr(CO)_3$ complex was reported by Bruce et al. [70]. The reaction of (η^6-benzo[*h*]quinoline)$Cr(CO)_3$ with Me–$Mn(CO)_5$ in refluxing toluene was reported to afford the resulting bimetallic product as a scarlet microcrystalline air-stable powder in 35% yield (Eq. (13)). Much later, further examples of the application of this *ortho*-metalation reaction to (η^6-arene)$Cr(CO)_3$ complexes were reported by Woodgate and co-workers [71] (Eq. (14)) who described the synthesis of a series of cyclomanganated (η^6-acetophenone)$Cr(CO)_3$ complexes in moderate to good yields. In some cases the manganating agent, e.g. $PhCH_2$–$Mn(CO)_5$, initiated an unexpected aldol condensation reaction between the two molecules of the starting derivatized acetophenone complex. Attempts to cyclomanganate (η^6-benzaldehyde)$Cr(CO)_3$ did not generate any new heterobimetallic product.



(14)

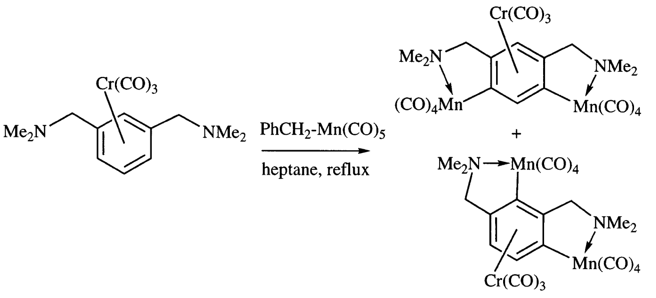


Scheme 20.

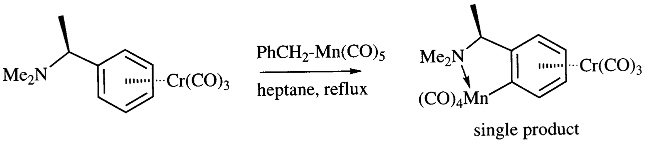


L= CH_2NMe_2; R_n= 2-Me, 6-Me; 15 %
L= CH_2NMe_2; R_n= 4-OMe; 52 %
L= CH_2NMe_2; R_n= 3-OMe, 5-OMe; 100 %
L= CH_2SMe; R_n= H; 40 %
L= C_5H_5N; R_n= H; 83 %
L= C_9H_7N; R_n= H; 65 %

(15)



(16)



(17)

The *ortho*-manganation of derivatives of *N*,*N*-dimethylbenzylamine such as $[\eta^6\text{-}(CH_3)_2NCH_2\text{–}C_6H_4R]Cr(CO)_3$ was reported to give the corresponding *ortho*-metalated products in satisfactory yields [72] (Eq. (15)). The chromium complex of the 'pincer' ligand developed by van Koten [73], when treated with excess amounts of $PhCH_2\text{–}Mn(CO)_5$ in refluxing heptane, yielded a mixture of two different di-manganated heterotrimetallic complexes, which demonstrated that the $(\eta^6\text{-arene})Cr(CO)_3$ moiety is capable of incorporating more than one bulky $Mn(CO)_4$ fragment (Eq. (16)). The *ortho*-manganation of chiral α-methylated benzylamine derivatives afforded, with total stereoselectivity, the cyclomanganated products in which the methyl group on the benzylic carbon was located *trans* to the $Cr(CO)_3$ tripod (Eq. (17)). The author proposed that the absence of the other stereoisomer was the consequence of a peculiar lability of the $Mn(CO)_4$ fragment upon thermal treatment favoring the most thermodynamically stable product. This hypothesis was confirmed by a reaction in which the $Mn(CO)_4$ moiety was transferred from one chelating ligand to another. On reacting a mixture of cyclomanganated *N*,*N*-dimethylbenzylamine with $(\eta^6$-4-methoxy-*N*,*N*-dimethylbenzylamine$)Cr(CO)_3$ in hot heptane, the hetero-bimetallic product resulting from the transfer of the $Mn(CO)_4$ moiety was obtained, along with some starting material and uncoordinated *N*,*N*-dimethylbenzylamine (Scheme 20). The reverse experiment was carried out under similar experimental conditions, the results of which suggested the absence of a strict thermodynamic equilibrium between the cyclometalated species. The *ortho*-manganation [74,75] and *ortho*-rhenation [76] reactions of derivatives of $2\text{-}[(\eta^6\text{-phenyl})Cr(CO)_3]$pyridine were also reported to give the corresponding binuclear products in good yields.

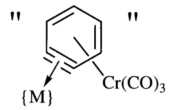
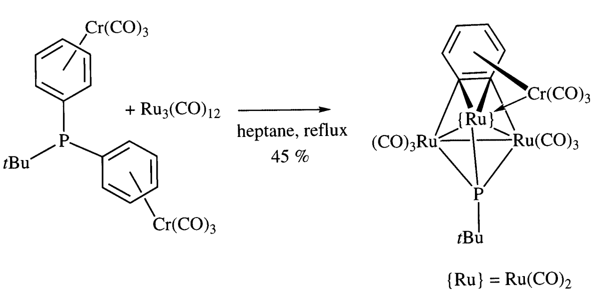
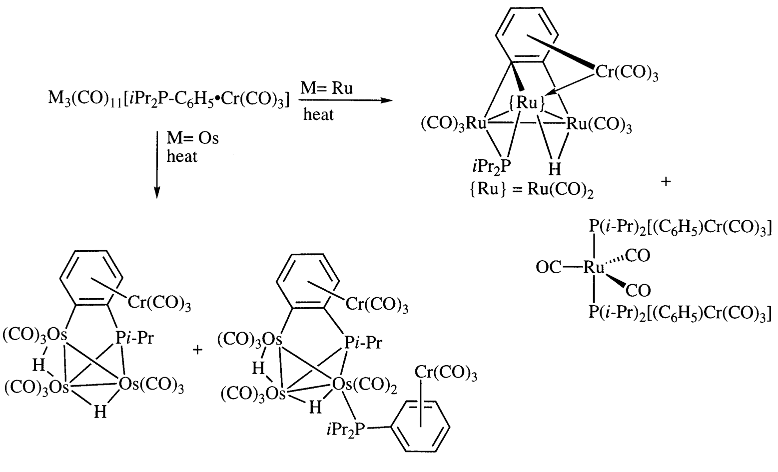


Fig. 2. A benzyne species stabilized by coordination to transition metals.

Cullen and co-workers synthesized transition metal stabilized benzyne complexes by the thermolysis of trinuclear complexes of either ruthenium or osmium carbonyl (Fig. 2). For instance thermolysis of $Ru_3(CO)_{12}$ in the presence of $PhP[C_6H_5\cdot Cr(CO)_3]_2$ afforded the stabilized benzyne pentanuclear complex $Ru_3(CO)_9\{\mu_3\text{-}P[C_6H_5\cdot Cr(CO)_3]\}[\mu_3\text{-}C_6H_4\cdot Cr(CO)_3]$ in 50% yield, which contains a 1,2-diruthenated $(\eta^6\text{-arene})Cr(CO)_3$ fragment [77a].

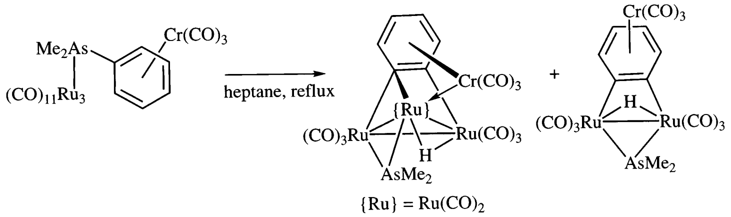


(18)



Scheme 21.

Similarly, the thermolysis of $Ru_3(CO)_{12}$ in the presence of t-BuP[$C_6H_5\cdot Cr(CO)_3]_2$ in heptane generated a new stabilized benzyne tetranuclear species $Ru_3(CO)_8[\mu_3\text{-}C_6H_4\cdot Cr(CO)_3][\mu_3\text{-}P(t\text{-}Bu)]$ in 45% yield; according to structural studies this complex contains a dative $Cr\rightarrow Ru$ interaction [77b] (Eq. (18)). The thermolytic reaction was thought to proceed via a preliminary mono-decarbonylation of the trinuclear $M_3(CO)_{12}$ species followed by the coordination of the phosphorus donor to the vacant coordination site created at a ruthenium atom. In the subsequent steps, the C_{Ar}–P bond that links an (η^6-arene)$Cr(CO)_3$ fragment to the phosphorus atom is cleaved. Thermolysis of $Ru_3(CO)_{11}L$ with $L = AsMe_2[C_6H_5\cdot Cr(CO)_3]$ generated, via C_{Ar}–H and C_{Ar}–As bond cleavages, two different stabilized-benzyne species [77c] (Eq. (19)).

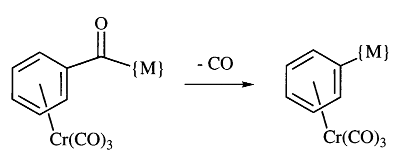


(19)

The first of these was the heterotetrametallic species $Ru_3(CO)_8(\mu\text{-}H)\{\mu_3\text{-}\eta^2\text{-}[(\eta^6\text{-}C_6H_4)Cr(CO)_3]\}(\mu\text{-}AsMe_2)$ in which, according to structural analysis, a coordinatively unsaturated Ru center appears to undergo dative bonding with the chromium atom. The second species, the heterotrinuclear complex $HRu_2(CO)_6\{\mu\text{-}\eta^2\text{-}[(\eta^6\text{-}C_6H_4)Cr(CO)_3]\}(\mu\text{-}AsMe_2)$, was described by the authors as being a stabilized form of benzyne. Significantly a different behavior was observed for ruthenium- and osmium-based $M_3(CO)_{11}[(i\text{-}Pr)_2PC_6H_5\cdot Cr(CO)_3]$ (M = Os, Ru) coordination complexes when treated under thermolytic conditions [78] (Scheme 21). The ruthenium complex afforded, in refluxing heptane, a mixture of two products $HRu_3(CO)_8[C_6H_4\cdot Cr(CO)_3][P(i\text{-}Pr)_2]$ and $Ru(CO)_3[(i\text{-}Pr)_2PC_6H_5\cdot Cr(CO)_3]_2$. The first product, a stabilized benzyne complex, resulted from the sequential C_{Ar}–H and C_{Ar}–P bond cleavages. The second product was presumably formed following the thermal mono-decarbonylation of the substrate and coordination of an $(i\text{-}Pr)_2P[C_6H_5\cdot Cr(CO)_3]$ species present in the reaction medium (Scheme 21).

The osmium complex yielded, upon thermolysis, two similar products resulting from the *ortho* directed C_{Ar}–H bond activation in the (η^6-phenyl) fragment and C_{Alkyl}–P bond activation in the isopropyl substituent of the phosphorus atom. The heterometallic tetranuclear products $H_2Os_3(CO)_9[i\text{-}PrPC_6H_4\cdot Cr(CO)_3]$ and $H_2Os_3(CO)_8[i\text{-}PrPC_6H_4\cdot Cr(CO)_3][(i\text{-}Pr)_2PC_6H_5\cdot Cr(CO)_3]$ both possess two μ-bridged hydrides that link the vicinal osmium atoms (Scheme 21).

2.8. Metalation by extrusion (retro-cis-migration) of CO from benzoyl–metal complexes

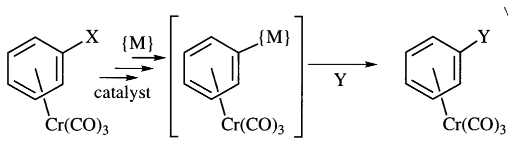


(20)

Extrusion of carbon monoxide in acyl–metal complexes (Eq. (20)) is a thermally favored process, which corresponds to the 'reversed' *cis*-migration of an aryl group from a carbonyl functionality coordinated to a metal center. A tetranuclear species containing three

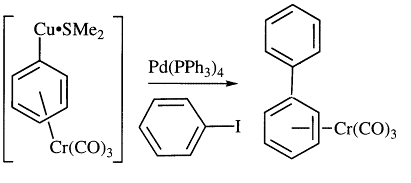
Cp(CO)$_2$Fe– (abbreviated Fp) σ-bonded groups was synthesized by Hunter and co-workers by reacting 1,3,5-[Fp–C(O)–]$_3$(C$_6$H$_3$) and Cr(CO)$_6$ in refluxing *n*-Bu$_2$O. The product was formed following the thermally promoted tridecarbonylation of Cr(CO)$_6$ and the thermally induced extrusion of the three iron-bonded CO ligands, and was eventually isolated in 15% yield [79]. One limitation of this method was the temperature sensitivity of the acyliron substrates. The same authors also described the syntheses of (η^6-1,4-C$_6$H$_4$PhFp)-Cr(CO)$_3$, (η^6-4,4′-C$_{12}$H$_8$Fp$_2$)Cr(CO)$_3$ and (η^6-2,6-C$_{10}$H$_6$Fp$_2$)Cr(CO)$_3$ in respective yields of 7, 28 and 24% starting from 1,4-C$_6$H$_4$Ph[C(O)Fp], 4,4′-C$_{12}$H$_8$[C(O)-Fp]$_2$, 2,6-C$_{10}$H$_6$[C(O)Fp]$_2$.

2.9. Bimetallic species as intermediates in palladium-mediated and Grignard-like processes



Scheme 22.

In this section we address those processes in which a reactive metalated (η^6-arene)Cr(CO)$_3$ complex (M ≠ Li) intervenes as a transient species in a catalyzed process or in Grignard-type reactions (Scheme 22). Widdowson and co-workers successfully reacted (η^6-arene)Cr(CO)$_3$ complexes with copper(I)bromide · dimethylsulfide at low temperature [80]. The analogous (η^6-aryl)Cr(CO)$_3$ copper(I) species were too sensitive to be isolated, but on reaction with acyl chlorides or allylic bromides gave the functionalized (η^6-arene)Cr(CO)$_3$ complexes in satisfactory yields. The in situ formed (η^6-aryl)Cr(CO)$_3$ Cu(I) complexes were also reacted with vinyl bromides (Scheme 23), iodoaryls (Eq. (21)) and bromopyridines in the presence of a Pd(0) cross-coupling reaction catalyst.



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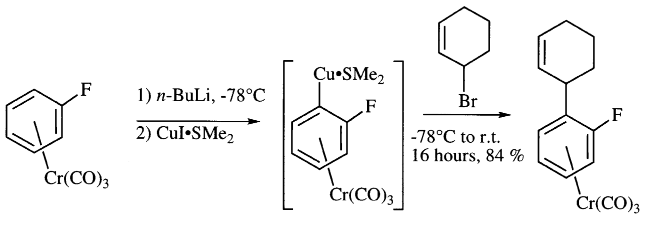
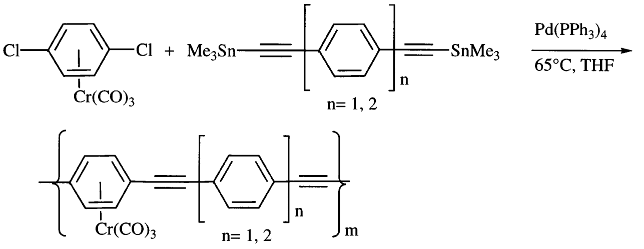


Scheme 23.

In situ formed Zn(II), Cr(0) bimetallic species were prepared by Uemura et al. [81] to take part in a palladium-mediated cross-coupling reaction with bromo-benzene which ultimately afforded biphenyl complexes in modest yields. The authors concluded that the best conversions for such Negishi-type cross-coupling reactions were obtained when (η^6-chloro- or bromo-arene)Cr(CO)$_3$ complexes were reacted with M–C$_6$H$_5$ (M = ZnCl, MgBr, etc...) in the presence of a Pd(II) or Pd(0) catalysts.

Palladium coupling reactions mediated by transient Pd(II), Cr(0) σ–π bimetallic species, such as the carbonylation of (η^6-halogenoarene)Cr(CO)$_3$ complexes, were studied by Basset and co-workers and later on by Mortreux and co-workers. The palladium-catalyzed carbonylation of (η^6-chloroarene)Cr(CO)$_3$ complexes described and patented by Basset [82] proceeded with turnover numbers ranging from 8.5 to 300 and yields from 17 to 80%, respectively. The experiments were usually carried out in Teflon coated steel autoclaves at pressures superior to 5 bar of either pure CO or CO + H$_2$ (for aldehyde formation), at temperatures ranging from 100 to 170 °C, and using Pd(II) pre-catalysts. The products were the corresponding esters, amides, α-oxo-amides and aldehydes in various ratios. Although under these conditions partial decoordination of the Cr(CO)$_3$ moiety was always evident, the authors proposed that the activation of the C$_{Ar}$–Cl bond by the Cr(CO)$_3$ was effected in the early stages of the catalytic reaction during the oxidative addition of the active Pd(0) species. Various mechanistic aspects of both the oxidative addition of Pd(0) and the insertion of CO into the C$_{Ar}$–Pd bond have been addressed comprehensively elsewhere [65].

In an interesting review [68], Mortreux and co-workers addressed a variety of cross-coupling reactions involving nucleophilic reagents such as copper acetylides and organostannanes [83] (Eq. (22)) as well as the catalytic Heck olefination of (η^6-halogenoarene)-Cr(CO)$_3$ complexes. The review also provides an extensive overview of a number of catalytic carbonylation (Eq. (23)) processes, which were recently applied to the kinetic resolution of racemic (η^6-arene)Cr(CO)$_3$ complexes [84].



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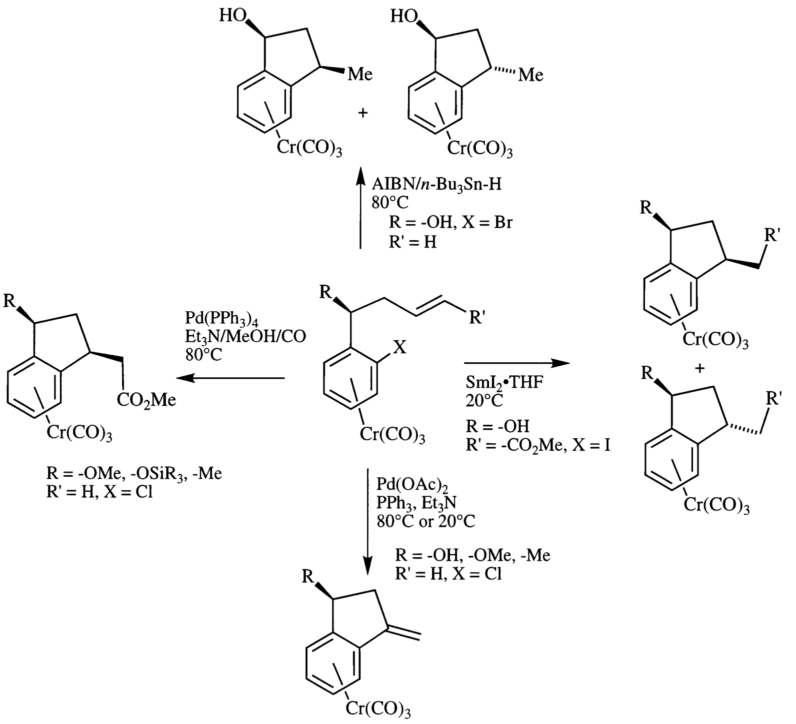
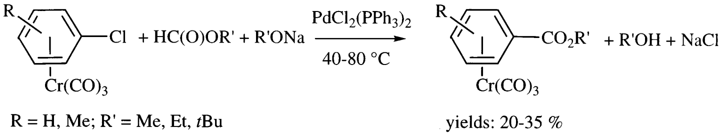
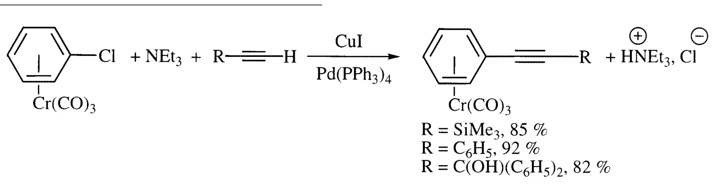


Scheme 24.



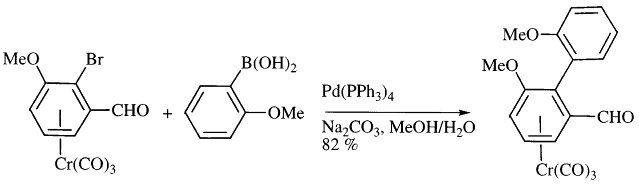
(23)

Several examples are known in which (η^6-halogenoarene)Cr(CO)$_3$ complexes are involved in Stille and Negishi-type reactions [85], in the Sonogashira-type catalytic coupling with terminal alkynes [86] (Eq. (24)) and in Suzuki–Miyaura-type coupling reactions (Eq. (25)) [87]. The mechanisms of these palladium-mediated C–C bond-forming reactions have not yet been elucidated. In general, the order of reactivity of (η^6-halogenoarene)Cr(CO)$_3$ complexes is as follows: $I > Br > Cl \gg F$. Johansson and co-workers observed that attempts to couple complexes of the (η^6-X–C$_6$H$_5$)Cr(CO)$_3$ (X = SnR$_3$ and Cl) type with mono-substituted benzene derivatives C$_6$H$_5$–Y (Y = I, OTf, SnR$_3$) in DMF at 100 °C under palladium-catalyzed Stille-type cross-coupling conditions afforded mainly a chromium-free benzophenone derivative resulting from a carbonylative coupling reaction. The authors demonstrated that CO was supplied mainly by the decomposition of the Cr(CO)$_3$ moiety. These results corroborated the earlier observations by Uemura and Kamikawa on the carbonylative coupling side-reactions that occurred in Suzuki–Miyaura-type palladium-mediated reactions [88]. More recently [85e], Rose and co-workers reported a similar side reaction in a series of Stille and Suzuki-type cross-coupling reactions catalyzed either by Pd(PPh$_3$)$_4$ or PdCl$_2$(PPh$_3$)$_2$. The carbonylative process was predominantly avoided in one case of Stille-type coupling by carrying out the reaction at r.t. in dimethylformamide with a mixture of Pd$_2$(dba)$_3$ and AsPh$_3$ as the catalytic system. An attempted cross-coupling reaction between the chlorobenzene complex and (n-Bu$_3$Sn)$_2$ in the presence of Pd$_2$(dba)$_3$ and AsPh$_3$ in refluxing THF yielded the n-butylbenzene complex in excellent yield instead of the expected tri(n-butyl)stannylbenzene complex [85g].



(24)

Kündig and co-workers recently reported a series of intramolecular Pd-catalyzed carbocyclization Heck-type



(25)

reactions and aryl-radical cyclizations with *ortho*-substituted planar chiral (η^6-butenylhalobenzene)Cr(CO)$_3$ complexes, which yielded a variety of indane complexes [89] (Scheme 24). The putative radical-mediated cyclizations were initiated by HSn(n-Bu)$_3$/AIBN or carried out with stoichiometric amounts of SmI$_2$ · THF. However, the authors did not produce any definite evidence for the radical formation. For the palladium-mediated reactions that involved complexes with a stereogenic benzylic center, the stereochemistry of the alkene carbopalladation was shown to be governed by the planar chirality of the substrate. These Heck-type reactions took place at 80 °C either in benzene or acetonitrile without the loss of the Cr(CO)$_3$ moiety (Scheme 24).

Table 1
Geometrical parameters of metalated (η^6-arene)tricarbonylchromium complexes

Compound	$d_{\mathrm{Cr–C}_{ipso}}$ (Å)	α_{ipso} (°)	{M}	Reference
1	2.286	115.9	–Fe(CO)$_2$Cp	[59]
2	2.278	115.7	–Fe(CO)$_2$Cp	[56]
3	2.294(2)	116.7	–Fe(CO)$_2$(CpMe)	[59]
4	2.300	116.6	–Fe(CO)$_2$(indenyl)	[59]
5	2.316(9)	115.6(8)	–Fe(CO)Cp-κO	[47]
6	2.307	115.9(4)	–TiClCp$_2$	[51b]
7	2.278	114.6	–TiClCp$_2$	[51a]
8	2.332	111.3	–TiClCp$_2$	[51a]
9	– [a]	117.5(3)	–TiClCp$_2$	[51c]
10	2.279(8)	116.2	–PdCl(dppe)	[67]
11	2.266	115.6	–PdCl(PCy$_3$)-μCl	[67]
12	2.307	114.7	–Mn(CO)$_4$(PPh$_3$)	[50a]
13	2.279(3)	115.6(2)	–Mn(CO)$_4$-κO	[71]
14	2.335(6)	114.5(6)	–Mn(CO)$_3$PPh$_3$-κO	[71]
15	2.291(2)	115.1(2)	–Mn(CO)$_4$-κN	[72]
16	2.266(8)	116.9(8)	bis-Mn(CO)$_4$-κN	[72]
17	2.353(13)	– [a]	–W(CO)$_5^-$	[61]
18	2.298(14)	– [a]	–TiCp$_2$-κC	[47]
19	2.251(7)	117.8(7)	–Hg–	[49]
20	2.326(2)	116.23 (19)	–Re(CO)$_3$[C(O)Ph]$^-$ -κN	[76]
21	2.281(8) [b]	117.6(7) [b]	1,3,5-[(Fe(CO)$_2$-Cp]$_3$	[79]

[a] Not available.
[b] Averaged value.

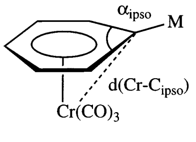


Fig. 3. Distorted arene ligands in (η^6-arene)Cr(CO)$_3$ complexes: typical geometrical parameters.

To our knowledge, the classical Grignard procedure was applied only once to the (η^6-arene)Cr(CO)$_3$ complexes [90]. The reaction between (η^6-iodobenzene)Cr(CO)$_3$ and magnesium turnings at r.t. in Et$_2$O led to a putative Grignard-type intermediate which was subsequently opposed to trimethylsilylchloride. The product of the reaction, (η^6-trimethylsilylbenzene)Cr(CO)$_3$, was isolated with a relatively poor yield (10%).

3. Structural and spectroscopic properties

3.1. Structural peculiarities of metalated (η^6-arene)Cr(CO)$_3$ complexes

The effects of a metal-centered substituent connected to an aromatic carbon of an (η^6-arene)Cr(CO)$_3$ complex over the geometry of the latter are similar to those generally noticed in complexes bearing classical organic groups [91]. Although moderate π-retrodonation of electronic density from the transition metal to the aromatic is expected, important steric interactions caused by the metal's ligand-retinue may also induce some distortions of the complexed arene ligand. These structural distortions can be of two types [92]: (1) an anomalous out-of-the-mean plane folding of the arene ligand involving the metalated *ipso* carbon; and (2) an electronegativity-induced decrease of the endocyclic angle centered at C$_{ipso}$, i.e. α_{ipso}. The first effect has been demonstrated to be dependent mostly on the π-donor property of the metal-centered arene substituent [91,92].

The second effect has been addressed by Lotz and co-workers [51b] who studied the influence of electronegativity of the corresponding titanium centered unit for a small series of Ti(IV) complexes over the value of α_{ipso}. Table 1 gives a list of structural parameters extracted from the X-ray diffraction molecular structures of the reported bimetallic complexes (Chart 1). In this table, d(Cr–C$_{ipso}$) is the Cr–C$_{ipso}$ interatomic distance, which characterizes the electronic repulsion between the two metallic fragments, α_{ipso} corresponds to the value of the endocyclic angle at the *ipso* position (Fig. 3). Note that the values of some structural parameters, which were missing in the original reports, have been extracted from the data deposited with the Cambridge Structural Data Bank for the purpose of the present review. Values of d(Cr–C$_{ipso}$) put together in Table 1 are all superior to 2.230 Å, the value found in (η^6-benzene)Cr(CO)$_3$. The highest values that are found in compounds **5** (2.316(9) Å), **8** (2.332 Å), **14** (2.335(6) Å), **17** (2.353(13) Å) and **20** (2.326(2) Å) compare well with those determined in complexes derived from anilines which are the only ones in which such large

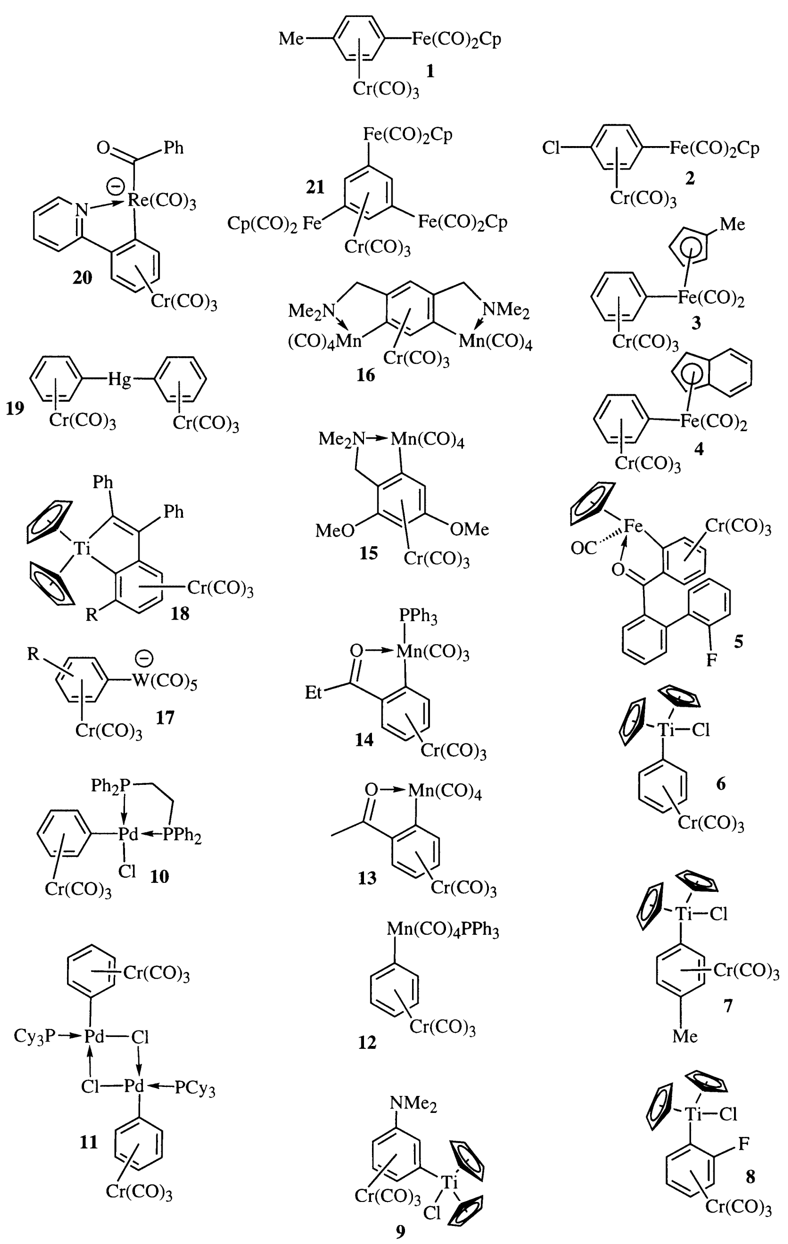


Chart 1.

Cr–C_{ipso} distances are found [92]. It is generally admitted that for strong π-donor substituents the conjugation of a pair of electrons with the arene π-system induces a repulsive interaction with the atom of Cr, by either pushing the latter away from C_{ipso} or by distorting the aromatic ligand [91]. A similar interpretation based on the electronic repulsions has been proposed recently to explain the distortions in other (η^6-arene)$Cr(CO)_3$ complexes [92]. Although almost all the values of α_{ipso} are smaller than the ideal endocyclic angle of 120 (Table 1) there is no straightforward correlation with the corresponding electronegativities of the corresponding metal-centered groups. Given the steric size of most metal ligands, crystal packing may also contribute to the distortions of the arene ring geometry (Charts 1 and 2).

3.2. IR spectroscopy of metalated (η^6-arene)$Cr(CO)_3$ complexes

IR spectroscopy of such bimetallic species provides one with a clear sight of the overall electronic effect of the σ-bonded metal moiety over the electron density distribution throughout the complex. Values of the $Cr(CO)_3$ carbonyl ligand C–O bond stretching force constant k_M calculated [93] from the IR spectra of a series of bimetallic complexes reported in the literature are given in Table 2. These data are presented with the corresponding values of the carbonyl C–O bond force constant k_H of the corresponding complex in which the σ-bonded metal moiety has been replaced by a hydrogen atom. The electronic consequence of the presence of a metal-centered substituent can be estimated from the value of $k_M - k_H$ that 'illustrates' the variation of the electron density at the carbonyl carbon. An electron-donor substituent should induce a flow of electron density towards the chromium atom, which should promote back-donation of electron density to the antibonding π* orbitals located at the CO carbons thus decreasing both the bond order and the bond force constant. A negative value of $k_M - k_H$ should denote an electron-donating character of the σ-bonded metal substituent. An electron-withdrawing group should produce a positive value of $k_M - k_H$. In the majority of cases the metal-centered arene substituents behave as electron donors (Table 2). To our knowledge, in only one case, when M = –HgCl (Chart 2), the σ-bonded metal behaves as a genuine electron-withdrawing substituent with a $k_M - k_H$ value of $+23 \times 10^3$ dyn cm^{-1} which compares well with that described by van Meurs and co-workers [94] for –CF_3 ($+28.5 \times 10^3$ dyn cm^{-1}). The nature of the ligands that surround the σ-bonded metal M clearly affects the amplitude of the electron density variation between M and the chromium atom. For instance, the value of $k_M - k_H$ for the μ-chloro bridged complex of Pd(II), **11**, is seven times larger than that of complex **10**, which bears a Pd(II) atom chelated by a σ-donor diphosphine ligand. A similar comparison can be made for the two Hg(II) complexes **19** and **24** (Chart 2). In other terms, the electronic effects of ligands coordinated to the metal center M σ-bonded to the arene ligand are readily transmitted via M to the CO ligands borne by the $Cr(CO)_3$ moiety and essentially through the σ-bond framework.

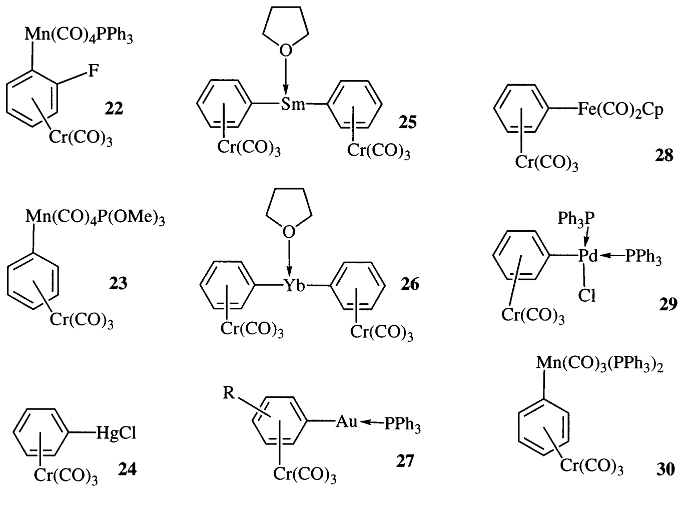


Chart 2.

Table 2
Effect of the metalation of (η^6-arene)$Cr(CO)_3$ complexes on the CO bond stretching force constant

Compound	k_M (10^6 dyn cm^{-1})	k_H (10^6 dyn cm^{-1})	$k_M - k_H$ (10^3 dyn cm^{-1})	{M}	Reference
1	1.447	1.461 [a]	−14	–$Fe(CO)_2Cp$	[59]
2	1.458	1.475 [a]	−17	–$Fe(CO)_2Cp$	[56]
6	1.457	1.489 [b]	−32	–$TiClCp_2$	[51b]
7	1.451	1.481 [b]	−30	–$TiClCp_2$	[51a]
8	1.466	1.503 [b]	−37	–$TiClCp_2$	[51a]
9	1.428	1.455 [b]	−27	–$TiClCp_2$	[51c]
10	1.420	1.462 [a]	−42	–PdCl(dppe)	[67]
11	1.456	1.462 [a]	−6	–PdCl(μ-Cl)PCy_3	[67]
19	1.444	1.462 [a]	−18	–Hg–	[41]
21	1.407	1.489 [b]	−82	1,3,5-(–$Fe(CO)_2Cp)_3$	[79]
22	1.464	1.503 [b]	−39	–$Mn(CO)_4PPh_3$	[50a]
23	1.464	1.489 [b]	−25	–$Mn(CO)_4P(Ome)_3$	[50a]
24	1.485	1.462 [a]	+23	–HgCl	[65a]
25	1.471	1.484 [c]	−13	–Sm–, · THF	[49]
26	1.484	1.484 [c]	0	–Yb–, · THF	[49]
27	1.463	1.489 [b]	−26	–$AuPPh_3$	[51a]

[a] In KBr.

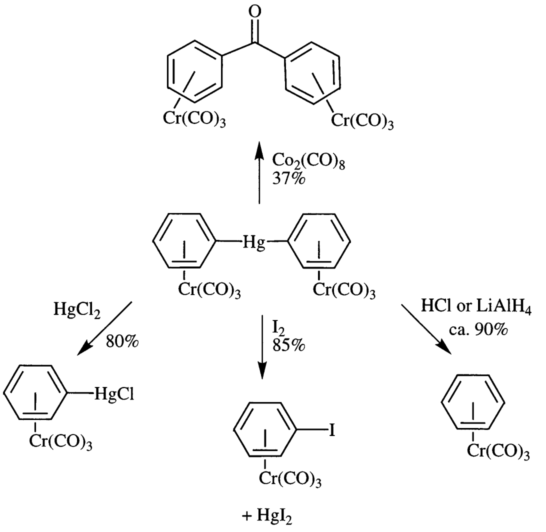
[b] In CH_2Cl_2.

[c] In THF.

Table 3
Comparison of the σ_p Hammett constants of metal-centered substituents {M}, computed from Neuse's relationship, i.e. σ_p^{IR}, with those obtained from ^{19}F-NMR spectra, i.e. $c\sigma_p$

Compound	k_M (10^6 dyn cm^{-1})	σ_p^{IR}	$c\sigma_p$	{M}
6	1.457	−0.74	–	–$TiClCp_2$
23	1.464	−0.58	−0.57	–$Mn(CO)_4P(OMe)_3$
28	1.452	−0.83	−0.65	–$Fe(CO)_2Cp$
30	1.480	−0.23	–	–$Mn(CO)_3(PPh_3)_2$
27	1.463	−0.61	−0.22 [a]	–$AuPPh_3$

[a] Determined in benzene.



Scheme 25.

It is well established that the carbonyl C–O bond stretching force constants k_M of (η^6-arene)$Cr(CO)_3$ complexes correlate with the substituent-parameters such as Hammett's σ_p constants. Neuse [95] established that the correlation of the k_M values with the corresponding σ_p constants of about 28 mono-substituted complexes analyzed in CH_2Cl_2 was particularly satisfactory (correlation coefficient: 0.957). He demonstrated that the two parameters were linked by the following linear relationship (k_M in dyn cm^{-1}):

$$k_M = (14.906 + 0.456 \times \sigma_p^M) \times 10^5$$

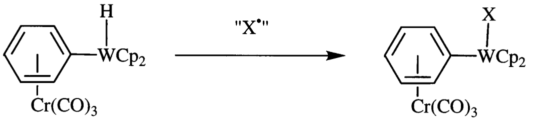
From this equation and from the k_M data determined from IR spectroscopic investigations of metalated and mono-substituted (η^6-arene)$Cr(CO)_3$ complexes, one may estimate the values of Hammett's σ_p constants of a series of transition metal centered substituents. The values of k_M, the σ_p constants established elsewhere from ^{19}F-NMR measurements [96] (written $c\sigma_p$), and the σ_p^{IR} constants computed with help of the relationship established by Neuse are given in Table 3. The latter equation yields −0.58 as the value of σ_p^M for –$Mn(CO)_4P(OMe)_3$ in complex **23**, which is consistent with that established by ^{19}F-NMR spectroscopy (−0.57). Similarly, a value of −0.83 for σ_p^M of –$Fe(CO)_2Cp$ in complex **28** compares reasonably well with that determined by ^{19}F-NMR spectroscopy ($c\sigma_p = -0.65$).

Similarly to the results obtained by Fedorov et al. for complexes substituted by the classical organic groups [97], Hunter and co-workers pointed out that the ^{13}C resonance of the $Cr(CO)_3$ tripod CO ligands is somewhat sensitive to the electronic effects of the transition metal σ-bonded to the bridging arene ligand [79b]. The electrochemical behavior (mostly oxidation) of the various metalated (η^6-arene)$Cr(CO)_3$ complexes has been studied intensively by Hunter and co-workers [98] and reviewed faithfully by Lotz and co-workers [5].

4. Stoichiometric reactions of Li-free metalated (η^6-arene)$Cr(CO)_3$ complexes

Organomercury derivatives of (η^6-arene)$Cr(CO)_3$ complexes have received limited attention probably owing to the famous toxicity of Hg compounds. Razuvaev et al. reported that $[(\eta^6\text{-}C_6H_5)Cr(CO)_3]_2Hg$ could react with $HgCl_2$ to afford in 80% yield (Scheme 25) the corresponding chloromercurio derivative $[(\eta^6\text{-}C_6H_5)Cr(CO)_3]HgCl$ [40]. Similarly, treatment of $[(\eta^6\text{-}C_6H_5)Cr(CO)_3]_2Hg$ with I_2 would afford surprisingly in 85% yield the iodobenzene chromium complex $(\eta^6\text{-}C_6H_5I)Cr(CO)_3$ (Scheme 25) [40]. Removal of mercury from the starting $[(\eta^6\text{-}C_6H_5)Cr(CO)_3]_2Hg$ could be carried out either by treatment with dry HCl or $LiAlH_4$. Seyferth and co-workers synthesized in one step the binuclear benzophenone complex $[(\eta^6\text{-}C_6H_5)Cr(CO)_3]_2C{=}O$ in 37% yield from a reaction between $[(\eta^6\text{-}C_6H_5)Cr(CO)_3]_2Hg$ and $Co_2(CO)_8$ (Scheme 25) [99].

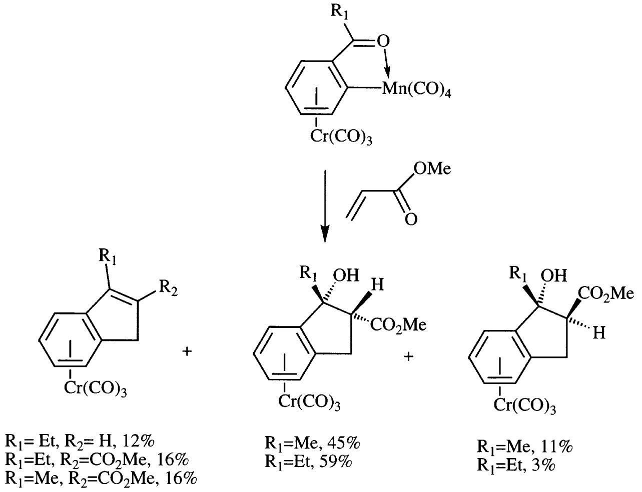
Smirnov et al. reacted $[(\eta^6\text{-}C_6H_5)Cr(CO)_3](H)WCp_2$ with various soft sources of the halogen radical X$^\bullet$ such as CCl_4, $CHBr_3$, and CH_3I [43]. The authors recovered the corresponding $[(\eta^6\text{-}C_6H_5)Cr(CO)_3](X)WCp_2$ products in 80, 76 and 71% yield, respectively (Eq. (26)).



(26)

sources of X$^\bullet$ (yields): CCl_4 (80%), $CHBr_3$ (76%), CH_3I (71%)

Clark et al. studied the reactivity of a series of cyclomanganated chromium complexes of acetophenone and benzaldehyde derivatives towards alkenes and alkynes in order to verify whether the $Cr(CO)_3$ could operate a stereochemical control over the so-called 'insertion' reaction of an alkene-or-alkyne into the C_{Ar}–Mn bond or not [71]. It is indeed well established that mononuclear cyclomanganated aromatic ketones may interact with alkynes to afford the metal-free indenol and indene derivatives with irreversible oxidation of the Mn(I) center. A series of experiments carried out with cyclomanganated $[(\eta^6\text{-}C_6H_5)Cr(CO)_3](R)C{=}O$ (R = Me, Et) and $H_2C{=}CH{-}C(O)OMe$ afforded the corresponding substituted indene and indanol chromium complexes with a reasonable conversion (Eqs. (27) and (28)). However, indanol derivatives were formed with moderate diastereoselectivity. The reaction of the cyclomanganated derivative of $[(\eta^6\text{-}C_6H_5)Cr(CO)_3](Et)C{=}O$ with either Ph–C≡C–CPh or Et–C≡C–Et afforded in 92% yield the corresponding indenol derivatives.



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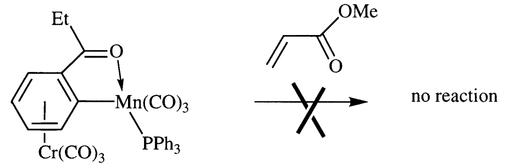
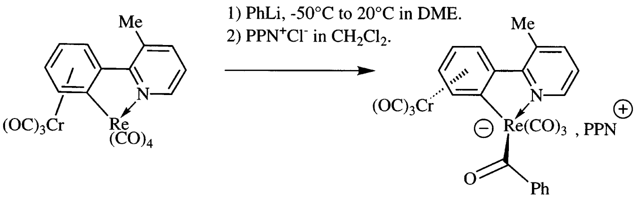
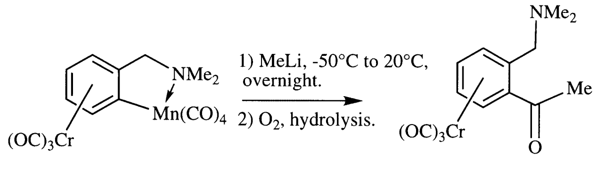


(28)

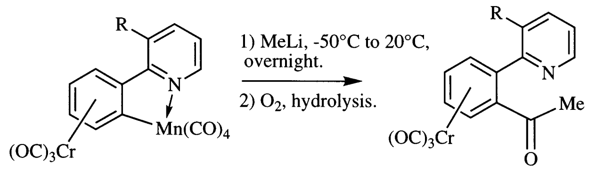
Cyclomanganated 2-phenylpyridine, and *N*,*N*-dimethylbenzylamine derivatives reacted readily with organolithium reagents to afford temperature sensitive acylmanganate species (Eq. (29)) [75,100]. The latter were shown to decompose at room temperature via a reductive-elimination process that affords the corresponding *ortho*-substituted aromatic ketones (Eqs. (30) and (31)).



(29)

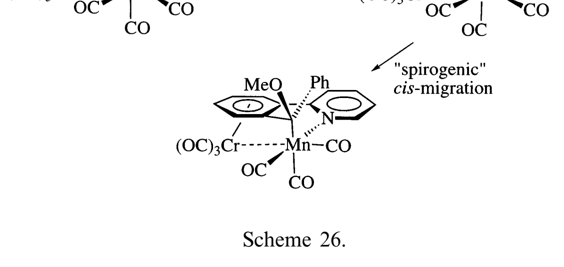


(30)



(31)

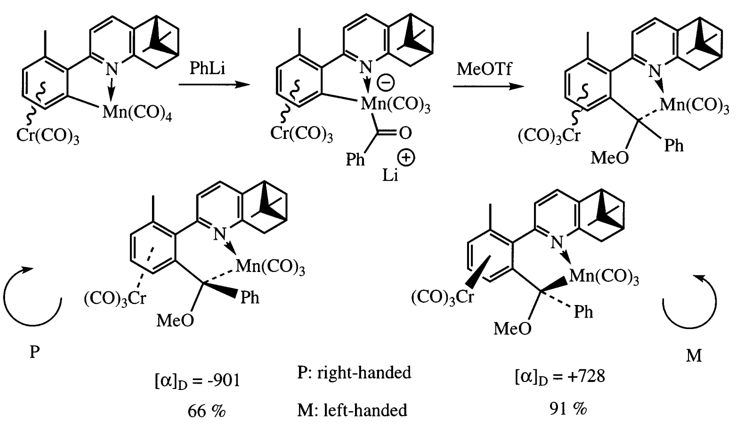
The regioselectivity of the nucleophilic attack of RLi to a CO ligand of the chelated $M(CO)_4$ group has been established on the basis of spectroscopic and X-ray diffraction investigations with a rhenium(I) complex (Eq. (29)). It has been shown that the addition of RLi occurs at the axial CO ligand located on the side opposite to the bulky $Cr(CO)_3$ moiety. The acylmanganate species may have another fate than decomposition if submitted to a hard alkylating agent. When the former anions were treated with MeOTf at low temperature, an *O*-alkylation reaction lead to a transient manganese(I) alkoxyphenylcarbene species that underwent the *cis*-migration of the vicinal aryl group π-coordinated by the $Cr(CO)_3$ moiety [101] and leading eventually to a stable product (Scheme 26). The latter, also accounted for as a 'Cr/Mn-spiralene' is a *syn*-facial heterobimetallic helical molecule (Fig. 4).



Scheme 26.

This structural feature stems from the spiroidal arrangement of the organic ligand around the C_{benzyl}–Mn axis. In this class of compounds, the two metals seem to interact electronically via a weak dative bond. The rotation of the $Cr(CO)_3$ tripod is sterically hindered by the proximal static $Mn(CO)_3$ fragment. The barrier to rotation of the tripod at 213 K of 15 kcal mol^{-1} has been determined with a ^{13}CO enriched sample [102]. Chiral 'Cr/Mn-spiralenes' of *P* and *M* helicity have recently been synthesized separately starting from the two diastereomeric chiral 2-phenyl-pyridine chromium complex derived from (−)-β-pinene (Scheme 27) [103].

It has been shown that cyclomanganated (η^6-arene)$Cr(CO)_3$ complexes derived from 2-phenyl-



Scheme 27.

pyridine react also with $Ph_2C{=}N_2$ in refluxing heptane to afford cleanly and in good yields the corresponding ‘Cr/Mn-spiralenes’ (Scheme 28) [103]. The reaction possibly involves first the decoordination of a CO ligand and secondly the coordination of the diazoalkane. Evolution of N_2 produces a highly reactive manganese(I) diphenylcarbene that undergoes *cis*-migration to yield the final ‘Cr/Mn-spiralene’.

5. Perspectives

The (η^6-arene)$Cr(CO)_3$ complexes differ from their chromium-free analogs in a variety of new transformations made possible because of the electron-withdrawing effect of and the stereochemical control introduced by the $Cr(CO)_3$ moiety. Two classes of applications have appeared: (1) those that use the $Cr(CO)_3$ group as an auxiliary that may be removed eventually upon completion of a sequence of reactions; and (2) those that aim at designing novel molecules incorporating a $Cr(CO)_3$ moiety and possessing specific stereochemical properties. For about 30 years, lithiated intermediates have been on the focus of ‘organic synthesis-oriented’ chemists. From the beginning of the 1990s until now, the design of planar chiral molecules justified further studies, among which many studies evolved towards the improvement of softer C_{Ar}–C bond-forming reactions offering a wider functional compatibility. Nevertheless arousing the interest of chemists, palladium-mediated cross-coupling reactions applied to (η^6-arene)$Cr(CO)_3$ complexes open new perspectives for the activation of C_{Ar}–Cl bonds. These catalyzed reactions also provide an effective tool for the stereoselective synthesis of new molecules possessing planar, axial and other types of asymmetry. However, attention should be drawn on the frailty of the $Cr(CO)_3$ group particularly when exposed to oxidizing agents [104], which may confine the application of the corresponding complexes to processes operating in relatively soft catalytic conditions. Apart from some fundamental investigations of physico-chemical properties (η^6-arene)$Cr(CO)_3$ complexes that encompass a σ-bonded transition metal have not inspired thorough synthetic applications. This tendency could significantly change in the near future given the increasing demand for both novel and elaborate organometallic molecules having a high potential for applications in optoelectronics and material sciences [105].

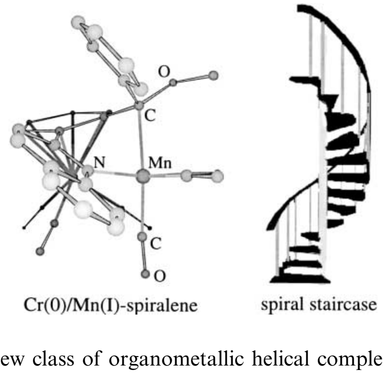
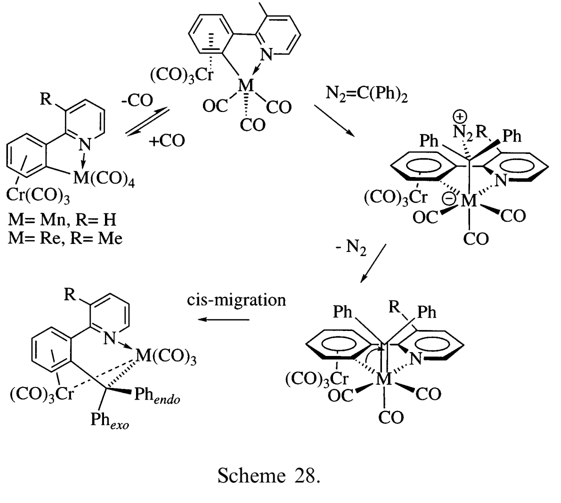


Fig. 4. A new class of organometallic helical complexes, the metallo-spiralenes.



Scheme 28.

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