C. R. Chimie 5 (2002) 137–141

S163107480201353X/FLA

Preparation of new (η^6-arene)$Mn(CO)_3^+$ complexes involving Pd-catalysed/*exo*-hydride abstraction sequence

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Received 19 June 2001; accepted 16 November 2001

Abstract – A novel methodology consisting in a selective palladium cross-coupling reaction starting from (η^5-chlorocyclohexadienyl)$Mn(CO)_3$ followed by rearomatisation allows the preparation of new cationic (η^6-arene)$Mn(CO)_3$ complexes, which cannot be obtained directly from the coordination of the corresponding free arenes. ***To cite this article: A. Auffrant et al., C. R. Chimie 5 (2002) 137–141*** © 2002 Académie des sciences / Éditions scientifiques et médicales Elsevier SAS

tricarbonylmanganese complexes / carbonylation / Stille reaction / hydride abstraction

Résumé – Une méthodologie novatrice consistant en une réaction de fonctionnalisation catalysée au palladium de complexes (η^5-chlorocyclohexadienyl) $Mn(CO)_3$ suivie d'une réaromatisation permet la préparation de complexes cationiques (η^6-arene)$Mn(CO)_3$ inédits, qui ne peuvent pas être obtenus directement par coordination des arènes libres correspondants. ***Pour citer cet article : A. Auffrant et al., C. R. Chimie 5 (2002) 137–141*** © 2002 Académie des sciences / Éditions scientifiques et médicales Elsevier SAS

complexes tricarbonylés du manganèse / carbonylation / réaction de Stille / arrachement d'hydrure

1. Introduction

Coordination of electrophilic $Mn(CO)_3$ group to an arene modifies its reactivity, allowing regioselective transformations impossible to perform in the case of the uncomplexed arenes [1, 2]. The main synthetic methods reported for the preparation of cationic (η^6-arene)$Mn(CO)_3$ complexes involve the direct coordination of $Mn(CO)_3$ to the corresponding free arene (Fig. 1, path **a**). When R is an electron-donating group such as alkyl, alkoxy or hydroxy substituent, complexation may occur in high yield [3]. Likewise arenes bearing weak electron-accepting groups such as chloride or non-conjugated carbonyl groups can be coordinated [3, 4], but for arenes substituted by resonance electron withdrawing groups, the strong electron deficiency of the ring prevents direct complexation of the metal, whatever the method employed [5]. An alternative route for functionalised (η^6-arene)$Mn(CO)_3^+$ complex syntheses could be an *ipso* nucleophilic aromatic substitution (Fig. 1, path **b**), which is known to occur on manganese complexes substituted by leaving group (LG), but only in the case of oxo, thio and amino nucleophiles [6]. More generally, nucleophiles add *anti* to the metal leading to neutral and stable (η^5-cyclohexadienyl)$Mn(CO)_3$ complexes that might generate cationic complexes by hydride abstraction (Fig. 1, path **c**). But this *endo*-hydride abstraction remains unsuccessful because of the difficult approach of a bulky electrophile, e.g triphenylmethyl carbocation, to the metal side.

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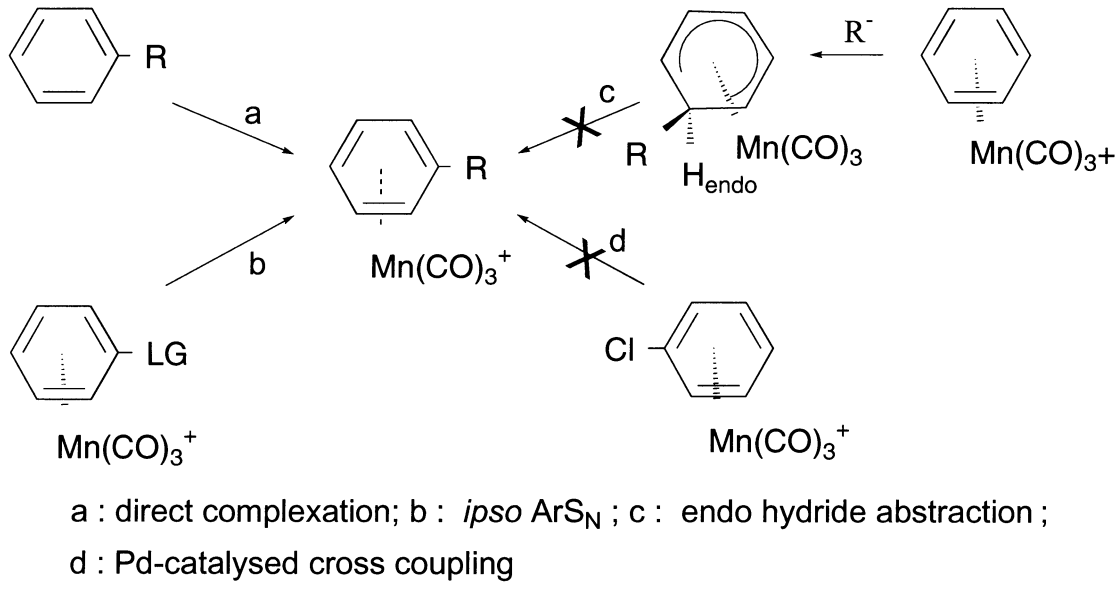

Fig. 1. Preparation of substituted (η^6-arene)$Mn(CO)_3^+$ complexes.

As part of our ongoing interest on cross coupling reactions [7, 8], we have shown the efficiency of bimetallic activation starting from (η^6-chloroarene)$Cr(CO)_3$ under smooth conditions avoiding side product formation and keeping intact the metal entity [9]. All our attempts to extend such catalytic transformations to cationic tricarbonyl(η^6-chloroarene)manganese complexes have unfortunately failed [10] up to now (Fig. 1, path **d**). Indeed, it has been shown that the catalytic process stops at the early oxidative addition step.

We considered that an alternative method to obtain substituted (η^6-arene)$Mn(CO)_3^+$ complexes could consist in the selective functionalisation of (η^5-chlorocyclohexadienyl)$Mn(CO)_3$, without alteration of the metal fragment. The corresponding (η^5-cyclohexadienyl)$Mn(CO)_3$ complexes could then undergo *exo*-hydride abstraction [11–13] to afford new substituted (η^6-arene)$Mn(CO)_3^+$ complexes that cannot be prepared directly by paths **a** to **d** (Fig. 1).

We now wish to report the synthesis of substituted (η^5-cyclohexadienyl) complexes **B** by Pd-catalysed cross coupling reaction starting from (η^5-chlorocyclohexadienyl)$Mn(CO)_3$ **A**, and then the transformation of these new complexes **B** into the corresponding cationic η^6 complexes **C** (Fig. 2).

2. Pd-catalysed functionalisation of (η^5-chlorocyclohexadienyl)$Mn(CO)_3$ complexes

(η^5-chlorocyclohexadienyl)$Mn(CO)_3$ complexes are prepared by hydride addition in THF to (η^6-chlorobenzene)$MnCO)_3^+$ complexes **1** (Fig. 3) leading generally to a mixture of separable regioisomers *ortho* **2** and *meta* **3** with respect to the Cl [14–16]. In the case of (η^6-*p*-chloroanisole)$Mn(CO)_3^+$, this addition afforded regioselectively complex **2** (Table 1, entry 2).

We first investigated the Stille cross coupling reaction and we showed that complexes **2a** and **2c** coupled with phenyltin reagents using 35 % $Pd_2(dba)_3$ in the presence of 10 % $AsPh_3$ [17] in DMF at room temperature to give the expected complexes **4a** and **4c**

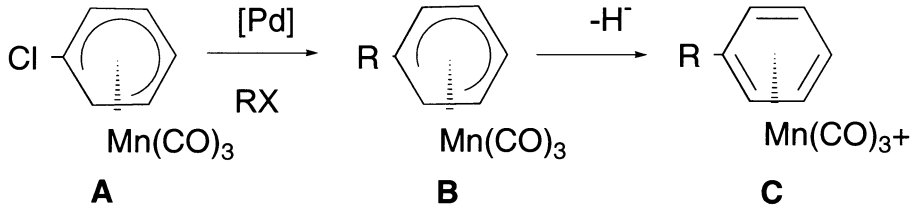

Fig. 2. General synthetic strategy.

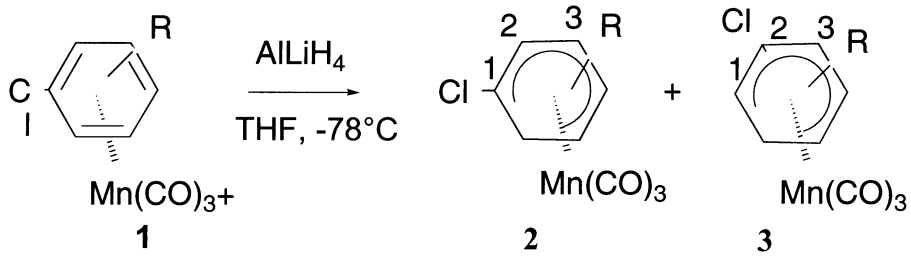

Fig. 3. Preparation of (η^5-chlorocyclohexadienyl)$Mn(CO)_3$ complexes.

(Fig. 4). Extending the reaction conditions to thienyltin reagents complexes **5a–5d** were obtained. The results gathered in Table 2 show that both substitution (entries 1, 7, 8 and 9) and steric hindrance (entries 10 and 11) of starting complex **2** did not affect the course of the reaction. Similarly, the reactivity of the chlorine atom towards the palladium catalysis in the oxidative addition does not seem to depend on its position in the π system [18]. Indeed, identical reaction conditions applied to complex **2a** (entry 1) or **3a** (entry 12) afforded the expected coupling product **4a** in 57% or **5'a** in 58% yield respectively. In contrast, it is worthy to note that the reaction course is greatly affected by the nature of the ligand. As shown in entries 3–6, using phosphorous ligands (PPh_3, dppf, $P(OEt)_3$, P^tBu_3) instead of $AsPh_3$ led in all cases to the decomposition of the starting material. The same reaction run without catalyst gave no arylation product (Table 2, entry 2), indicating that complexes **4** arose from a Pd-catalysed process.

We next turned our attention to the preparation of (η^5-cyclohexadienyl)$Mn(CO)_3$ complexes substituted by conjugated electron-withdrawing groups. We first synthesized (η^5-cyclohexadienyl)$Mn(CO)_3$ complexes **6** substituted by conjugated keto, ester and amide groups using a Pd-catalysed carbonylation of neutral (η^5-chlorocyclohexadienyl)$Mn(CO)_3$ (Fig. 5). Complex **2b** reacted under CO atmosphere in the presence of $Pd_2(dba)_3$ 35% and $AsPh_3$ 10% and 2-tributylstannylthiophene to deliver after 2 h complex **6a** in 90% yield (Table 3, entry 1). Under the same conditions, complex **2c** gave complex **6b** in 90% yield (Table 3, entry 2). This reaction has been extended to the preparation of alkyl ketones using Bu_4Sn as nucleophile (Table 3, entry 3).

Since the reaction pathway may involve an acyl palladate as an intermediate, we thought it could be trapped by classical nucleophiles [19, 20] in order to prepare carboxylic acid derivatives. Indeed reacting morpholine with complex **2b** under the same catalytic conditions afforded amide derivative **6d** (entry 4) in 48% yield [21].

Table 1.

Entry	R	Complex **1**	Ratio **2**:**3**	Yield (%)
1	H	**1a**	100:0	80
2	4-OMe	**1b**	100:0	95
3	4-Me	**1c**	60:40	90
4	2-Me	**1d**	25:75	91

3. Synthesis of unprecedented cationic (η^6-arene)$Mn(CO)_3$ complexes

In order to use these Pd-catalysed reactions as alternative methods for the preparation of functionalised cationic η^6 manganese complexes, it was crucial, at this point of our study, to ascertain if the new neutral η^5 complexes could be easily transformed into the

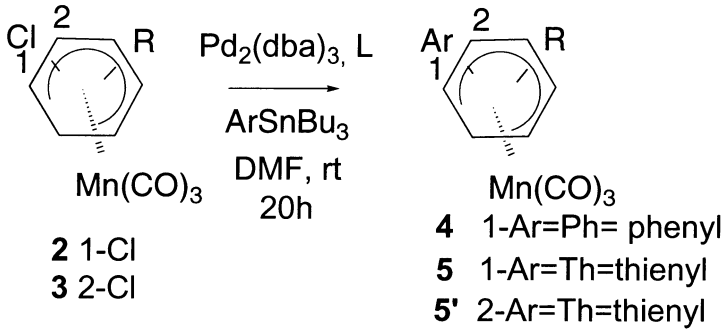

Fig. 4. Stille cross coupling reaction of (η^5-1-chlorocyclohexadienyl)$Mn(CO)_3$ complexes.

Table 2.

Entry	Complex	R	Ar	L	Yield (%)
1	**2a**	H	Ph	$AsPh_3$	**4a** (57)
2	**2a**	H	Ph	—	—
3	**2a**	H	Ph	PPh_3	—
4	**2a**	H	Ph	dppf	—
5	**2a**	H	Ph	$P(OEt)_3$	—
6	**2a**	H		P^tBu	—
7	**2a**	H	Th	$AsPh_3$	**5a** (51)
8	**2b**	4-OMe	Th		**5b** (78)
9	**2c**	4-Me	Ph		**4c** (45)
10	**2c**	4-Me	Th		**5c** (48)
11	**2d**	2-Me	Th		**5d** (53)
12	**3a**	H	Th		**5'a** (58)

corresponding cationic complex. The hydride abstraction proceeded very nicely in CH_2Cl_2 at room temperature (Fig. 6). The rearomatisation of complex **5c** gave quantitatively the unprecedented complex **7c** (Table 4, entry 1), which cannot be obtained by direct complexation of the corresponding free arene, since the manganese entity coordinates either the phenyl or the thienyl ring or both, giving a mixture of three inseparable products.

Performing the hydride abstraction from complexes **6** arose the matter of the coexistence of two strong acceptor groups (the $Mn(CO)_3^+$ entity and the carbonyl function) on the same ring. But the rearomatisation could be achieved in good yields from 70 to 95% yield by using CPh_3BF_4 as hydride abstracting reagent (Table 4, entries 2–4) to deliver stable cationic Mn complexes **7** bearing ketone or amide substituent.

As a conclusion we developed a high yield two step methodology to prepare unprecedented (η^6-arene)$Mn(CO)_3^+$ complexes starting from (η^5-chlorocyclohexadienyl)$Mn(CO)_3$ complexes consisting in Pd coupling reactions followed by *exo*-hydride abstraction.

4. General experimental procedure

4.1. Stille cross-coupling reaction: preparation of tricarbonyl(4-methyl(1-thienyl)cyclohexa dienyl)manganese complex 5c

Pd_2dba_3 (0.019 g, 0.02 mmol) and $AsPh_3$ (0.21 g, 0.07 mmol) were added to a solution of complex **2c** (0.063 g, 0.2 mmol) in degased DMF (7 ml). After 10 min, 2-tributylstannyl thiophene (0.071 g, 0.2 mmol) was introduced. The reaction mixture was stirred at room temperature for 20 h, poured into ice cold water (100 ml) and extracted with 50 ml pentane, the organic phase was washed with water (2×50 ml), dried over magnesium sulphate, filtered. Solvents were evaporated under reduced pressure. The residue obtained was purified by silica gel chromatography (pentane) to deliver complex **5c** as a yellow solid in 48% yield.

RMN ^1H ($CDCl_3$): 1.90 (3H, s, CH_3); 2.51 (1H, d, $J = 12$ Hz, H_{6exo}); 3.15(1H, d, $J = 6$ Hz, H_5); 3.24 (1H, dd, $J = 6$ and 12 Hz, H_{6endo}); 5.22 (1H, d, $J = 6$ Hz, H_2); 5.74 (1H, d, $J = 6$ Hz, H_3); 6,83 (1H, t, $J = 5$ Hz, H_{10}); 6,90 (1H, t, $J = 5$ Hz, H_9); 7,17 (1H, d, $J = 5$ Hz, H_8).

Elemental analysis: calculated, C 53.51, H 3.53; found, C 53.59, H 3.75.

Table 3.

Entry	Complex	R	R'Y	COR'	Yield (%)
1	**2b**	4-OMe	$ThSnBu_3$	COTh	**6a** (90)
2	**2c**	4-Me	$ThSnBu_3$	COTh	**6b** (90)
3	**2c**	4-Me	$SnBu_4$	COBu	**6c**(56)
4	**2b**	4-OMe	$HN(C_2H_4)_2O$	$CON(C_2H_4)_2O$	**6d** (48)

4.2. Carbonylation reaction: preparation of (4-methoxy-cyclohexadienyl)$Mn(CO)_3$thiophen-2-yl methanone complex 6a

Pd_2dba_3 (44 mg, 0,048 mmol) and $AsPh_3$ (51 mg, 0,17 mmol) were added to a solution of complex **2c** (135 mg, 0,48 mmol) in THF (10 ml). CO was bubbled into the reaction mixture, which was stirred at room temperature for 15 min, before introducing 2-tributylstannyl thiophene (343 mg, 1 mmol). The mixture was stirred at 60 °C overnight, then poured into ice-cold water (100 ml) and extracted with 50 ml ethyl ether. The organic phase was washed with water (2×50 ml), dried over magnesium sulphate and filtered. The solvents were evaporated under reduced pressure. The residue obtained was purified by silica gel chromatography (pentane 90%, ether 10%) to deliver complex **6a** as a yellow solid in 90% yield.

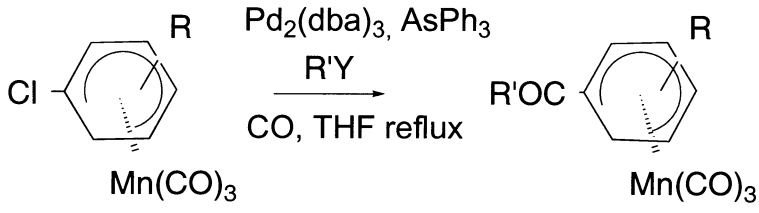

Fig. 5. Carbonylation of (η^5-1-chlorocyclohexadienyl)$Mn(CO)_3$ complexes.

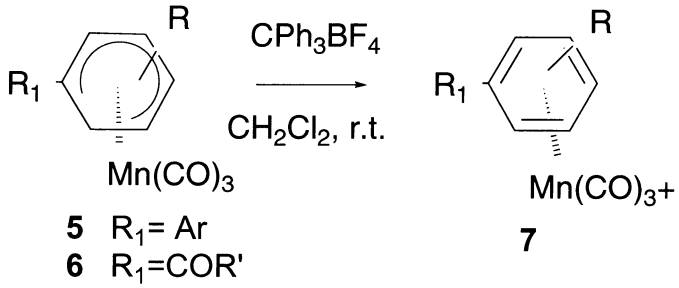

Fig. 6. Preparation of cationic complexes **7** by rearomatisation.

RMN ^{1}H ($CDCl_3$): 2.36(1H, d, J = 13 Hz, H_{6exo}); 3.20 (1H, dd, J = 6 et 2 Hz, H_5); 3.50 (1H, dd, J = 6 et 13 Hz, H_{6endo}); 3.48 (3H, s, OCH_3); 6.03 (1 H, d, J = 6 Hz, H_2); 6.14 (1H, d, J = 6 Hz, H_3); 7.07 (1H, dd, J = 4 and 5 Hz, Ar–H); 7.48 (1H, dd, J = 4 and 5 Hz, Ar–H); 7,55 (1H, m, Ar–H).

Elemental analysis: calculated, C 50.29, H 3.12; found, C 50.84, H 3.71.

Table 4.

Entry	Complex	R	R_1	Yield (%)
1	**5c**	4-OMe	Th	**7c** (>99)
2	**6a**	4-OMe	COTh	**7a** (95)
3	**6b**	4-Me	COTh	**7b** (70)
4	**6d**	4-OMe	$CON(C_2H_4)_2O$	**7d** (85)

4.3. Hydride abstraction: preparation of tricarbonyl(4-methoxy(1-thienyl)arene)manganese complex 7a

A solution of complex **6a** (108 mg; 0.15 mmol) in CH_2Cl_2 (5 ml) is introduced into a solution of CPh_3BF_4 (96 mg, 0.3 mmol) in CH_2Cl_2 (5 ml). The reaction mixture was stirred overnight, half the solvent was then evaporated. After cooling at 0°C, anhydrous Et_2O was added, a yellow solid precipitated. The solution was filtered and washed with anhydrous Et_2O and dried, complex **7a** was obtained as a yellow solid in 95% yield.

RMN ^{1}H (*acetone* d_6): 4.27 (3H, s, OMe); 6.57 (2H, d, J = 7.5 Hz, H_2 and H_6); 7.37 (1H, m, Ar–H); 7.66 (2H, d, J = 7.5 Hz, H_3 and H_5); 8.09 (1H, m, Ar–H); 8.23 (1H, m, Ar–H).

Elemental analysis: calculated, C 40.42, H 2.42; found, C 40.52, H 2.59.

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