Organometallics **2001,** *20,* 1901−1903

(η^5-Halogenocyclohexadienyl)Mn(CO)$_3$ Complexes: Halogen Substitution by Arene Derivatives

Damien Prim,[†] Audrey Auffrant,[†] Françoise Rose-Munch,[†] Eric Rose,*[,†] and Jacqueline Vaissermann[‡]

Laboratoire de Synthèse Organique et Organométallique , UMR CNRS 7611, Université Pierre et Marie Curie, Tour 44-1er étage, 4 Place Jussieu, 75252 Paris Cedex 05, France, and Laboratoire de Chimie Inorganique et Matériaux Moléculaires, ESA CNRS 7071, Université Pierre et Marie Curie, Bat. F, 4 Place Jussieu, 75252 Paris Cedex 05, France

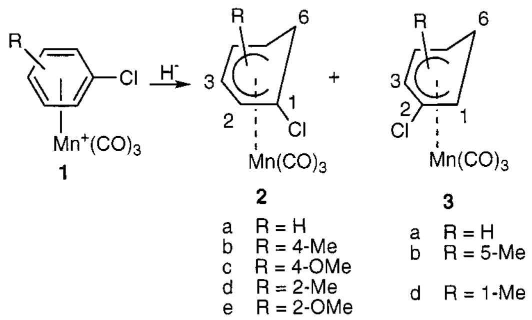
Received September 26, 2000

Summary: Unprecedented coupling reactions on (η^5-chlorocyclohexadienyl)tricarbonyl manganese complexes with arenes create a new carbon−carbon bond on the conjugated system, keeping intact the η^5-chlorocyclohexadienyl moiety; thus, the removal of the exo hydrogen bond of the sp^3 CH$_2$ group yields efficiently new cationic (η^6-arene) manganese complexes which cannot be prepared directly from the free arene.

The activation of arenes by coordination to transition metals is a well-established phenomenon. The manganese-mediated functionalization of arenes is particularly attractive because of the very high electrophilicity of the relevant complexes which undergo high-yield nucleophilic additions.[1] The corresponding tricarbonyl(η^5-cyclohexadienyl)manganese complexes are stable and relatively inert.[2] Only a few examples of the reactivity of their carbon π-system are described in the literature with stabilized nucleophiles[3] or hydrides.[4−6]

As part of our current studies on organochromium complexes[1a,6b] and on cross-coupling reactions,[7] we have shown the potentiality of bimetallic activation under smooth reaction conditions at room temperature, which avoids side product formation and decomplexation.[8] We now report the use of Pd$_2$(dba)$_3$ in the presence of AsPh$_3$ for the arylation of neutral (η^5-chlorocyclohexadienyl)Mn(CO)$_3$ complexes through a regioselective substitution of the chlorine atom by an aryl group.

Scheme 1



This unprecedented functionalization of an η^5-halogenocyclohexadienyl complex occurred without loss of the tricarbonylmanganese entity. This allowed us to stress the potentiality of these new substituted η^5-cyclohexadienyl complexes, particularly in the formation of substituted cationic (η^6-arene) manganese complexes.

(η^5-Chlorocyclohexadienyl)Mn(CO)$_3$ complexes were readily prepared by hydride addition to variously substituted cationic (η^6-chlorobenzene)Mn(CO)$_3$ complexes **1** according to Scheme 1:[4,6,9] mixtures of two regioisomers *ortho* and *meta* with respect to Cl were obtained in various ratios and were separated by silica gel chromatography column, whereas addition of hydride to (η^6-*ortho*- or *para*-chloroanisole)Mn(CO)$_3$ complex affords a single regioisomer, **2e** or **2c**, respectively.[6a]

Complex **2a** coupled with tributylphenyltin using 10% Pd$_2$(dba)$_3$ and 35% AsPh$_3$[10] in freshly distilled and degassed DMF at room temperature for 23 h, affording tricarbonyl(1-phenyl η^5-cyclohexadienyl)manganese complex **4a** in 52% yield (Table 1, entry 1). Control experiments conducted under the same conditions but in the absence of the catalyst gave no arylation product (Table 1, entry 2).

These first observations prompted us to extend this strategy by using various substituted starting complexes **2** as well as heterocyclic tributyltin reagents. The results are gathered in Table 1. Several points warrant comments: thienyltributyltin behaved similarly and reacted with complex **2a** to give the expected coupling product **5a** (Table 1, entry 3). Furthermore, the reaction path seems to be independent of the nature and the position of the starting substitution pattern (Table 1, entries

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* Corresponding author. E-mail: rose@ccr.jussieu.fr.

[†] Laboratoire de Synthèse Organique et Organométallique , UMR CNRS 7611.

[‡] Laboratoire de Chimie Inorganique et Matériaux Moléculaires, ESA CNRS 7071.

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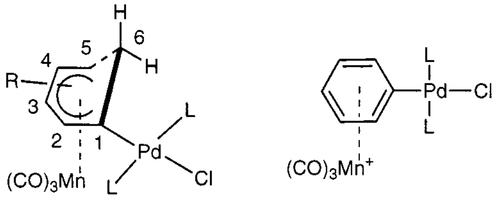
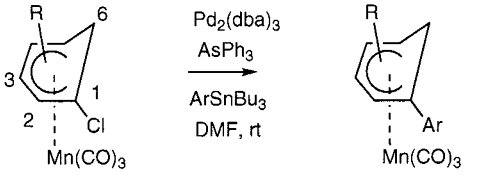
10.1021/om000831d CCC: $20.00
Publication on Web 04/12/2001



6 **7**

Figure 1.

Table 1. Stille Coupling Reactions of Complexes 2



2

4 Ar = Ph = phenyl
5 Ar = Th = thienyl

entry	2	R	Ar	time (h)	yield (%)
1	**2a**	H	Ph	23	**4a** (52)
2	**2a**	H	Ph	no catalyst	–
3	**2a**	H	Th	18	**5a** (51)
4	**2b**	4-Me	Ph	24	**4b** (45)
5	**2b**	4-Me	Th	20	**5b** (48)
6	**2c**	4-OMe	Th	20	**5c** (78)
7	**2d**	2-Me	Th	20	**5d** (53)

4–7). No steric hindrance effect was detected, and yields ranged between 48 and 78%. From there it follows that the withdrawing ability of the $Mn(CO)_3$ entity allowed the oxidative addition of Pd(0) into the C–Cl bond with formation of a transient η^5-bimetallic intermediate **6** (Figure 1).

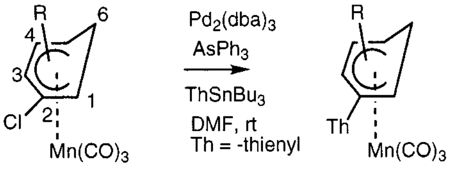
An easy activation of the C–Cl bond toward zerovalent palladium complex insertion has been described[11] in the case of cationic (η^6-chloroarene)$Mn(CO)_3$ derivatives, but the corresponding (η^6-arene)bimetallic adduct **7** was so stable that no further reaction was possible (Figure 1).

According to our results, η^5-bimetallic intermediate **6** could react very smoothly with stannyl derivatives and the X-ray structure of **5b**[15] allowed us to verify the following points: (a) the reaction of stannyl derivatives occurred on the carbon C(1), which bore the halogeno group in the starting material; (b) the η^5-cyclohexadienyl structure was preserved, in good agreement with literature data.[12] The five ring carbon atoms C(1), C(2), C(3), C(4), and C(5) are almost coplanar, while the remaining atom C(6) lies on the opposite side of this plane from the $Mn(CO)_3$ moiety. The plane makes a 40° angle with that defined by C(1), C(6), and C(5) carbon atoms.

Unexpectedly, the use of phosphorus-based ligands (such as $P(OEt)_3$, PPh_3, dppf, P^tBu_3) instead of $AsPh_3$ gave no coupling products. We observed instead disappearance of the starting material with decomposition of the metallic entity.

The use of the above-mentioned catalytic conditions allowed the reaction of the regioisomer complexes **3**

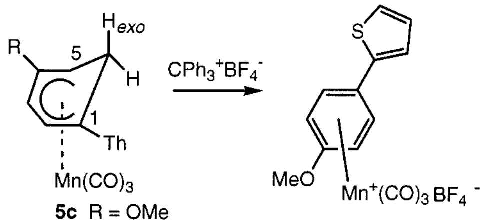
Table 2. Stille Coupling Reactions of Complexes 3



3 **8**

entry	3	R	yield (%) after 20 h
1	**3a**	H	**8a** (58)
2	**3b**	5-Me	**8b** (30)
3	**3d**	1-Me	**8d** (43)

Scheme 2



5c R = OMe

9

(Table 2) with a thienyltin derivative for example, leading to the formation of the desired coupling products regioselectively at the C(2) carbon. As already underlined for complexes **2**, both substitution of the η^5 ring and steric hindrance did not seem to affect the arylation process (Table 2, entries 2, 3).

(η^5-Cyclohexadienyl)Mn complexes such as **4**, **5**, and **8** are very useful in synthesizing new cationic (η^6-arene)-$Mn(CO)_3$ complexes. For example, by reacting CPh_3-BF_4[13] with complex **5c**, we obtained the formation of the cationic complex **9** in 93% yield by abstracting the *exo* hydrogen at C(6) (Scheme 2). This is the key point of our approach: the introduction of a new group (Ar or Th) at the π-carbon system leaves the sp^3 carbon

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(15) Typical arylation procedure: preparation of tricarbonyl(4-methyl(1-thienyl)cyclohexadienyl)manganese complex **5b.** $Pd_2(dba)_3$ (0.019 g, 0.02 mmol) and $AsPh_3$ (0.21 g, 0.07 mmol) were added successively to complex **2b** (0.063 g, 0.2 mmol) in 10 mL of anhydrous degassed DMF. After 15 min at room temperature, 2-tributylstannylthiophene (0.071 g, 0.2 mmol) in 1 mL of DMF was added. The mixture was stirred at room temperature for 20 h, poured into 100 mL of ice cold water, and extracted twice with 50 mL of diethyl ether. The combined organic phases were dried over magnesium sulfate, filtered, and evaporated under reduced pressure. The residue was then purified by flash chromatography on silica gel (pentane) to afford complex **5b** (R_f = 0.29). The pale yellow solid was finally recrystallized from diethyl ether with petroleum ether in 48% yield. IR (CH_2Cl_2) ν(CO): 1917, 1998 cm^{-1} . ^1H NMR ($CDCl_3$, 200 MHz): δ 1.90 (s, 3H, CH_3), 2.51 (d, $J = 12$ Hz, 1H, H-6*exo*), 3.15 (d, $J = 6$ Hz, 1H, H-5), 3.24 (dd, $J = 12$, 6 Hz, 1H, H-6*endo*), 5.22 (dd, $J = 3$, 6 Hz, 1H, H-2), 5.74 (d, $J = 6$ Hz, 1H, H-3), 6.84 (d, $J = 4$ Hz, 1H, H-10), 6.92 (m, 1H, H-9), 7.15 (d, $J = 4$ Hz, 1H, H-8). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 21.9 (CH_3), 29.3 (C-6), 50.8 (C-5), 77.9 (C-3), 94.1 (C-2), 97.8 (C-4), 106.2 (C-1), 122.3 (C-10), 124.8 (C-9), 127.7 (C-8), 133.8 (C-7), 223.2 (CO). UV/vis (CH_2Cl_2): λ_{max} (ϵ) 232 nm (10800), 318 (6200). Anal. Calcd: C 53.51, H 3.53. Found: C 53.59, H 3.75. Crystal data for **5b**: $C_{14}H_{11}O_3SMn$, $M = 314.24$, crystal dimensions 0.30 × 0.60 × 0.60 mm, monoclinic, space group $P2_1/n$, $a = 11.579(2)$ Å, $b = 9.819(2)$ Å, $c = 11.988(1)$ Å, $\alpha = 94.95(1)°$, $V = 1357.9(4)$ Å^3, $Z = 4$, $\rho = 1.54$ g cm^{-3}, $\mu = 1.08$ mm^{-1}, θ range 1–28°, 192 variables were refined for 2312 independent reflections with $I > 3\sigma(I)$ to $R = 0.0441$, $R_w = 0.0562$, and GOF = 0.79. Data were collected on a CAD4 Enraf-Nonius diffractometer at 295 K with Mo Kα radiation, refinements based on F were carried out with CRYSTALS.

unsubstituted and then allows an *easy change of hapticity* (η^5 into η^6) by removing the *exo* hydride. This avoids the use of oxidative processes with consequent loss of the Mn moiety as usually reported.[1b,2]

In conclusion, we have discovered the first Stille coupling reactions involving (η^5-halogenocyclohexadienyl)$Mn(CO)_3$ complexes giving rise to an overall "*ipso*" substitution of the chloro group by an aryl group. This process could represent an interesting alternative and complementary method of selective preparation of substituted tricarbonyl(η^6-arene) manganese complexes when they cannot be synthesized using direct complexation[14] of a $Mn(CO)_3$ entity with the starting organic product. Examination of the detailed mechanism of this reaction as well as its generalization to other examples is currently underway.

Supporting Information Available: Text giving spectral data for the new compounds and tables of crystal data, atomic coordinates, and bond distances and angles for compound **5b**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM000831D