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Tetrahedron
Tetrahedron 60 (2004) 3325–3347

Tetrahedron report number 676

Bimetallic Pd/Cr and Pd/Mn activation of carbon–halide bonds in organochromium and organomanganese complexes

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Received 19 December 2003

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1. Introduction

Activation of haloarene, halocyclopentadienyl (Cp) or halocyclohexadienyl (Ch) carbon–halide bonds using palladium-catalysed reactions and coordination of the organic ligand to tricarbonyl-chromium or -manganese moieties is now commonly defined as bimetallic Pd/Cr or Pd/Mn activation.[1,2] A combination of the two transition metals greatly expanded the scope of arene–chromium and -manganese chemistry and allowed completion of the reactivity panel of organo-chromium and -manganese complexes.

It is well established that the presence of a tricarbonyl–Cr or -Mn fragment dramatically activates the carbon–halogen bond and opens up the possibilities for nucleophilic attack.[3–7] The very high electrophilicity of these complexes has been exemplified and gave rise to an unprecedented and convenient access to numerous natural products[8–14] and elaborated polymetallic structures with potential applications in materials science.[15–18] Despite intense research, however, the preparation and reactivity of such complexes still lack generality and selective access to vinyl, alkynyl, aryl and electron-withdrawing group (EWG) substituted complexes remains unsolved. Indeed, direct complexation of phenyl-substituted alkynes, alkenes or arenes generally proceeds with low yields and with poor chemo- and regioselectivity. Additionally, the low electronic density of aromatics bearing EWGs prevents direct complexation of the metal.

Keywords: Bimetallic activation; Palladium-catalysed reactions; Organomanganese complexes; Organochromium complexes.
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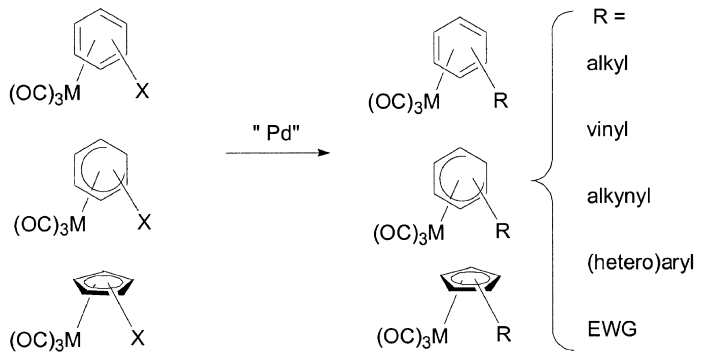
0040–4020/$ - see front matter
doi:10.1016/j.tet.2004.02.002



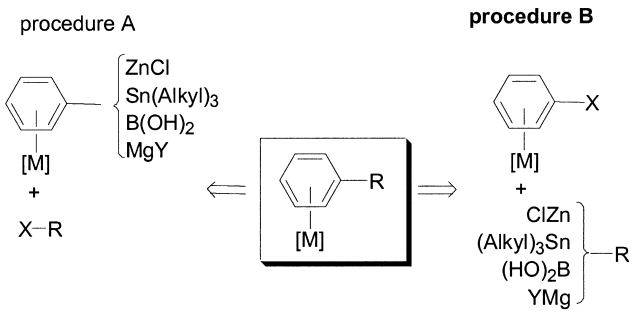
Scheme 1.

In 1985, Villemin[19] first proposed a palladium-catalysed selective and elegant access to phenylalkyne–tricarbonylchromium complexes. Undoubtedly, this pioneering work signalled the early beginnings of a tremendous amount of studies on bimetallic activation of arenes. Since these studies, the scope of bimetallic Cr/Pd activation has not only been applied to the introduction of substituents on arene rings, but has also been employed with Cp and Ch substrates. More recently, the less toxic Mn/Pd combination has been reported to be efficient for the introduction of various substituents on organic ligands. Although a few other bimetallic combinations involving metal carbonyl complexes ($Re(CO)_3$,[20–23] $Mo(CO)_3Me$,[22,23] $W(CO)_3Me$,[22–24] $Fe(CO)_2Me$[22–24] and $Fe(CO)_3$.[25–30]) and palladium are reported in the literature, this article intends to overview palladium-catalysed introduction of sp, sp^2 and sp^3 carbon-based substituents and soft nucleophiles (O-, N-, P- and S-based) on η^6-organochromium complexes and on η^5- and η^6-organomanganese complexes (Scheme 1). The literature is covered up to the begining of 2003.

2. Coupling partners

Palladium-catalysed carbon–carbon bond formation between two partners including an arene–tricarbonylmetal complex can be envisioned owing to two retrosynthetic disconnections: coupling of the (metalloaryl)$M(CO)_3$ with R-halide according to procedure A or coupling of (haloaryl)$M(CO)_3$ with R-metal as illustrated in procedure B (Scheme 2).

Although, in the case of chromium complexes, some type A procedures were successful,[31,32] they mainly afforded the expected coupling product in poor yield or led to demetallation or even no reaction.[33,34] As a consequence, this review will only focus on the type B procedures.

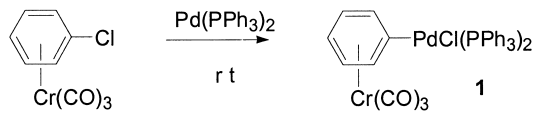


Scheme 2.

3. Pd/Cr Bimetallic activation

3.1. Oxidative addition

The $(\eta^6\text{-}C_6H_5R)Cr(CO)_3$ unit behaves as a strongly EWG.[3–7,35] The withdrawing ability of the $Cr(CO)_3$ moiety being generally comparable to a nitro group.[4] It has been reported that the oxidative addition of the carbon–halogen bond of an aryl halide to palladium(0) is dramatically accelerated by coordination of the highly electrophilic $Cr(CO)_3$ fragment to the arene ring.[36] Indeed, whereas the oxidative addition of chlorobenzene to palladium(0) species requires either elevated temperatures[37] or the use of elaborated basic and bulky phosphine ligands,[38,39] the presence of the $Cr(CO)_3$ fragment allows oxidative addition to take place at room temperature on $(\eta^6\text{-}C_6H_5Cl)Cr(CO)_3$, furnishing complex **1** (Scheme 3).[37]

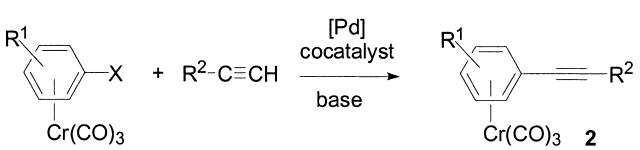


Scheme 3.

Moreover, due to the presence of the $Cr(CO)_3$ fragment, complexed chloroarenes have been shown to react about 15-fold faster than the free iodoarenes in palladium-catalysed carbon–carbon bond formation reactions under very mild experimental conditions.[40]

3.2. Introduction of alkynyl groups

3.2.1. Sonogashira reaction. Alkynylated $(\eta^6$-arene)-$Cr(CO)_3$ complexes **2** have received much attention in



Scheme 4.

Table 1. Coupling conditions for the preparation of alkynylated complexes using the Sonogashira procedure

Entry	R^1	X	R^2	Conditions	Yield (%)	Reference
1	H	Cl	H, $SiMe_3$, Ph, $CH(OH)Ph$, $C(OH)Ph_2$, $(CH_2)_8CO_2H$	$Pd(PPh_3)_4$ or $PdCl_2(PPh_3)_2$, Et_3N, CuI, 18 h, rt	80–92	18,19,41,42, 46
2	*m*- and *p*-NMe_2, *m*- and *p*-^{t}Bu	I	$SiMe_3$	$Pd(PPh_3)_4$, Et_3N, CuI, 16 h, rt	[a]	46
3	H	Cl	Ph, 4-NO_2Ph, 4-MeOPh, 4-NMe_2Ph, 2-thienyl, 2-furyl, ferrocenyl	$PdCl_2(PPh_3)_2$, Et_3N, THF, CuI, 18 h, rt or reflux	58–91	35
4	H, *o*-, *m*- and *p*-Me	Cl	CH_2OH, $C(OH)Me_2$, $C(OH)Ph_2$,$C(OH)(CH_2)_5$	$PdCl_2(PPh_3)_2$, Et_3N, THF, CuI, 18 h, reflux	69-quant.	43,44
5	*o*-$CH(OMe)_2$	I	$SiMe_3$	$PdCl_2(PPh_3)_2$, Et_3N, THF, CuI, 18 h, reflux	69	45
6	H	Cl	$(\eta^6\text{-}C_6H_5)Cr(CO)_3$	$Pd(PPh_3)_4$, Et_3N, CuI, 24 h, reflux	34	42

[a] Yields not indicated.

recent years, due to their beneficial introduction into building blocks with potential application in materials science.[18,35,41] In this context, most studies were devoted to the palladium-catalysed coupling methodologies, which allow highly chemo- and regioselective alternatives over direct complexation (Scheme 4).

Indeed, classical direct complexation does not tolerate alkyne substituents[42] and thus affords phenylacetylene complexes in low yields (<5%).[19] The Sonogashira procedure appeared to be the most appropriate approach to the regioselective preparation of alkynylated complexes **2** in good to excellent yields (Table 1). The starting arene complexes were usually unsubstituted or substituted by electron-releasing groups and both chloro- and iodoarene complexes were used. Coupling of trimethylsilyl-, aromatic, heteroaromatic and organometallic acetylenes furnished the expected alkynylated complexes. In addition, variously substituted propargylic alcohols were successfully used (entries 1 and 4).[43,44]

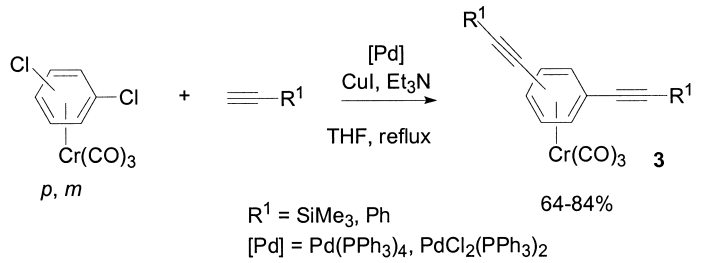
Generally, the catalytic systems are based on Pd(0) or Pd(II) species in combination with CuI as cocatalyst and triethylamine as base in THF. It is noteworthy that some interesting difunctional planar chiral arenes were also obtained using this methodology (entry 5).[45]

Dialkynylated $(\eta^6\text{-arene})Cr(CO)_3$ complexes **3** were efficiently prepared from 1,3- and 1,4-(dichlorobenzene)$Cr(CO)_3$ complexes through 'one-pot' bis-Sonogashira coupling (Scheme 5).[45] High yields (64–84%) of the dicoupled adducts were obtained using either Pd(0) or Pd(II) precatalysts in classical coupling conditions.

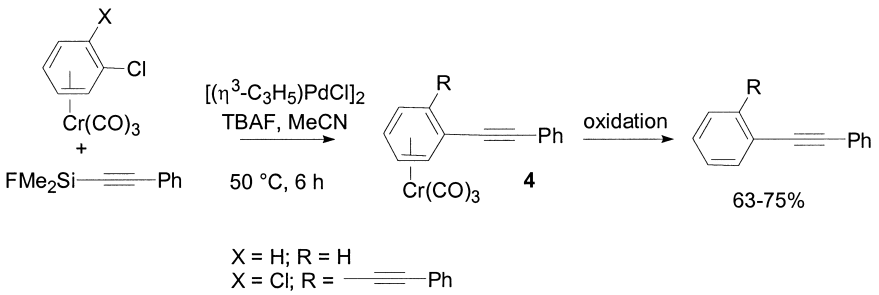
$Cr(CO)_3$-complexed mono- and dichloroarenes were also used in cross-coupling reactions involving organofluorosilanes (Scheme 6).[47] In this case, mono- and di- 'sila type' Sonogashira reactions took place in the presence of $[(\eta^3\text{-}C_3H_5)PdCl]_2$ and TBAF as a fluoride source. The complexed alkynylated adducts **4** were obtained as intermediates, but they immediately reacted with iodine, affording the free acetylenic ligands in 63–75% yield.

Recently, Müller[40] reported the first Sonogashira coupling reaction of the $(\eta^6\text{-chlorobenzene})Cr(CO)_2PPh_3$ complex **5** with terminal alkynes (Scheme 7). Although replacing the CO residue by a phosphane ligand reduced the electron-withdrawing ability of the metallic fragment, the $(\eta^6\text{-chlorobenzene})Cr(CO)_2PPh_3$ complexes were found to be efficient coupling partners. Nevertheless, as a consequence of the reduced electron-withdrawing ability, longer reaction times were required to ensure completion of the coupling and formation of the products **6**.

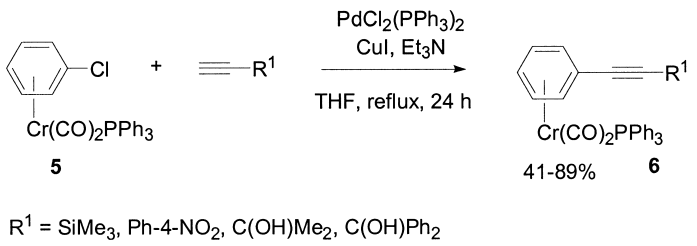
Alkynyl$(\eta^6\text{-arene})Cr(CO)_3$ complexes **7** obtained using a Sonogashira coupling reaction between $(\eta^6\text{-}C_6H_5Cl)Cr(CO)_3$ and propargylic alcohols have recently been shown to undergo base-catalysed isomerisation into the final enone **9** through an allenol intermediate **8** in a one-pot coupling-isomerisation sequence (Scheme 8).[48] Moreover, starting from the same coupling partners, addition of hydrazine after completion of the coupling-isomerisation sequence allowed



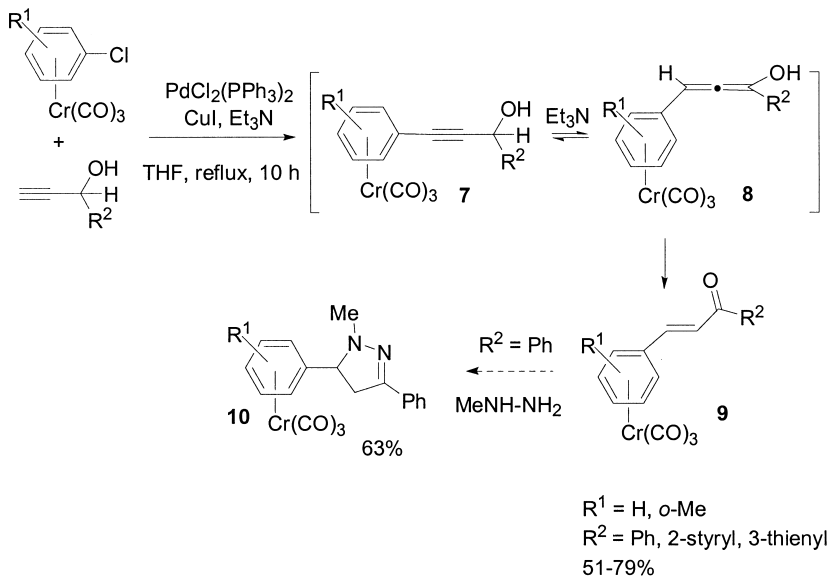
Scheme 5.



Scheme 6.



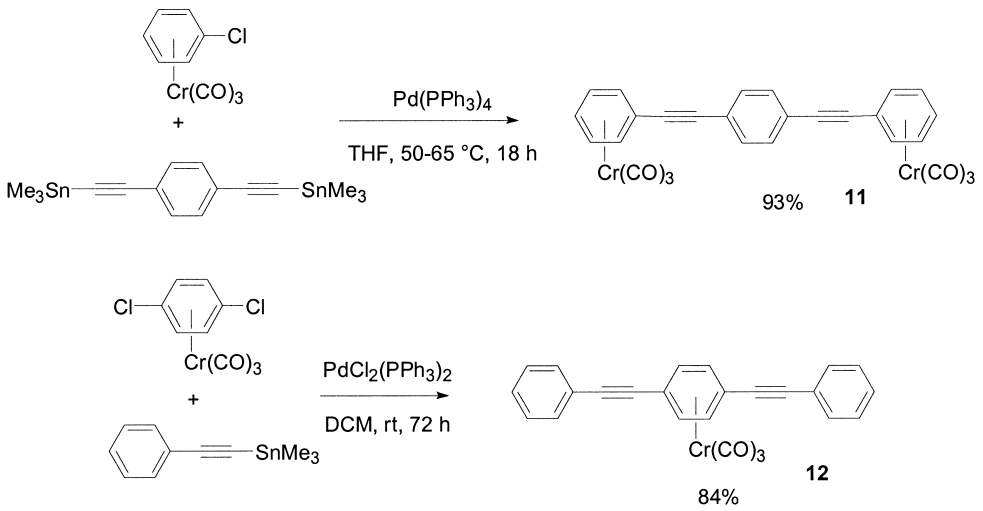
Scheme 7.



Scheme 8.

a one-pot three-component access to the substituted pyrazolines **10**.

3.2.2. Stille reaction. Complementary to the Sonogashira methodology, Stille couplings between trimethylstannyl-acetylenes and $(\eta^6\text{-}C_6H_5Cl)Cr(CO)_3$ have been used to prepare organometallic-substituted acetylenes (Scheme 9). In one example, two molar equivalents of $(\eta^6\text{-}C_6H_5Cl)$-$Cr(CO)_3$ were reacted with 1,4-di-(trimethylstannyl-ethynyl)benzene, affording the corresponding dichromium

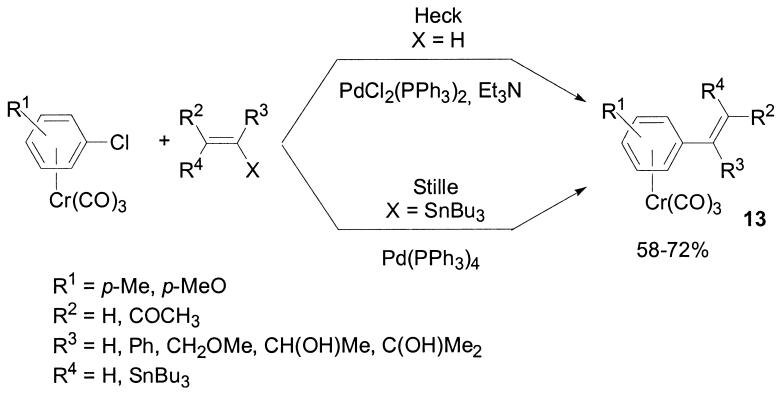


Scheme 9.

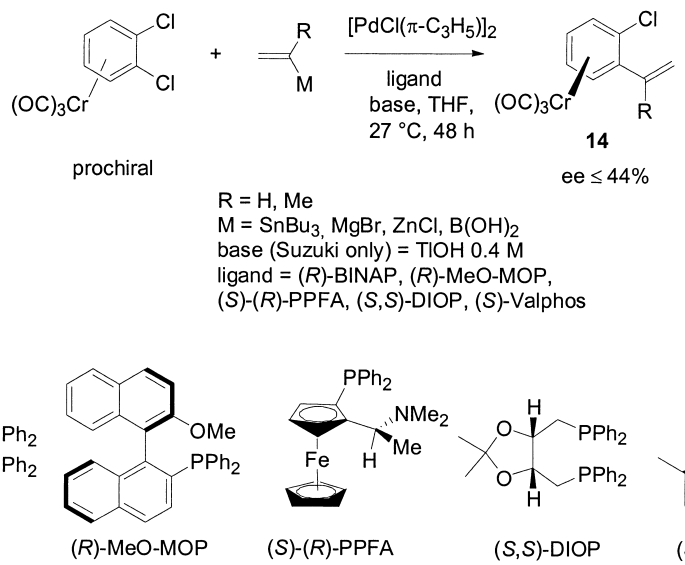
complex **11** in 93% yield.[49] Similar couplings using complexed 1,4-dichlorobenzene and trimethylethynylphenylstannane gave the corresponding monochromium complex **12** in 84% yield.[50]

3.3. Introduction of alkenyl groups

Stille reactions and Heck olefinations have been described to introduce vinyl substituents using vinylstannanes and



Scheme 10.



Scheme 11.

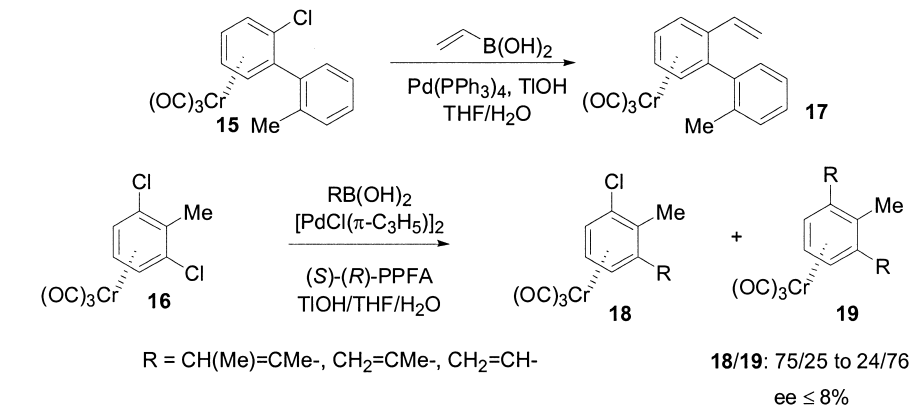
alkenes, respectively. Treatment of methyl vinyl ketone under typical Heck olefination conditions afforded the desired keto complex **13** (Scheme 10; R^2=COMe, R^3=R^4=H, X=H) in 58% yield.[51,52]

Variously substituted styrene complexes **13** could be selectively prepared in high yield by reacting (η^6-C_6H_5Cl)-$Cr(CO)_3$ complexes with vinylstannanes in the presence of Pd(0).[51,53]

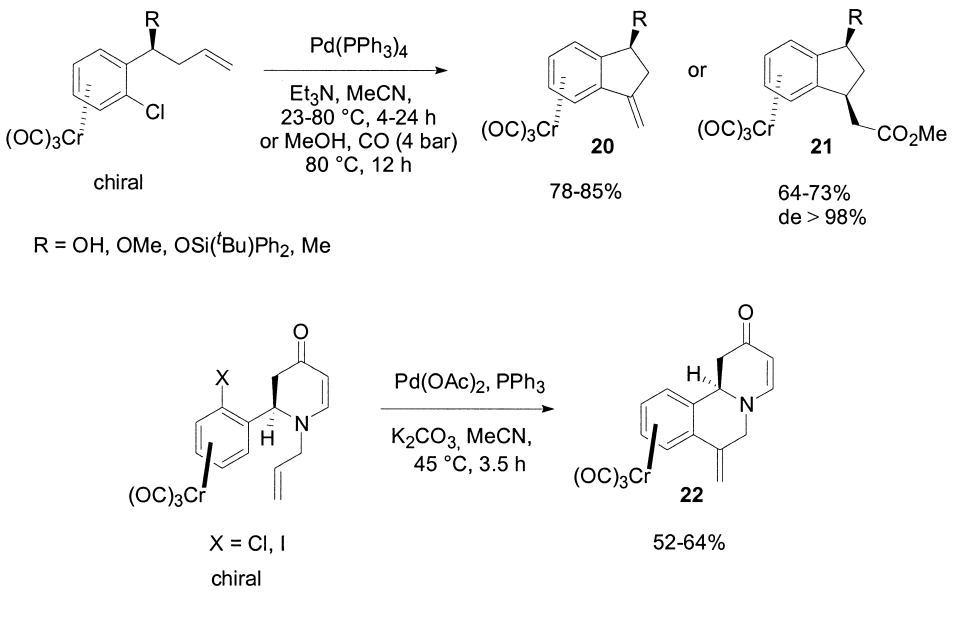
Planar chiral complexes were obtained from prochiral precursors such as (η^6-dichlorobenzene)$Cr(CO)_3$ complex shown in Scheme 11 and the palladium-catalysed mono-substitution of one of the enantiotopic chlorine atoms in this complex affords the optically active complexes **14**. These chiral complexes were obtained in moderate enantioselectivity (up to 44% ee) under Stille (Sn), Corriu-Kumada-Tamao (Mg), Negishi (Zn) or Suzuki (B) conditions, using chiral ligands.[54,55]

Uemura also investigated the couplings between vinyl-metals and enantiomerically pure tricarbonylchromium complexes.[56] He particularly exemplified the enantio-selective couplings of chloro- **15** or dichlorobenzene **16** tricarbonylchromium complexes with various vinyl boronic acids to afford complexes **17**-**19** (Scheme 12).

An intramolecular version of Heck olefination has only recently attracted much attention and it has been shown that $Cr(CO)_3$ complexes successfully undergo an



Scheme 12.

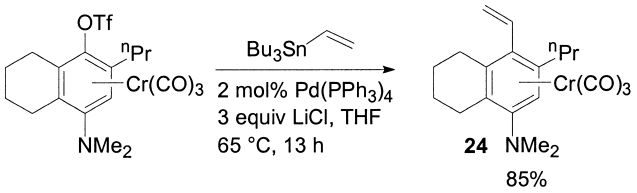


Scheme 13.

intramolecular palladium-catalysed Heck reaction, affording indane, (*iso*)quinolines and benzofuran heterocyclic complexes (Scheme 13).

Kündig first showed that palladium-catalysed intramolecular cyclisations could be performed without decomplexation. Under classical Heck conditions, the methyleneindane complexes **20** were obtained keeping the stereogenic benzylic centre intact.[57,58] Trapping the alkylpalladium species under carbonylative conditions in methanol selectively afforded a single methyl ester diastereomer **21**. The same strategy using the enantiomerically pure chromium complex gave the enantiopure hydro(*iso*)quinolines **22**,[59] whilst the benzofuran skeleton **23** was prepared from the dichloroaryl ether complex in 47% yield under classical Heck conditions.[60]

Another interesting feature of the tricarbonylchromium complexation is illustrated in the preparation of vinyl tricarbonyl complexes from triflates. It is well known that the cross-coupling between electron-rich aryl triflates and stannanes generally requires extreme conditions, but proceeds rather smoothly when a tricarbonyl-chromium moiety is coordinated to the arene. Using this approach, in 1994, Wulff reported that the cross-coupling between a tricarbonylchromium-complexed electron rich arene triflate and a vinylstannane affords compound **24** in excellent yields (Scheme 14).[61]



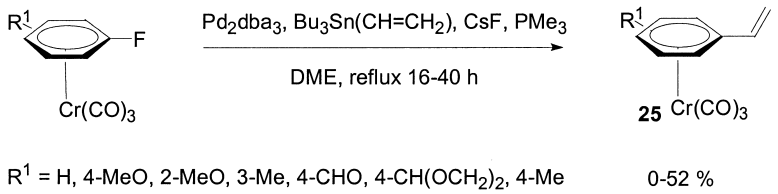
Scheme 14.

Stille olefinations involving (fluoroarene)tricarbonylchromium complexes were also reported by Widdowson (Scheme 15).[62] The coupled adducts **25** were, however, isolated in poor to moderate yields (0–52%). For a general discussion about the use of C–F bonds, see Scheme 32.

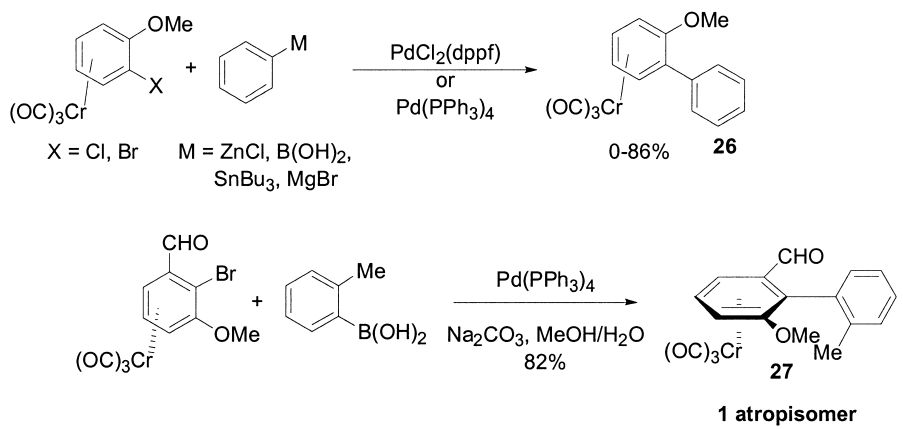
3.4. Introduction of aryl groups

Biphenyl and binaphthyl derivatives are not only attractive compounds as chiral ligands for asymmetric reactions, but are also commonly found in biologically active natural compounds. It has been extensively demonstrated that the presence of a chromium-coordinated arene ligand drastically influences the regioselectivity of chemical reactions on the arene, but also allows unexpected reactions such as aromatic nucleophilic substitutions.[4] Additionally, the coordination of a $Cr(CO)_3$ moiety to a phenyl group differentiates the two prochiral faces of *ortho*- or *meta*-disubstituted arenes and induces a planar chirality. As a consequence, the monochromium complexes of *ortho*- or *meta*-disubstituted biphenyl compounds are expected to exhibit both axial and planar chiralities that could be useful in asymmetric reactions. Since the selective tricarbonylchromium complexation of a biphenyl compound remains elusive and leads to complex mixtures,[63] direct couplings between an arenechromium complex and another arene would provide an elegant route to elaborated biphenyl complexes.

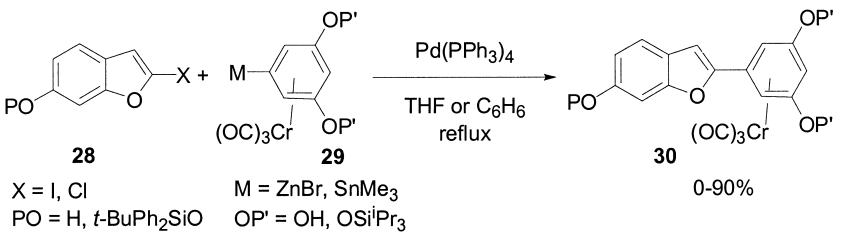
One of the first report describing this approach appeared in 1994 when Uemura et al. described the palladium-catalysed coupling between a haloarene and a metallated (Zn, B, Sn or Mg) species (Scheme 16).[63,64] The expected monochromium biphenyl complex **26** was isolated in poor to excellent yields (up to 86%), along with the dehalogenated or the demetallated arenechromium complex. The best result was obtained by coupling the phenylboronic acid with the



Scheme 15.



Scheme 16.



Scheme 17.

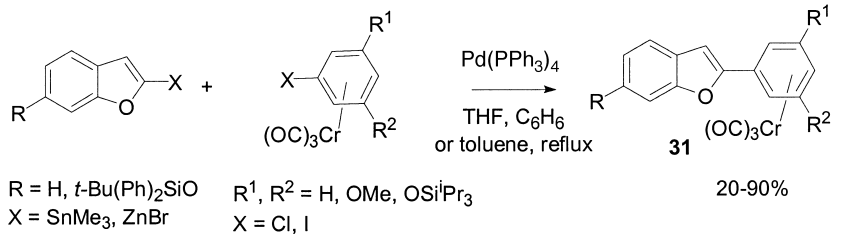
o-bromoanisole chromium complex using $Pd(PPh_3)_4$ as a catalyst in a mixture $MeOH/H_2O$ in the presence of Na_2CO_3.

Interestingly, the stereochemistry of the coupling was investigated for the chiral (3-methoxy-2-bromobenzaldehyde)$Cr(CO)_3$. Using the conditions described above, the expected coupled product **27** was isolated in 82% yield, as a single atropisomer and characterised by X-ray crystallography structure.[63]

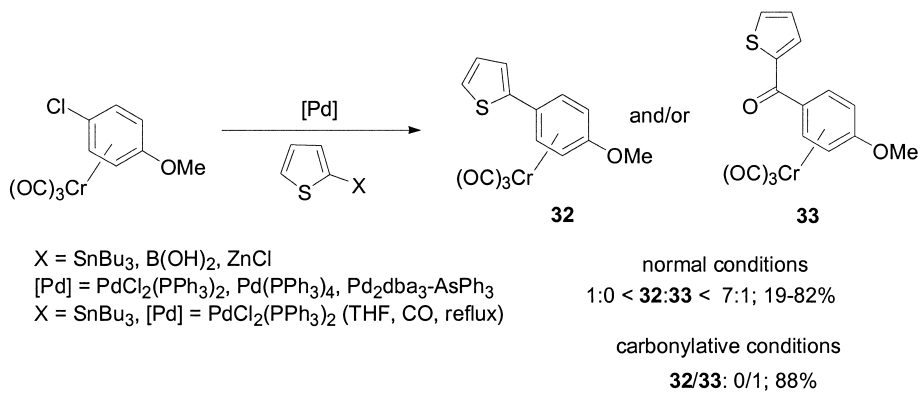
A few years earlier, Widdowson et al. had already investigated the coupling reactions between the halobenzofurans **28** and metallo-resorcinols **29** (Scheme 17).[65] The best conditions were found to involve the triisopropylsilyl-protected iodoresorcinol and a stannylated benzofuran partner. In the presence of $Pd(PPh_3)_4$, the cross-coupling compound **30** was isolated in 90% yield.

Later, the same group investigated further the coupling conditions between 2-trimethylstannyl- or 2-bromozincbenzofurans with the appropriately functionalised 5-iodoresorcinols (Scheme 18).[66] The best coupling conditions appeared to involve the trimethylstannylbenzofurans. Using these conditions, the coupled compounds **31** were isolated in moderate to very good yields (20–90%).

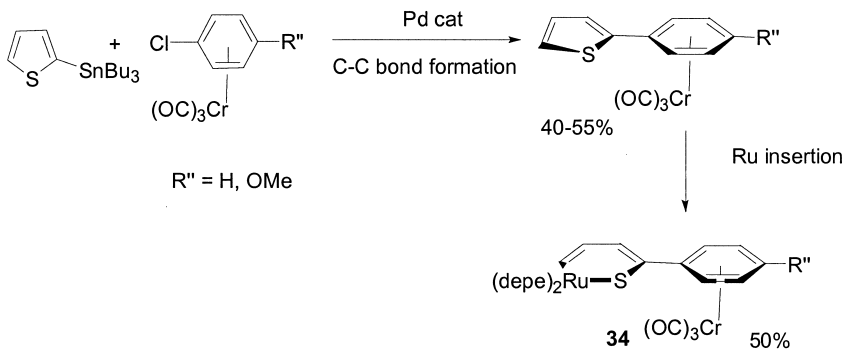
The couplings between heterocycles and tricarbonylchromium complexes have been further studied in recent years. In particular, Rose et al. reported that the couplings between 2-metallated thienyl derivatives (Scheme 19; X=$SnBu_3$, $B(OH)_2$ or ZnCl) and (*p*-chloroanisole)tricarbonylchromium complexes afforded not only the expected tricarbonyl-η^6-[(thiophenyl)arene)] **32**, but also the tricarbonyl-η^6-[(thiophenyl)carbonylarene)] complex **33**, resulting from the insertion of the carbonyl moiety during the coupling (Scheme 19).[67,68] The coupling conditions were investigated and the authors demonstrated that the reaction of stannyl, boronic or zinc derivatives with (*p*-chloroanisole)-chromium complexes generally affords a mixture of the carbonylated and non-carbonylated coupled compounds. The use of the catalytic system $Pd_2(dba)_3$, $AsPh_3$ in DMF at room temperature, however, allowed the exclusive preparation of the expected non-carbonylated species in 82% yield. Additionally, when the reaction was performed under a CO atmosphere in the presence of $PdCl_2(PPh_3)_2$ as the catalyst, only the carbonylated compound was isolated in excellent (88%) yield.



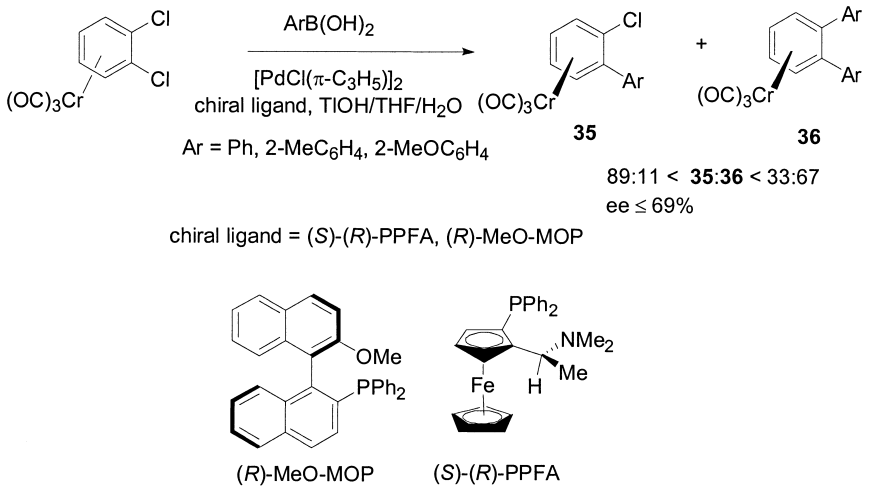
Scheme 18.



Scheme 19.



Scheme 20.

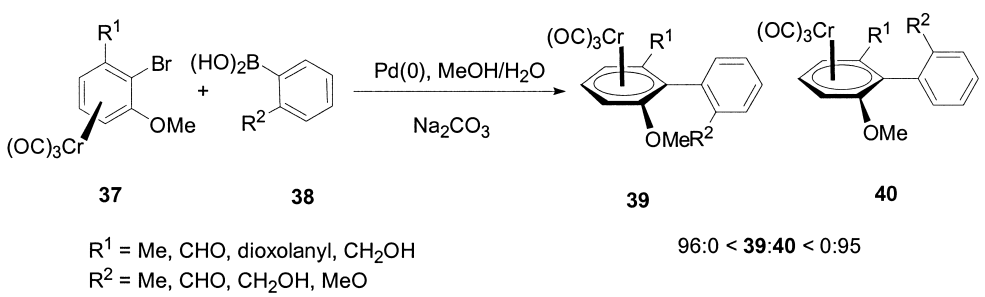


Scheme 21.

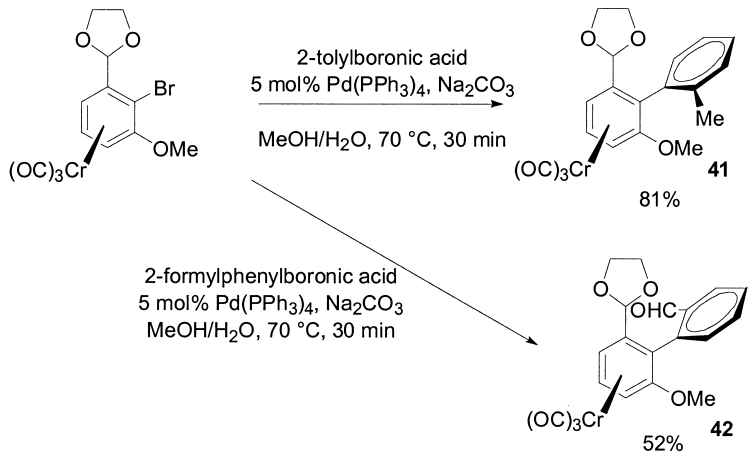
The same group then investigated further the reactivity of the (thienylanisole)chromium complex.[69,70] In particular, the regioselective insertion of ruthenium into the thienyl S–C bond was evidenced (Scheme 20). The arenechromium thiaruthenacycle **34** was isolated in 50% yield and it has been suggested that the regioselectivity of the ruthenium insertion might have been directed by steric factors, as already observed by other workers.[71]

As described earlier, *ortho*- and *meta*-disubstituted arene-chromium complexes exist in two enantiomeric forms and can give rise to biaryl complexes with both planar and axial chiralities. This property has been extensively demonstrated over the years. In 1994, Uemura et al. reported the synthesis of the bi- or triphenyl complexes **35** and **36**, starting from the *ortho*-dichlorobenzenechromium complex (Scheme 21).[56] Under palladium catalysis, the expected biaryl structures were isolated in moderate to good yields with enantiomeric excesses up to 69%.

Following a similar approach, chiral biaryl compounds were prepared using Suzuki coupling conditions.[72] These conditions appeared to be rather effective and were applicable to a wide variety of substrates. The disubstituted anisole-chromium complexes **37**, bearing either electron-withdrawing or electron-releasing groups, were reacted with the *ortho*-substituted boronic acids **38** under palladium catalysis and afforded the coupled compounds **39** and **40** in reasonable to good yield (Scheme 22). During the couplings, the steroselectivity of the reaction appeared to be controlled by the nature of the *ortho*-substituent of the phenylboronic acid used. It is worth noting, however, that



Scheme 22.



Scheme 23.

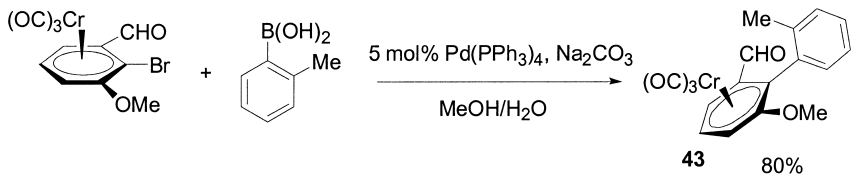
up to 40% of the CO-inserted compound was obtained when R^1=dioxolanyl and R^2=CH_2OH.

This result therefore provides a promising approach for the preparation of the enantiomerically pure biphenyl compounds, with axial chirality, **41** and **42**. The biphenyls obtained using this methodology and depicted in Scheme 23 were recently shown to undergo further selective functionalisation and were isolated as single diastereomers.[73]

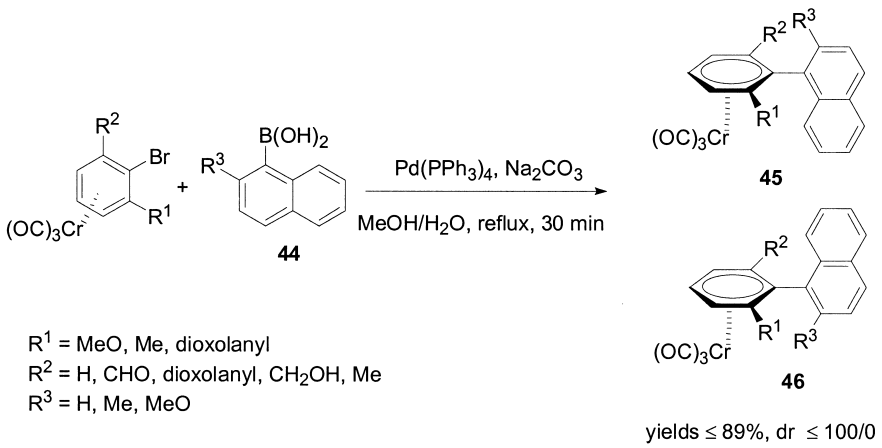
More elaborated structures were prepared using Suzuki cross-coupling[74] and enantiomerically pure (+)-(*R*,*R*)-tricarbonyl[1,2,3,4,5,6-η^6)(2-methoxy-2′-methyl-6-formylbiphenyl]-chromium **43** was synthesised by reacting 2-tolylboronic acid and the enantiomerically pure (−)-(2-bromo-3-methoxybenzaldehyde)chromium complex, under palladium catalysis, in 80% yield (Scheme 24).

The same methodology was successfully applied to the coupling of naphthylboronic acids with substituted arenechromium complexes (Scheme 25).[75] Many natural products including korupensamines or ancistrocladine possess naphthyltetrahydroquinoline substructures in their skeleton. Access to the naphthyl-substituted arenechromium complexes **45** and **46** was successfully achieved by coupling naphthylboronic acids with substituted arenechromium complexes in good to excellent yields. The stereochemistry of the coupling products was also investigated. It appeared that the major coupling compound is the complex **45** (Scheme 25). In this isomer, the naphthalene substituent R^3 lies in the opposite plane with respect to the $Cr(CO)_3$ fragment.

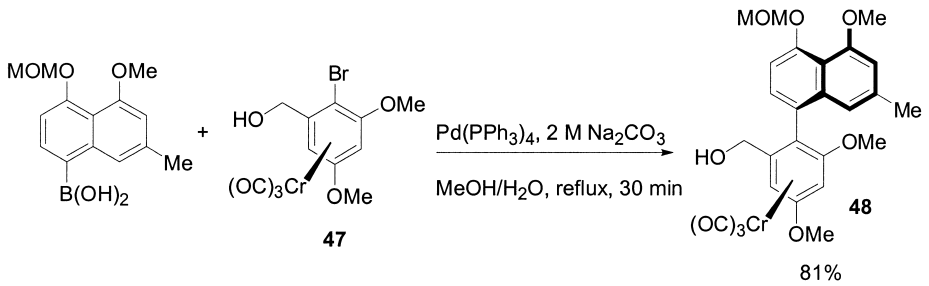
When an enantiomerically pure tricarbonylchromium derivative **47** was used, the coupling compound **48** was



Scheme 24.

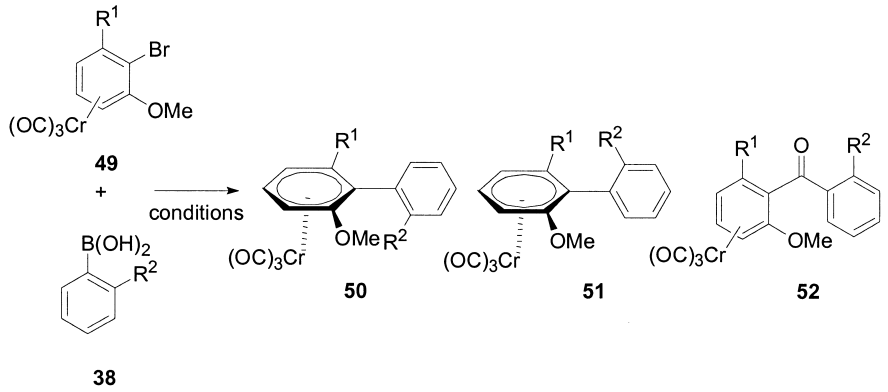


Scheme 25.



Scheme 26.

Table 2. Arylation of arylmetal$Cr(CO)_3$ complexes using phenylboronic acids: selected examples



conditions: $Pd(PPh_3)_4$, Na_2CO_3, $MeOH/H_2O$, reflux 30 min

Entry	Complex	Phenylboronic acid	R^1	R^2	Ratio **50/51/52**	Yield (%)
1	**49a**	**38a**	Me	Me	100:0:0	96
2	**49b**	**38a**	CHO	Me	92:0:8	89
3	**49c**	**38a**	$\overline{CHO(CH_2)_2O}$	Me	100:0:0	81
4	**49d**	**38a**	CH_2OH	Me	100:0:0	77
5	**49a**	**38b**	Me	CHO	0:100:0	95
6	**49b**	**38b**	CHO	CHO	0:100:0	43
7	**49c**	**38b**	$\overline{CHO(CH_2)_2O}$	CHO	0:100:0	52
8	**49a**	**38c**	Me	CH_2OH	81:0:19	68
9	**49c**	**38c**	$\overline{CHO(CH_2)_2O}$	CH_2OH	0:0:100	40[68]
10	**49a**	**38d**	Me	OMe	97:3:0	94
11	**49b**	**38d**	CHO	OMe	4:96:0	85
12	**49d**	**38d**	CH_2OH	OMe	94:6:0	90

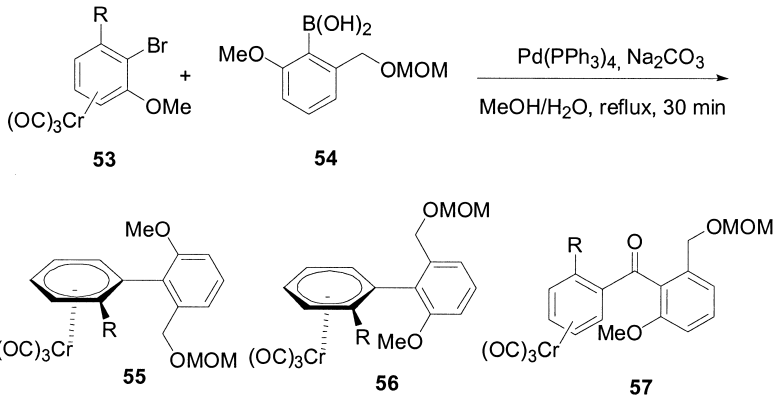
isolated as a single enantiomer without racemisation (Scheme 26).

The use of chiral tricarbonylchromium complexes was then further exemplified. In particular, Uemura et al. reported the stereoselective synthesis of the enantiomers of axially-chiral biaryls using this route.[76] The effects of the different substituents of the coupling partners and the coupling conditions were thoroughly studied (Table 2). As shown in Table 2, Suzuki couplings were proved to be particularly efficient.

The stereoselectivity of the coupling reaction was investigated. From the results gathered in Table 2, it appears that the stereoselectivity of the process is again strictly driven by the bulkiness of the *ortho*-substituents adjacent to the coupling positions. Interestingly, when a 2,6-disubstituted phenylboronic acid **54** was used, the stereochemical differentiation appeared to be lower (Table 3). On the other hand, the reaction of a (2,6-disubstituted aryl halide)$Cr(CO)_3$ **53** with *ortho*-monosubstituted phenylboronic acids proved to be more efficient than the coupling of a monosubstituted aryl halide chromium complex with a disubstituted boronic acid. The authors proposed that the lower yield in the latter coupling reaction could be attributed to the lower propensity for displacement of the palladium intermediate during the transmetallation step.

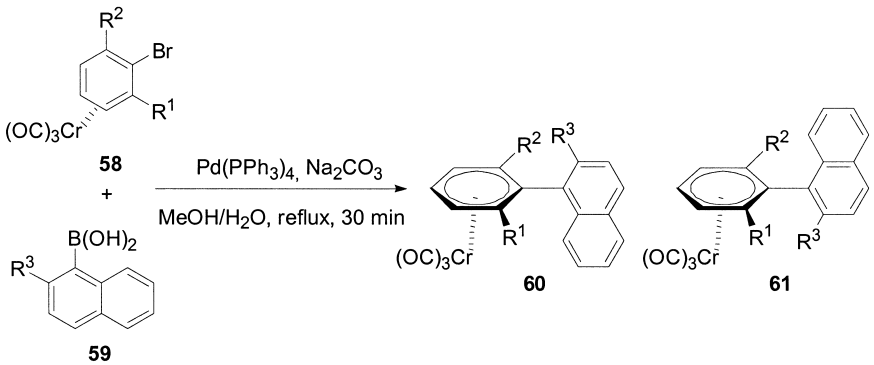
Naphthylboronic intermediates were also investigated in this study (Table 4). As already reported by the same

Table 3. Arylation of arylmetalCr(CO)$_3$ complexes using (2,6-disubstitued)phenylboronic acids

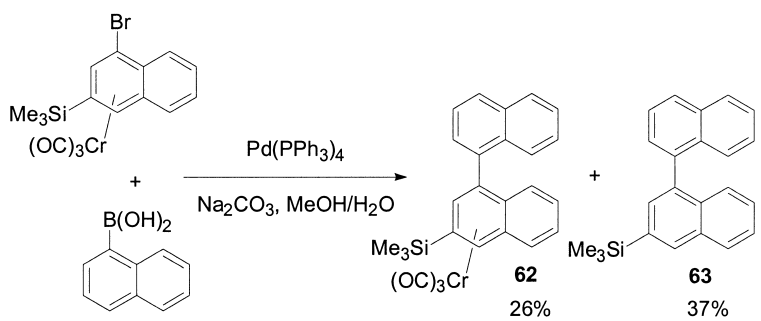


Entry	R	Conditions	Ratio **55/56/57**	Yield (%)
1	Me	Na_2CO_3/MeOH/H_2O	94:6:0	77
2	OMe	$Ba(OH)_2$, DME, H_2O	55:22:23	86
3	CHO	Na_2CO_3/MeOH/H_2O	0:0:100	40[68]

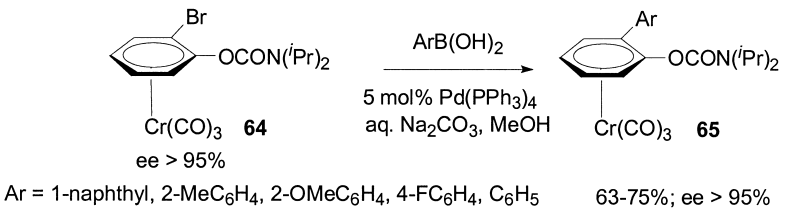
Table 4. Coupling of naphthylboronic acids with arylmetalCr(CO)$_3$ complexes



Entry	Complex **58**	Naphthylboronic acid **59**	Ratio **60/61**	Yield (%)
1	R^1=MeO, R^2=Me	R^3=H	100:0	88
2	R^1=MeO, R^2=CHO	R^3=H	100:0	89
3	R^1=MeO, R^2=CH_2OH	R^3=H	100:0	86
4	R^1=MeO, R^2 = $\overline{CHO(CH_2)_2O}$	R^3=H	100:0	85
5	R^1=Me, R^2=H	R^3=Me	95:5	25
6	R^1=MeO, R^2=H	R^3=Me	71:29	71
7	R^1 = $\overline{CHO(CH_2)_2O}$, R^2=H	R^3=Me	100:0	57
8	R^1=Me, R^2=H	R^3=MeO	97:3	78



Scheme 27.



Scheme 28.

authors in previous studies, the coupling appeared to be really efficient. According to Uemura, the stereochemistry controlled by the bulkiness of the larger fragment near the biaryl axis was determined in a *syn* orientation to the $Cr(CO)_3$ moiety.[77]

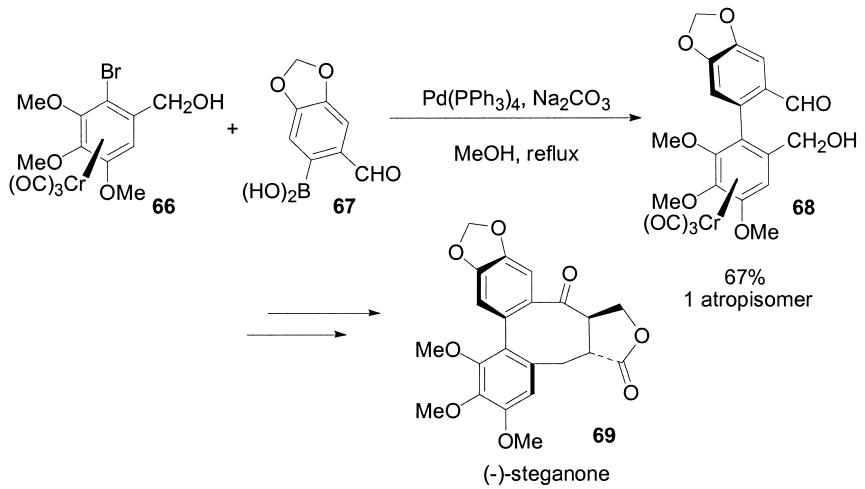
The preparation of binaphthyl derivatives was attempted according to the same procedure (Scheme 27). Unfortunately, the coupling afforded a mixture of the complexed and decomplexed binaphthyl compounds **62** and **63**, respectively, in 26 and 37% yield.

Over the years, Suzuki coupling conditions involving more elaborated partners have appeared in the literature. Nelson reported, in 1999, a Suzuki cross-coupling between an enantiomerically enriched ($95 < ee < 97$) *ortho*-bromocarbamate–chromium complex **64** and various boronic acids (Scheme 28).[78] In general, the coupled products **65** were isolated in good yields without racemisation.

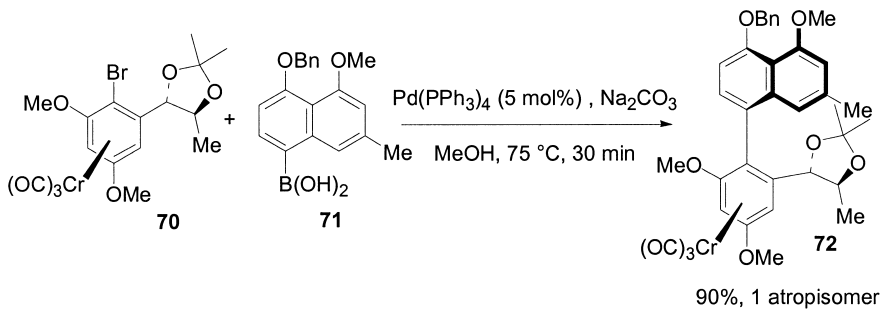
Additionally, the carbamates were shown to be displaced by Ph_2PLi, affording the corresponding diphenylphosphino derivatives in good yield without racemisation.

The versatile character of the cross-couplings involving chiral or non-chiral arenechromium complexes, and the possible preparation of decomplexed products rendered this methodology extremely attractive for the preparation of biologically active compounds. Pioneering work in this area was reported about a decade ago by Uemura et al.,[12] who applied this approach to the synthesis of (−)-steganone.[12] They first prepared the enantiomerically pure pentasubstituted arenechromium complex **66** from the commercially available trimethoxybenzaldehyde. Coupling the haloarenechromium complex **66** with the boronic acid **67** under palladium catalysis afforded the expected coupling compound **68** in 67% yield, without the formation of the other atropisomer. With this key synthon in hand, the authors were able to access to the (−)-steganone structure **69** in a very elegant manner (Scheme 29).

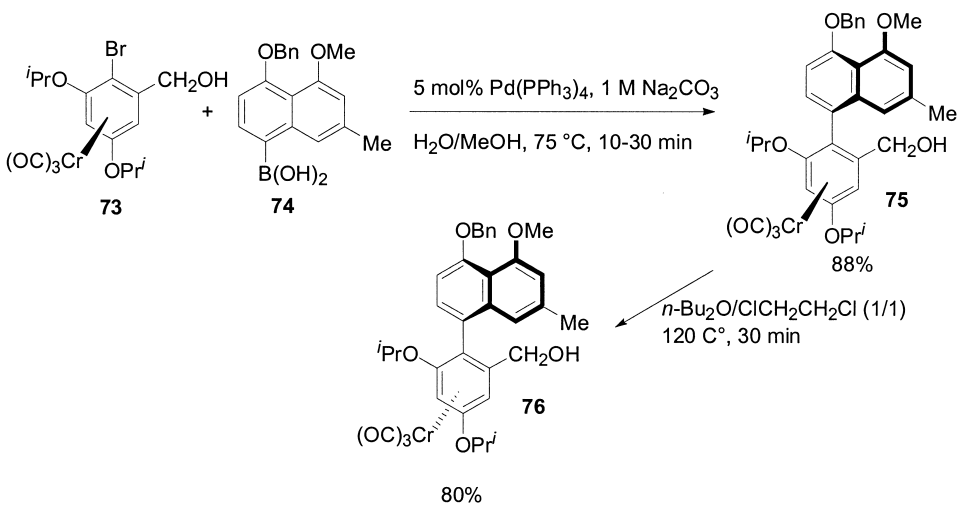
A few years later, the same group used a similar approach



Scheme 29.



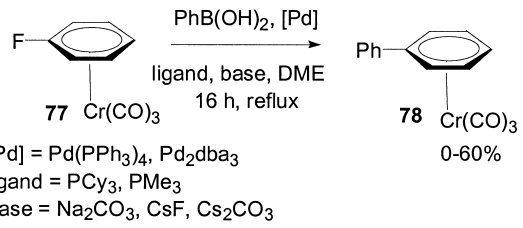
Scheme 30.



Scheme 31.

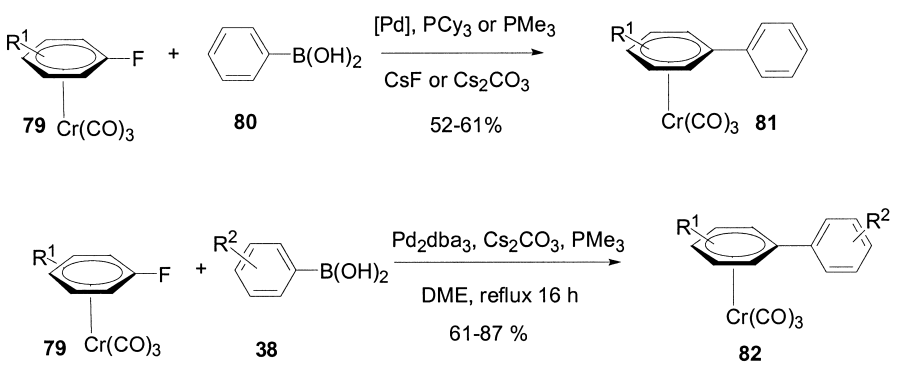
for the preparation of *O*,*O*-dimethylkorupensamine, which is known to exhibit both antimalarial and anti-HIV activities.[79] A key step in the synthesis involved the preparation of a chiral arenechromium-substitued naphthyl complex **72**, a precursor of the naphthyltetrahydroisoquinoline present in the dimethylkorupensamine (Scheme 30). The latter complex was efficiently prepared in a stereoselective manner by coupling the chiral arenechromium complex **70** with the 4-benzyloxy-5-methoxy-6-methylnaphthylboronic acid **71** in the presence of $Pd(PPh_3)_4$ and sodium carbonate in 90% yield.

Key building blocks giving access to the antimalarial korupensamine A and *ent*-korupensamine B were also prepared from chiral planar arenechromium complexes (Scheme 31).[80] Interestingly, the same complex was used in the two parallel syntheses. Both enantiomers of the chiral tricarbonyl(2-bromo-3,5-diisopropoxybenzaldehyde)chromium complex **73**, prepared according to classical organometallic chemistry, were reacted with the naphthylboronic acid derivative **74** under Suzuki coupling conditions. As exemplified, the expected *syn* coupling product **75** was isolated in high yield (88%) as a single diastereomer. The other diastereomer **76** was isolated after a selective atropoisomerisation performed by heating at 120 °C for 30 min.

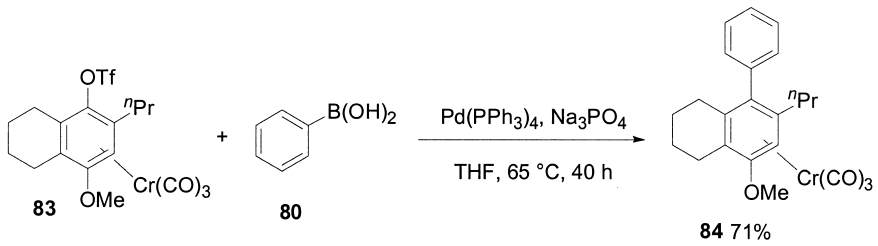


Scheme 32.

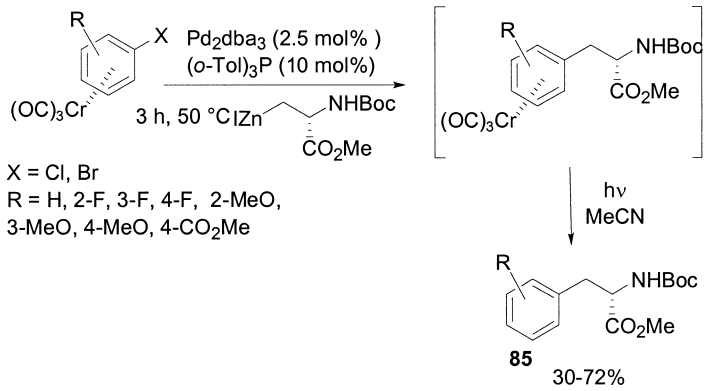
Numerous advantages of arene coordination by a $Cr(CO)_3$ moiety have been listed above. Nevertheless, some other properties of arenechromium complexes remain to be exemplified. In particular, the electronic effects brought about by the coordination of $Cr(CO)_3$ weaken the aromatic bonds and allow remarkable chemical sequences. One of the most striking examples concerns the oxidative addition of palladium involved in aromatic C–F bonds that offers attractive and efficient cross-couplings involving fluoroarenes. Widdowson et al. were among the first chemists to investigate this opportunity and in 1999, they reported Suzuki-type couplings between a phenylboronic acid, and the fluorobenzenetricarbonylchromium complex **77** (Scheme 32).[81] Different coupling conditions were tested. The best results were obtained using Pd_2dba_3 as the



Scheme 33.



Scheme 34.



Scheme 35.

palladium source, PMe_3 as the ligand and Cs_2CO_3 as the base. Under these conditions, the coupling products such as **78** were isolated in about 60% yield (see also Scheme 15).

More recently, the same authors investigated further the potential of this approach with substituted arenechromium complexes and boronic acids.[62,82] In particular, both the catalytic conditions and the effect of substitution on the arenechromium moiety **79** were investigated. Two different sets of catalytic conditions appeared to be the most suitable: Pd_2dba_3–PCy_3, CsF and Pd_2dba_3–PMe_3, Cs_2CO_3. The use of the latter gave an access to monocomplexed biphenyls **81** and **82** (Scheme 33).

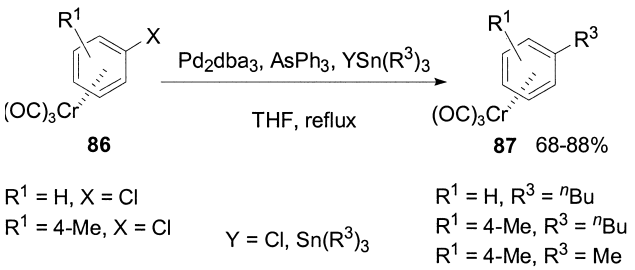
To the best of our knowledge, very few examples of couplings involving arenechromium complexes bearing non-halogenated leaving groups have been reported. It should be mentioned, however, that triflates were found to be good alternative partners for the couplings and, in 1994, Wulff et al. reported the coupling between an arenechromium triflate complex **83** and phenylboronic acid **80** in 71% yield (Scheme 34).[61]

3.5. Introduction of alkyl groups

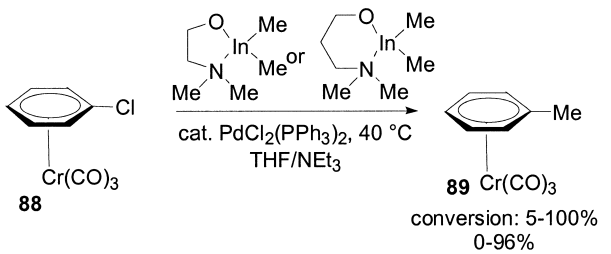
The versatility of the arenechromium chemistry has been extensively exemplified in the former part of this review with the observation of very efficient arene–arene couplings. Another feature of the arene chromium activation by a tricarbonylchromium moiety concerns the coupling of alkyl groups on arenes using palladium catalysis.

To the best of our knowledge, this methodology was first reported in 1996 by Jackson et al. who described the alkylation of halo-arenechromiumtricarbonyl complexes by zinc-activated aminoacid residues. Under classical catalytic conditions (Pd_2dba_3, $(o\text{-Tol})_3P$), the coupling compounds **85** were obtained in 30–72% yield after decomplexation (Scheme 35).[83]

More recently, Rose et al. reported a different arene alkylation involving a very efficient and selective alkyl group migration from the stannylated reactant, $(alkyl)_3SnCl$ or $[(alkyl)_3Sn]_2$, on a chloroarenetricarbonylchromium complex **86** (Scheme 36).[84] In this case, alkyl-substituted complexes **87** were obtained in 68–88% yield.



Scheme 36.

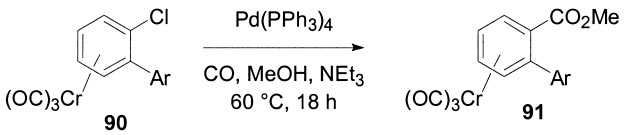


Scheme 37.

Finally, in 2002, Schmaltz et al. reported methyl *ipso* substitutions of the chlorotricarbonylchromium complex **88** using methylindium derivatives and affording complexes **89** (Scheme 37).[85] The reactions took place in good to excellent yields at 40 °C in THF.

3.6. Introduction of carboxylated groups

The association of palladium and arenechromium chemistries has been widely used in the preparation of aromatic esters, amides, aldehydes or α-oxo-amides. In a typical experiment, a haloarenetricarbonylchromium complex is reacted with a nucleophile under palladium catalysis and a carbon monoxide atmosphere. Uemura et al. described a pioneering result in this area in 1994.[56] Using the strategy described above, they reported the preparation of a benzoate methyl ester tricarbonylchromium complex **91**, starting from the corresponding chloroarene derivative **90** (Scheme 38). No yield concerning the reaction was mentioned.



Scheme 38.

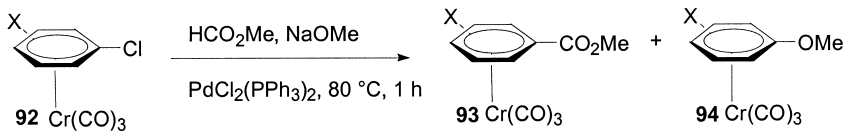
The same year, Carpentier et al. reported a similar approach using substituted chloroarenetricarbonylchromium complexes **92**.[86] Interestingly, the conditions they used not only afforded the expected esters **93**, but also the corresponding anisoles **94** in good combined yields. In the case of chloroarenes substituted by EWGs, the anisoles were isolated as the major compounds (Scheme 39).

Using the same catalytic conditions, this group further investigated the effect of the substituents.[87,88] They observed that the presence of electron-donating groups on the starting chloroarene favoured the formation of the esters **95** and **96** at the expense of the anisole **97** (Scheme 40).

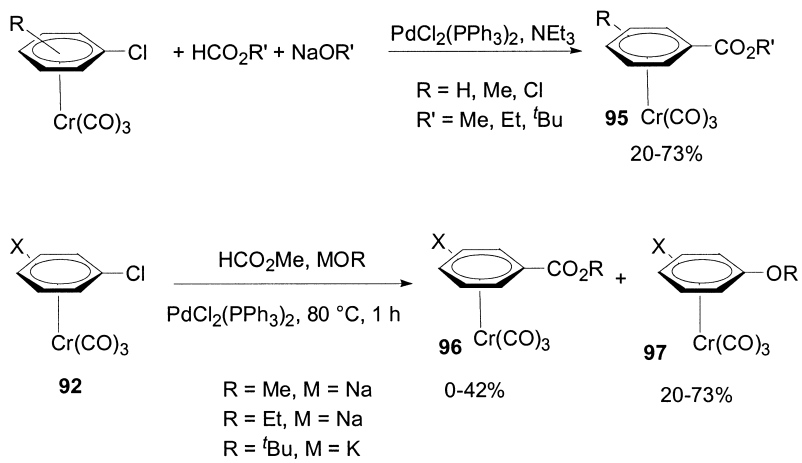
3.7. Introduction of carbonylated groups

Carbonylation of haloarenetricarbonylchromium complexes can additionally be achieved via a similar strategy. The mechanistic insights of the strategy were thoroughly investigated in 1991 by Basset et al.[37] and the first reports appeared in 1993 when Carpentier et al. described the preparation of the benzaldehyde derivatives **98**, starting from substituted chloroarenetricarbonylchromium complexes (Scheme 41).[51]

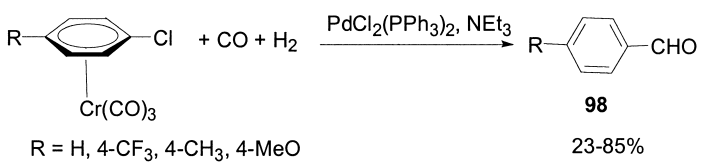
Using a similar strategy, Carpentier et al. reported that the amide **99** and α-oxo-amide **100** could be prepared through an aminocarbonylation sequence (Scheme 42).



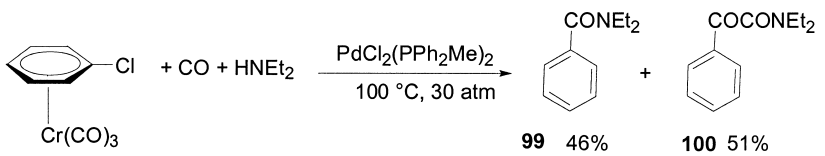
Scheme 39.



Scheme 40.



Scheme 41.



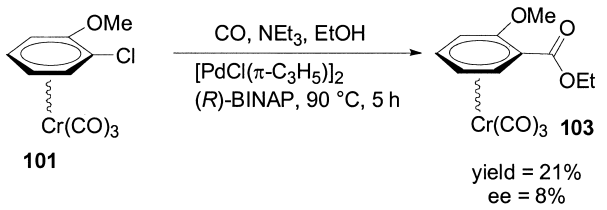
Scheme 42.

Aminocarbonylations were also described by Basset et al. (Scheme 43).[37] These authors pointed out that the ratio between the amide and the α-oxo-amide depends on the carbon monoxide pressure used during the reaction.

Later, they pursued their investigations further and generalised the methodology (Scheme 43).[89]

In 1996, Carpentier et al. developed a chiral version of alkoxycarbonylation for the kinetic resolution of 2(-chloroanisole)tricarbonylchromium complexes such as **101** (Scheme 44).[90] In this approach, they took advantage of the efficiency of esterification reactions of electron-rich chloroarene complexes. In particular, they reported the preparation of diastereomeric esters, for example, **102**, from (*S*)-2-methyl-1-butanol and the (*o*-chloroanisole)chromium complex (Scheme 44) in good yields, but with poor enantiomeric excesses.

In a similar manner, the asymmetric reaction catalysed by the palladium–(*R*)-BINAP complex in ethanol gave the expected ester **103** with an interesting selectivity, but a poor yield (Scheme 45).

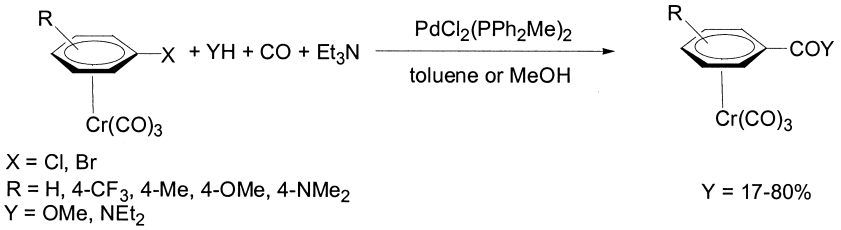


Scheme 45.

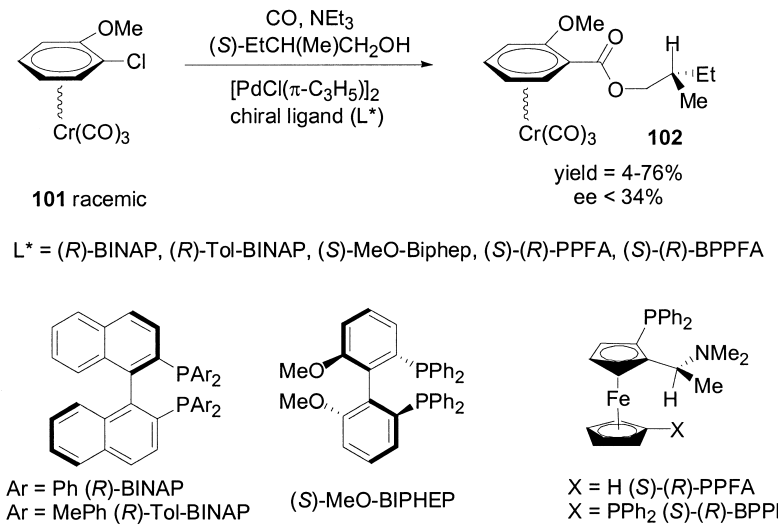
4. Pd/Mn Bimetallic activation

4.1. Introduction

$Mn(CO)_3$ complexes have been known since the early 1970s. $Mn(CO)_3$ or $Mn^+(CO)_3$ fragments have been described as even more electrophilic than the corresponding $Cr(CO)_3$ moiety.[4,91] Palladium-catalysed reactions involving $Mn(CO)_3$ complexes were, however, scarcely described until recently. Taking into account the withdrawing ability of the $Mn(CO)_3$ fragment and by analogy with arene-chromium chemistry, Mn-complexed chloroarenes were expected to undergo oxidative addition from palladium(0)



Scheme 43.

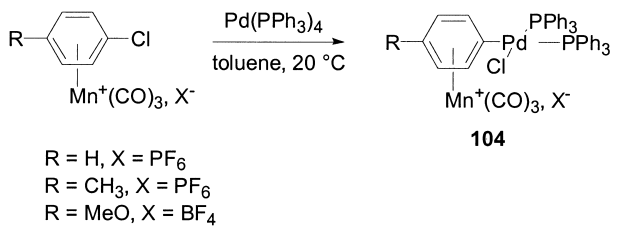


Scheme 44.

species and allow palladium-catalysed reactions. This section is devoted to recent progresses in palladium catalysis using cationic (η^6-chloroarene)$Mn(CO)_3$, (η^5-chloroCp)$Mn(CO)_3$ and (η^5-chloroCh)$Mn(CO)_3$ complexes.

4.2. Cationic (η^6-arene)$Mn(CO)_3$ complexes

As recently described, oxidative addition products are easily obtained from cationic (η^6-chloroarene)$Mn(CO)_3$ and Pd(0) species (Scheme 46).[92] The formation and stability of the *cis*-adducts **104** have been attributed to the X^- ligand bulkiness in the (η^6-arene)$Mn^+(CO)_3$ complex. The first intermediate in the catalytic cycle was easily reached, but no further catalytic transformations could be induced.

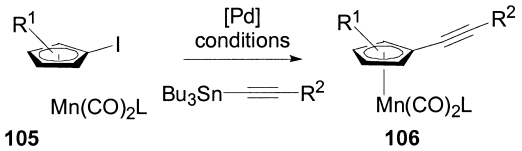


Scheme 46.

These results are in sharp contrast with Espinet's studies[93] that demonstrated that the first-formed *cis*-adduct rapidly isomerises into the more stable *trans* isomer.

4.3. Neutral (η^5-Cp)$Mn(CO)_3$ complexes

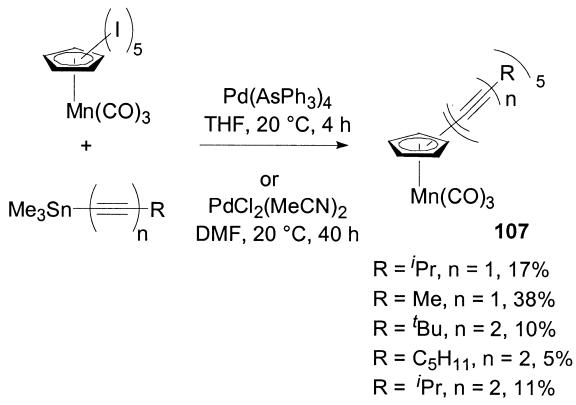
To the best of our knowledge, palladium-catalysed reactions starting from manganese-complexed Cp rings exclusively concern the introduction of alkynyl groups by Stille methodology.



Scheme 47.

The easily accessible (iodoCp)$Mn(CO)_3$ complexes **105** are useful starting material in coupling sequences (Scheme 47). As shown in Table 5, the catalytic systems are based on $PdCl_2(MeCN)_2$ or Pd_2dba_3-$AsPh_3$. A wide range of stannylated alkynes (entries 1–4) and organometallics (entries 5 and 6) have been used as coupling partners, affording disubstituted mono- and bimetallic alkynes **106** in 26–92% yields. Modification of the metal-withdrawing ability by changing from a carbonyl to a phosphane ligand does not influence the palladium-catalysed reactions. Indeed, (iodoCp)$Mn(CO)_2PPh_3$ complexes, subjected to classical coupling conditions, afforded the expected alkynylated complex (entry 6).

By analogy with hexaethynylbenzene, (pentaethynylCp)-$Mn(CO)_3$ complexes **107** could be prepared in 5–38% yield (Scheme 48). The coupling reactions between (pentaiodoCp)$Mn(CO)_3$ complexes and alkyl-substituted acetylenes and butadiynes using $Pd(AsPh_3)_4$ or $PdCl_2$-$(MeCN)_2$ afforded the corresponding star-shaped complexes.[26,95]



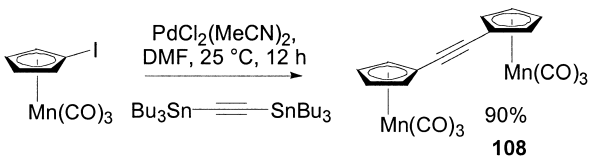
Scheme 48.

To close this section, the homobimetallic Mn–Mn complex **108**, shown in Scheme 49, was efficiently prepared in 90% yield by the coupling of the (iodoCp)$Mn(CO)_3$ complex and bis(tributylstannyl)acetylene using $PdCl_2(MeCN)_2$ as a catalyst in DMF at room temperature.[23]

Table 5. Introduction of alkynyl groups by Stille reaction

Entry	L	R^1	R^2	Conditions	[Pd]	Yield (%)	Reference
1	CO	H	H	DMF, 25 °C, 2 h	$PdCl_2(MeCN)_2$	92	22,25,94
2	CO	H	$SiMe_3$	THF, 25 °C, 4 h	Pd_2dba_3-$AsPh_3$	79	26
3	CO	2-$SiMe_3$	$SiMe_3$	DMF, 25 °C, 1 h	$PdCl_2(MeCN)_2$	57	26,94
4	CO	3-$SiMe_3$	$SiMe_3$	DMF, 25 °C, 1 h	$PdCl_2(MeCN)_2$	26	26,94
5	CO	H	[M]	DMF, 25 °C, 8–12 h	$PdCl_2(MeCN)_2$	70–81	22
6	PPh_3	H	$MnCO_2PPh_3$	DMF, 25 °C, 12 h	$PdCl_2(MeCN)_2$	[b]	24

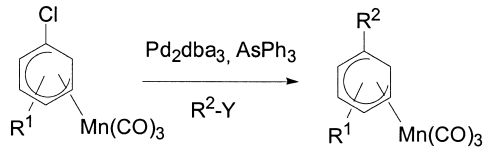
[a] [M]=$Mn(CO)_3$, $Re(CO)_3$, $W(CO)_3Me$, $Fe(CO)_2Me$.
[b] Yield not mentioned.



Scheme 49.

4.4. Neutral (η^5-Ch)Mn(CO)$_3$ complexes

Among the different classes of arenetricarbonylmetal complexes, (η^5-chloroCh)Mn(CO)$_3$ complexes have only recently received much attention. Until the first palladium-catalysed functionalisation was reported,[96] reactions at the π-system were restricted to nucleophilic additions and substi-tutions.[91,97] It has been shown that (η^5-chloro-Ch)Mn(CO)$_3$ complexes can be readily coupled with aryltributylstannanes in Stille reactions (Scheme 50).[96]



R^1 = H, 4-Me, 4-OMe, 2-Me
R^2 = thienyl, phenyl; Y = $SnBu_3$ 45-78%
R^2 = alkenyl; Y = H, $SnBu_3$ 13-32%
R^2 = alkynyl; Y = H, ZnCl, $SnBu_3$ 40-91%

Scheme 50.

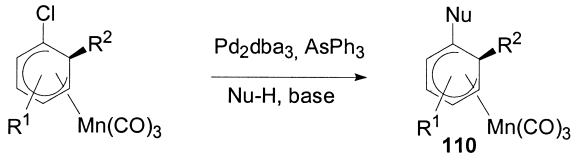
The major outcome of the studies directed towards the determination of effective catalytic systems are listed below:

- The Pd_2dba_3–$AsPh_3$ combination smoothly catalyses coupling reactions, affording the functionalised complexes in high yields. Arsine ligands are already known to accelerate transmetallation steps due to their higher decoordination ability.[98,99]
- The use of various phosphorous-based ligands such as PPh_3, dppf, P^tBu_3 or $P(OEt)_3$ only led to decomplexation of the starting material. A possible interaction between Mn, Pd and the P-based ligand seems to be responsible for the observed decomplexation and lack of efficiency.[91,100]
- When $AsPh_3$ was replaced by $SbPh_3$, high yields of the expected coupling products and shorter reaction times were observed. The reaction was less chemoselective, however, giving rise to the formation of decomplexed and carbonylated side products.[100]

As shown in Scheme 50, Stille arylation afforded good to high yields of the thienyl- and phenyl-substituted (η^5-Ch)Mn(CO)$_3$ complexes **109**, regardless of the starting substitution pattern.

The use of the same catalytic system also allowed the introduction of alkenyl and alkynyl substituents through Stille-, Heck- or Negishi-type reactions.

This methodology was extended to Buchwald–Hartwig-type reactions (Scheme 51).[101] Palladium-catalysed amination, as well as etherification, thioetherification and phosphorylation, were successfully performed. The preparation of the unprecedented N-, O-, S- and P-substituted (η^5-Ch)Mn(CO)$_3$ complexes **110** was achieved in 31–93% yield, using a non-elaborated catalytic system (Pd/As).[102]

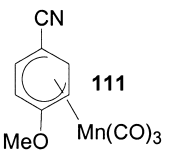


R^1 = H, 4-Me, 4-MeO, 2-MeO
R^2 = H, Ph
Nu-H = morpholine, $HNEt_2$, $NH_2(C_6H_4)OMe$
PhOH, *iso*amylOH, $C_5H_{11}SH$, *p*-tolylSH
$HP(O)(OEt)_2$, $HP(O)(Ph)_2$, $HP(Ph)_2$
base = Cs_2CO_3, NaH

"N" 42-90%
"O" 31-38%
"S" 73-93%
"P" 43-77%

Scheme 51.

Attempts to use carbon nucleophiles such as ketone enolates or malonitrile anions under similar catalytic conditions failed. In contrast, a nitrile function could be introduced using potassium cyanide in the presence of the Pd/As catalytic system and 18-C-6 crown ether affording the expected cyano complex **111** (Scheme 52).[100]



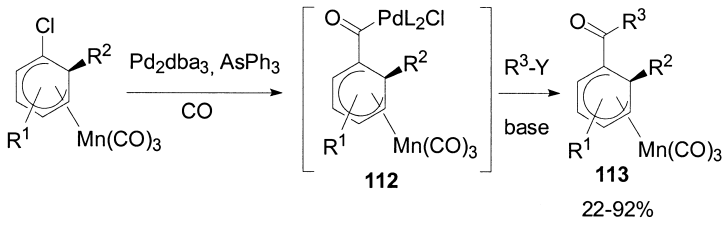
Scheme 52.

Taking advantage of the facile palladium-catalysed *ipso* substitution of the chlorine atom in the (η^5-chloro-Ch)Mn(CO)$_3$ complexes, the same strategy was applied under carbonylative conditions (Scheme 53).[103] The acylpalladate intermediate **112**, generated from (η^5-chloro-Ch)Mn(CO)$_3$ complexes and the Pd/As catalytic system under a CO atmosphere was reacted with various nucleophiles affording EWG-substituted (η^5-Ch)$MnCO_3$ complexes **113**.

Aryl and alkyl ketones, yne- and ene–ones, as well as carboxylic esters, thioesters and amides, were obtained in 22–92% yield. It is worth noting that the palladium-catalysed functionalisation of (η^5-chloroCh)Mn(CO)$_3$ complexes keeps the Ch moiety intact. It is therefore possible to abstract the *exo* hydrogen atom of the sp^3 group. This methodology offers an original approach for the preparation of substituted (η^6-arene)Mn(CO)$_3$ complexes that cannot be synthetised using direct complexation of a Mn(CO)$_3$ entity of the starting organic product.

5. Concluding remarks

This review covers 18 years of intense research in bimetallic Pd/Cr and Pd/Mn activation of the carbon–halide bond in organo-chromium and -manganese complexes from the pioneering work of Villemin until the more recent



R^1 = H, 4-Me, 4-OMeO, 2-Me
R^2 = H, Ph
R^3 = aryl, alkyl, vinyl, alkynyl; Y = $SnBu_3$
OPh, MeO, N(CH_2CH_2)O, *p*-tolylS; Y = H; base = NaH, Et_3N, K_2CO_3

Scheme 53.

discoveries. There is no doubt that this expanding area at the frontier of organic and organometallic chemistry will shortly reveal a variety of spectacular applications, ranging from the synthesis of natural compounds to more straightforward accesses to original polymetallic molecules. Considering this potential, the coming years will definitely witness a radical development in this chemistry.

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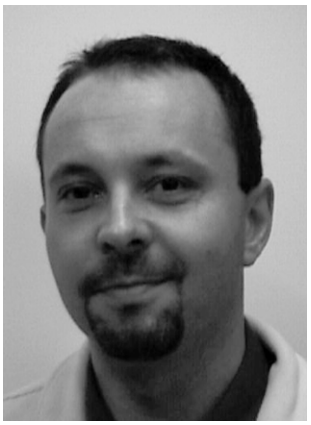
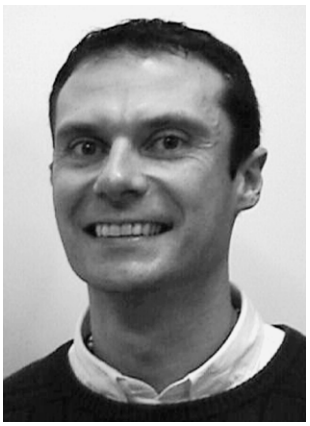
Biographical sketch



Damien Prim received his PhD degree at the University of Metz in 1994. After a postdoctoral period at the University Catholique de Louvain with Professor L. Ghosez, he returned to the University of Metz as Assistant Professor (1995–1999). Then, he moved to the university Pierre et Marie Curie in Paris as CNRS research associate for 2 years and joined the University of Versailles as Assistant Professor in Prof. F. Couty's group. His current research includes organic synthesis in aqueous media and transition metal-assisted catalytic transformations.

Françoise Rose-Munch was born in Metz, France. She entered the CNRS in 1975 and received her PhD degree in 1976 from the University Pierre et Marie Curie, Paris. After a postdoctoral period in 1976 and 1977 at the University of Stanford, California, USA with Prof. Jim Collman, she returned to Paris and was promoted CNRS Research Director. Her research interests concern the organometallic chemistry of Pd, Fe, Cr and Mn complexes and the nucleophilic substitutions of arene–Cr and –Mn complexes, as well as their application in non linear optics.



Bruno Andrioletti was born in Troyes-France in 1968. He studied chemistry at the University of Burgundy (Dijon-France) and received his PhD degree in 1997 under the supervision of Prof. R. Guilard and Dr. B. Boitrel. His PhD focused on the development of new porphyrinic models of the cytochrome c oxidase active centre. Afterwards, for 2 years, he joined Prof. J. L. Sessler's group at the University of Texas at Austin, Austin, Texas for postdoctoral training. There, he studied the chemistry of expanded porphyrins and carried out the development of new anion sensors. In 1999, he was appointed CNRS researcher at the University Pierre et Marie Curie in Paris, France in Dr. E. Rose's group. His current interests mainly concern the development of new porphyrin and other oligopyrrolic macrocycles and their use in asymmetric catalysis and molecular recognition.

Eric Rose was born in Nancy, France. He entered the CNRS in 1970 and obtained his PhD degree in 1975 from the University P. et M. Curie, Paris. After postdoctoral training in 1976 and 1977 at the University of Stanford, California, USA with Prof. Jim Collman, he then moved back to Paris and was promoted to CNRS Research Director in 1985. His research interests are focused on the preparation of models of hemoproteins (Mb, Hb and cyt P450) and of new chiral porphyrins as catalysts for the epoxidation of terminal olefins, as well as nucleophilic substitutions in arene-metal complexes.

François Couty was born in 1963 in Caen (France). He studied chemistry at the University Pierre et Marie Curie in Paris and received his PhD degree in 1991 in Prof. Agami's group. The same year, he obtained a position of Assistant Professor in this University. He spent a year in Namur (Belgium) as a postdoctoral fellow with Prof. A. Krief. After having completed his Habilitation (1999), he was promoted to full Professor at the University of Versailles (2001). His research interests are in the field of asymmetric synthesis, synthetic methodology and enantioselective catalysis.