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Oxidative addition of cationic (η^6-chloroarene)tricarbonylmanganese compounds to palladium(0) complexes. Synthesis, characterisation and reactivity

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Abstract

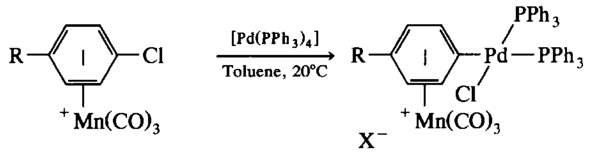
The oxidative addition of the coordinated chloroarene in $[(4\text{-}RC_6H_4Cl)Mn(CO)_3][X]$ ($R = H, OCH_3$; $X = PF_6, BF_4$) to $[Pd(PPh_3)_4]$ proceeds readily at room temperature to give $[\{\eta^6\text{-}[\{PdCl(PPh_3)_2\}(4\text{-}RC_6H_4)(Mn(CO)_3)][X]$. $^{31}P\{^1H\}$ NMR analysis of these square-planar palladium complexes revealed that the phosphorus ligands are *cis*. In contrast to their tricarbonylchromium analogues, these manganese complexes could not be carbonylated because the electron-withdrawing effect of the $Mn(CO)_3^+$ moiety is too strong.

Keywords: Manganese; Palladium; Oxidative addition; Chloroarene; Carbonylation; Catalysis

1. Introduction

The activation of aryl chlorides towards palladium-catalysed carbon–carbon bond formation through coordination of the arene ring to an electron-deficient transition metal is now well documented [1]. Much attention has been focused on (η^6-chloroarene)tricarbonylchromium complexes [1,2]. The reactions studied, essentially carbonylation reactions, could be conducted smoothly with a catalytic amount of palladium, and lead to functionalized arenes in good yields. The possibility of using (η^6-chlorobenzene)(η^5-cyclopentadienyl)iron(II) hexafluorophosphate has also been reported [3,4], but the reactions were not catalytic. Since it is well-established that nucleophilic displacement of chlorine on cationic (η^6-chloroarene)tricarbonylmanganese complexes proceeds under very mild conditions [5], we investigated the reaction between compounds **1a**–**c** and a zerovalent palladium complex.

Complexes **1a** and **1b** were found to react with an equimolar amount of $[Pd(PPh_3)_4]$ to give the oxidative-addition products **2a** and **2b** in nearly quantitative yields. The reaction proceeded in toluene at room temperature in a few hours, as indicated by precipitation of the product. In the case of the *para*-chloroanisole complex **1c**, the reaction rate was slower and a higher temperature (35°C) as well as a small excess of $[Pd(PPh_3)_4]$ (20%) were required to achieve completion. The ^1H, $^{13}C\{^1H\}$, $^{31}P\{^1H\}$ NMR and IRFT spectra, and elemental analyses, indicated that complexes **2a**–**2c** have the expected formula. These results show that the tricarbonylmanganese cation actually activates chloroarenes to bring about the oxidative addition of the C–Cl bond to Pd(0) species. Its effect is far greater than that of the



1a $R = H, X = PF_6$
1b $R = CH_3, X = PF_6$
1c $R = OCH_3, X = BF_4$

2a $R = H, X = PF_6$
2b $R = CH_3, X = PF_6$
2c $R = OCH_3, X = BF_4$

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(η^5-cyclopentadienyl)iron(II) cation (which requires THF reflux [3] or 100°C in DMF [4]), and is at least comparable to that of the tricarbonylchromium moiety (25°C in toluene, [6]). The lower reactivity of **1c** is attributable to the strong electron-donating effect of the *para*-methoxy group which partly reduces the activating effect of $Mn(CO)_3^+$. The $^{31}P\{^1H\}$ NMR data indicated that in all the complexes **2a–2c**, the two PPh_3 are *cis* in the square plane. This geometry in bis(monophosphine) palladium(II) complexes is very rare [7], but it has also been observed in the corresponding complex obtained from (η^6-chlorobenzene)(η^5-cyclopentadienyl)iron(II) hexafluorophosphate and $[Pd(PPh_3)_4]$ [3], and is probably due to the bulky $(\eta^6\text{-}RC_6H_4)Mn(CO)_3^+$ ligand.

Further carbonylation of complexes **2a–2c** was also investigated. Whatever the reaction conditions used (acetone, acetonitrile, methanol, 25–80°C, 1–50 atm CO), we could neither isolate nor detect the expected $[\{\eta^6\text{-}RC_6H_4CO(Mn(CO)_3)\}PdCl(PPh_3)_2][X]$ ($X = PF_6$ or BF_4) and starting material **2a–2c** was recovered. Several attempts to produce (η^6-methyl 4-methylbenzoate)tricarbonylmanganese hexafluorophosphate from **1b** in $CH_3OH\text{–}NEt_3$ (10 ml : 0.14 ml) under 50 atm of CO at 80°C with a catalytic amount of $[Pd(PPh_3)_4]$ or $[PdCl_2(PPh_3)_2]$ resulted in trace amounts of methyl 4-methylbenzoate (uncoordinated ester) and variable amounts of 4-methoxytoluene (S_NAr product). This reactivity of complexes **2a–2c** towards carbon monoxide is very different from that of their chromium analogues, which easily produce carbonylation derivatives [6]. The insertion of a carbon monoxide molecule into a metal–carbon bond is believed to proceed through intramolecular nucleophilic attack of the aryl residue on coordinated CO [8]. In our case, the impossibility of inserting a carbon monoxide into the Pd–C(aryl) bond may be due to the strong electron-withdrawing effect of the tricarbonylmanganese cation which reduces considerably the electron density on the arene ring (as shown by the easy oxidative-addition step) and consequently its nucleophilicity towards coordinated CO.

These results clearly illustrate the difficulty of achieving catalytic carbonylation of chloroarenes, since the two first elementary steps of the catalytic cycle (oxidative addition and CO insertion) require opposite electronic characteristics of the arene ring. However, the easy activation of the C–Cl bond in (chloroarene)tricarbonylmanganese derivatives by zerovalent palladium complexes suggests the potential of various palladium-catalysed carbon–carbon bond formation processes.

2. Experimental details

Chloroarene(tricarbonylmanganese) complexes **1a** and **1b** [5a] and **1c** [9] were synthesised according to literature methods.

2.1. *General procedure for oxidative addition of chloroarene complexes to $[Pd(PPh_3)_4]$*

A toluene solution (8 ml) of tetrakis(triphenylphosphine)palladium(0) (40 mg, 0.035 mmol) under N_2 was transferred to a Schlenk tube containing the (chloroarene)tricarbonylmanganese complex **1** (0.035 mmol). The resulting clear suspension was protected from daylight and stirred at room temperature, giving rise (after a few h) to a precipitate. After 18 h stirring, the precipitate was filtered off, washed with Et_2O (2 × 3 ml) and dried under vacuum to give an off-white to pale-yellow solid in nearly quantitative yield.

2a: Anal. Calc. for $C_{45}H_{35}ClF_6MnO_3P_3Pd$: C 52.6, H 3.43; Found: C 52.7, H 3.42% ^1H NMR (300 MHz, CD_3COCD_3, ppm): 5.79 (m, 2H), 6.20 (m, 1H), 6.77 (m, 2H), 7.1–7.7 (m, 30H, PPh_3). $^{13}C\{^1H\}$ NMR (75.5 MHz, CD_3COCD_3, ppm): 95.8 (d, $J(CP) = 6.1$ Hz, C_o), 100.2 (s, C_p), 112.7 (d, $J(CP) = 4.3$ Hz, C_m), 128.8–136.3 (PPh_3), 219.1 (s, MnCO). $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_3COCD_3, ppm): 20.6 (d, $J(PP) = 30.5$ Hz), 36.3 (d, $J(PP) = 30.5$ Hz). IR (KBr, cm^{-1}): 2066, 2018, 1993 (vs, $Mn(CO)_3$).

2b: Anal. Calc. for $C_{46}H_{37}ClF_6MnO_3P_3Pd$: C 53.0, H 3.58, P 8.92; Found: C 53.7, H 3.93, P 8.40% ^1H NMR: 2.30 (s, 3H, CH_3), 5.64 (m, 2H), 6.75 (m, 2H), 7.1–7.8 (m, 30H, PPh_3). $^{13}C\{^1H\}$ NMR: 19.0 (s, CH_3), 95.5 (d, $J(CP) = 6.7$ Hz, C_o), 112.2 (d, $J(CP) = 4.5$ Hz, C_m), 118.2 (s, C_p), 128.4–136.2 (PPh_3), 219.1 (s, MnCO). $^{31}P\{^1H\}$ NMR: 20.5 (d, $J(PP) = 30.5$ Hz), 35.8 (d, $J(PP) = 30.5$ Hz). IR: 2060, 2010, 1997 (vs, $Mn(CO)_3$).

2c: MS/FAB$^+$: 911 (isotopic mass of $C_{46}H_{37}ClMnO_4P_2Pd$). ^1H NMR: 3.88 (s, 3H, OCH_3), 5.54 (m, 2H), 6.82 (m, 2H), 7.1–8.0 (m, 30H, PPh_3). $^{13}C\{^1H\}$ NMR: 56.4 (s, OCH_3), 80.0 (d, $J(CP) = 6.3$ Hz, C_o), 111.6 (s, C_p), 117.0 (d, $J(CP) = 14$ Hz, C_m), 128.8–139.2 (PPh_3), 219.1 (s, MnCO). $^{31}P\{^1H\}$ NMR: 20.6 (d, $J(PP) = 30.5$ Hz), 35.7 (d, $J(PP) = 30.5$ Hz). IR: 2057, 1999, 1983 (vs, $Mn(CO)_3$).

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