Palladium catalysed cross-coupling of (fluoroarene)tricarbonylchromium(0) complexes

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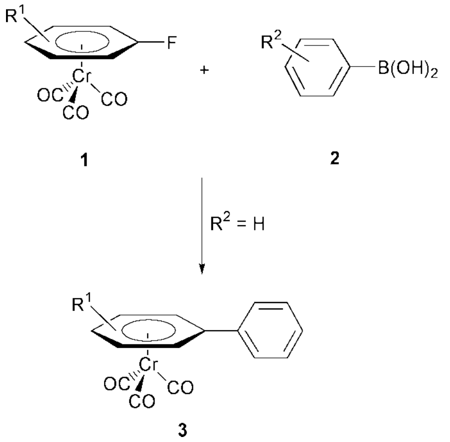
(Fluoroarene)tricarbonylchromium(0) complexes were found to undergo Suzuki and Stille cross-coupling reactions to form functionalised biaryl and styrene complexes in up to 87 and 52% yields, respectively. The Suzuki reactions were optimal with dipalladium tris(dibenzylideneacetone)–trimethylphosphine–caesium carbonate in DME at reflux. The Stille reactions were optimal with dipalladium tris(dibenzylideneacetone)–trimethylphosphine–caesium fluoride in DME at reflux and neither was adversely affected by a methoxy group on the complexed ring. The Suzuki reaction tolerated a chloro group on the arylboronic acid ring but not a bromo group.

Introduction

The Suzuki and Stille reactions are the most widely used and successful processes for the synthesis of biaryls.[1,2] Although aryl iodides, bromides and triflates are the most commonly used halide partners in these reactions, in some remarkable recent developments, aryl chlorides, hitherto regarded as inert to palladium cross-coupling reactions, have been shown to be effective participants provided there is an electron withdrawing group on the aryl ring[3] (including the η^6-tricarbonylchromium group)[4] and/or a basic phosphine ligand for palladium[5–10] is present. In the latter case, it has been shown that hindered phosphine ligands are particularly effective, even with electron rich aryl chlorides.[5,6]

We now report[11] that aryl fluorides, as their tricarbonylchromium(0) complexes **1**, will also undergo palladium catalysed cross-coupling with arylboronic acids **2** (Suzuki coupling, Scheme 1) and with vinyltributylstannane (Stille coupling, see Scheme 4).



Scheme 1 *Reagents and conditions*: 5 mol% $Pd_2(dba)_3$, base, ligand, DME reflux, 16 h (dba = dibenzylideneacetone).

Results and discussion

Suzuki reactions of (fluoroarene)tricarbonylchromium(0) complexes

Initially, we used standard conditions for Suzuki coupling[1] by which tetrakis(triphenylphosphine)palladium, fluorobenzenetricarbonylchromium(0) **1**, $R^1 = H$, and phenylboronic acid **2**, $R^2 = H$, together with sodium carbonate as base, gave the coupled complex **3**, $R^3 = H$, but only in trace amounts (Table 1, Run 1). When the reaction was repeated with dipalladium tris(dibenzylideneacetone) and caesium fluoride as the base and with tricyclohexylphosphine (Run 2; conditions reported by Fu and Littke[5]), no coupled product was detectable but dipalladium tris(dibenzylideneacetone)–trimethylphosphine, a phosphine not previously used for this purpose (Run 3), did produce biphenyltricarbonylchromium(0) complex in 52% yield.

Table 1 Control experiments for Suzuki couplings of (fluorobenzene)tricarbonylchromium(0)

Run	Pd	Added ligand	Base (equiv.)	Yield (%)
1	$Pd(PPh_3)_4$		Na_2CO_3 (2.2)	Trace[a]
2	$Pd_2(dba)_3$	PCy_3	CsF (4)	0
3	$Pd_2(dba)_3$	PMe_3	CsF (4)	52
4	$Pd_2(dba)_3$	—	CsF (4)	0
5	$Pd_2(dba)_3$	PMe_3	—	0[b]
6	$Pd_2(dba)_3$	PMe_3	Cs_2CO_3 (2.2)	61
7	—	PMe_3	Cs_2CO_3 (2.2)	0
8	—	—	Cs_2CO_3 (2.2)	0

[a] Toluene as solvent. [b] 4-Methoxyphenylboronic acid instead of phenylboronic acid.

The participation of a fluoroarene, albeit as its tricarbonylchromium complex, in a palladium catalysed cross-coupling is unprecedented[12] and required careful evaluation. The ready displacement of fluoride in these complexes by other nucleophiles,[13–16] particularly higher halides, which could then undergo cross-coupling, required that the system be free of any source of such nucleophiles. Thus no solvent/additive which might release higher halide was used and initially, either high purity (99.9%) caesium fluoride or caesium carbonate was used as the base. In principle, fluoride should be catalytic but attempts to demonstrate this have so far failed.

Control experiments covering the more obvious factors were carried out and the results are summarised in Table 1. The ineffectiveness of the normally active tricyclohexylphosphine as ligand (Run 2)[5,17] could be a consequence of steric hindrance between the bulky tricarbonylchromium unit and the bulky phosphine, and trimethylphosphine, with its lower cone angle, was used in all subsequent experiments. In the absence of any

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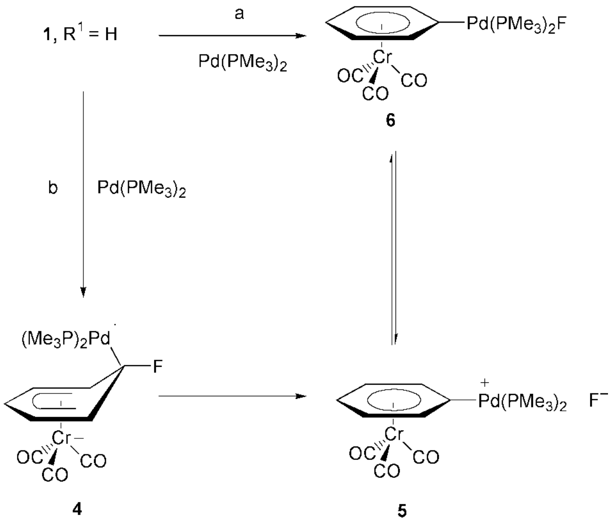
phosphine, the coupling failed (Run 4). Reaction without a base (Run 5) also failed but the use of caesium carbonate (Run 6) increased the yield to 61%. Reactions in the presence of base and phosphine but without palladium (Run 7) or in the absence of palladium and phosphine (Run 8) gave no coupled product.

Run 7 suggested that the neutral phosphine was unreactive towards the fluoro complex but to reinforce this conclusion a direct reaction between trimethylphosphine (1 equiv.) and fluorobenzene complex **1**, $R^1 = H$, under cross-coupling conditions was attempted. The fluoro complex was recovered unchanged in 98% yield. This precludes a process of phosphonium salt formation and participation of this salt in the cross-coupling process.[18,19]

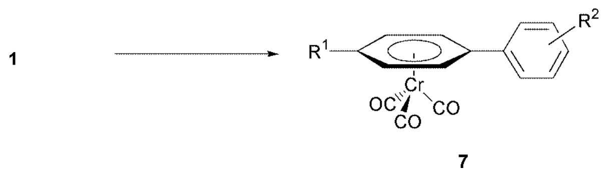
The presence of unchanged starting material from Run 8 also discounted the possibility that the arylborate anion was displacing the fluoride group from the complex and that the resultant $[Cr(CO)_3]$phenyl arylborate was the active cross-coupling partner.

These experiments provide strong evidence for the direct participation of the fluorobenzene complex in the coupling process with the implication of an unprecedented oxidative addition of the C–F bond to the palladium(0) intermediate.[20] Whether this is a concerted insertion (Scheme 2: path a) or an addition–elimination sequence (Scheme 2: path b) *via* an *exo* addition[21] of palladium to form **4** followed by fluoride loss to produce **5** cannot be determined at this point. The insertion product could be active in the catalytic cycle in either neutral **6** or cationic **5** form.[12]



Scheme 2

With suitable conditions established, the (fluorobenzene)-chromium complex **1**, $R^1 = H$, was coupled with a series of electron rich arylboronic acids **2** (Scheme 3, Table 2). The conditions finally developed were to stir a solution of fluorobenzene complex **1**, $R^1 = H$, the boronic acid **2**, caesium carbonate, 5 mol% $Pd_2(dba)_3$ and 20 mol% trimethylphosphine in deoxygenated DME under reflux for 16 h. Normal work-up gave the purified coupled product. Both unhindered (Table 2, Runs 1, 2, 3) and moderately hindered (Table 2, Runs 4, 5) boronic acids gave good yields of **7**. The polymerisation of 4-bromophenylboronic acid **2**, $R^2 = 4$-Br under the reaction conditions can be attributed to the greater reactivity of the C–Br bond over the C–F bond. However when 4-chlorophenylboronic acid **2**, $R^2 = 4$-Cl, was used the coupled product **7**, $R^2 = 4$-Cl, was isolated in 64% yield, which suggests that the reactivity of the C-F bond in the complex **2**, $R^1 = H$, is greater than that of the C–Cl bond under these reaction conditions.



Scheme 3 *Reagents and conditions*: 5 mol% $Pd_2(dba)_3$; 2 equiv. boronic acid **2**; 2.2 equiv. Cs_2CO_3; 20 mol% PMe_3; DME reflux 16 h.

Table 2 Suzuki couplings of (fluorobenzene)tricarbonylchromium(0) complexes **1** (Scheme 3)

	Boronic acid **2**		Product **7**	
Run	R^2	R^1	R^2	Yield (%)
1	H	H	H	61
2	4-MeO	H	4-MeO	87
3	4-Me	H	4-Me	81
4	2-MeO	H	2-MeO	78
5	2-Me	H	2-Me	79
6	4-Br	H	4-Br	0[a]
7	4-Cl	H	4-Cl	64
8	H	4-MeO	H	76
9	2-Me	4-MeO	2-Me	77
10	4-Me	4-MeO	4-Me	74

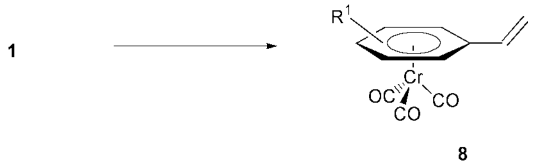
[a] Polymeric products derived from boronic acid **2**, $R^2 = Br$, were isolated.

To investigate more fully the scope of this process, the more electron rich (4-methoxyfluorobenzene)tricarbonylchromium complex **1**, $R^1 = 4$-MeO, prepared as before[22] in an improved 68% yield, was chosen for further study. A solution of this complex **1**, $R^1 = 4$-MeO, the boronic acid **2**, caesium carbonate, 5 mol% $Pd_2(dba)_3$ and 20 mol% trimethylphosphine in deoxygenated DME was stirred under reflux for 16 h (Scheme 4).

The yields with both the moderately hindered [Table 2, Run 9, $R^2 = 2$-Me, (77%)] and the unhindered [Runs 8, $R^2 = H$ (76%) and 10, $R^2 = 4$-Me (74%)] boronic acids were comparable to those of the parent complex **1**, $R^1 = H$ (79, 61 and 81% respectively) despite the expected reduction in reactivity by the 4-methoxy group.

Stille reactions of (fluorobenzene)tricarbonylchromium complexes

The Stille reaction is generally less facile than the Suzuki reaction[23] and in line with this, aryltributylstannanes failed to react with the complex **1**, $R^1 = H$. However, complex **1**, $R^1 = H$ was found to couple with vinyltributylstannane, using the conditions established for the Suzuki reactions, to give the styrene complex **8**, $R^1 = H$, albeit in only 5% yield after 16 h reflux. The use of DMF at 130 °C or dioxane at reflux led to the decomplexation of the complex.



Scheme 4 *Reagents and conditions*: 5 mol% $Pd_2(dba)_3$; 2 equiv. $Bu_3Sn(CH{=}CH_2)$; 4 equiv. CsF; 20 mol% PMe_3; DME reflux 16–40 h.

On the basis that an 'ate' complex of the stannane is the active coupling partner,[9] the caesium carbonate was replaced by caesium fluoride and gratifyingly, after 16 h reflux, complex **8**, $R^1 = H$, was isolated in 48% yield (Table 3, Run 1).

With Stille coupling established, a series of functionalised complexes, **1**, $R^1 = 2$-MeO, 4-MeO, 3-Me, 4-Me, 4-CHO, was prepared according to literature methods.[22] The yields are given in Table 3. The previously unknown complex **1**, $R^1 = 4$-$CH(OCH_2)_2$, was prepared from 2-(4-fluorophenyl)-1,3-

Table 3 Synthesis and Stille couplings of (fluoroarene)tricarbonylchromium(0) complexes **1**

	Complex **1**		Product **8**	
Run	R^1	Yield (%)	R^1	Yield (%)
1	H	[a]	H	48
2	2-MeO	[a]	2-MeO	42
3	4-MeO	68	4-MeO	40
4	3-Me	[a]	3-Me	52
5	4-Me	[a]	4-Me	52
6	4-CH($OCH_2)_2$	52	4-CH($OCH_2)_2$	37
7	4-CHO	92 [b]	4-CHO	0 [c]
8	H	[a]	[d]	13 [e]
9	4-MeO	68	[f]	6 [e]

[a] See ref. 22. [b] For the acid catalysed hydrolysis of **1**, R^1 = 4-CH($OCH_2)_2$. [c] **1**, R^1 = 4-CHO was unstable to the reaction conditions. [d] Product: **3**, R^1 = H. [e] From phenyltrimethylstannane. [f] Product: **3**, R^1 = 4-MeO.

dioxolane[24] by refluxing the ligand in a mixture of dibutyl ether and THF (20 : 1) with hexacarbonylchromium(0) for 24 h. To further assess electronic effects in the chromium complex, the electron deficient formyl analogue **1**, R^1 = CHO, was prepared by acid (2 M sulfuric acid) catalysed hydrolysis of the dioxolane complex **1**, R^1 = 4-CH($OCH_2)_2$, in THF during 1 h at room temperature, in 92% yield. However, this complex proved to be too fragile and was decomposed on attempted cross-coupling (Table 3, Run 7) as it was by simply heating it for 30 min in refluxing DME. Using the optimised conditions, the remaining complexes were coupled with vinyltributylstannane (as in Scheme 4). The results are shown in Table 3, Runs 2–6.

To address again the potential of the Stille reaction in biaryl formation, the less hindered phenyltrimethylstannane[25] was prepared from phenyllithium (iodobenzene, BuLi) and trimethyltin chloride in 99% yield. Coupling of this under the above conditions with complex **1**, R^1 = H, and **1**, R^1 = 4-MeO, did give the products **3**, R = H and **3**, R^1 = 4-MeO but in only 13 and 6% yield respectively (Table 3, Runs 8, 9). The low yield compared to the vinyltributylstannane can be related to the known lower reactivity of phenylstannanes compared with vinylstannanes in Stille couplings.[26] The use of phenylethynyltributylstannane, which is more reactive than vinylstannane[26] led only to partial polymerisation and residual starting material.

These results clearly raise intriguing mechanistic questions, which we continue to address. The couplings demonstrate the versatility of the (arene)tricarbonylchromium(0) complexes and add further possibilities to the exploitation of their already widely established role in synthesis.

Experimental

Reactions carried out under nitrogen were performed using standard vacuum line techniques.[27] THF and DME were distilled from sodium benzophenone ketyl. Dibutyl ether was distilled from sodium. Caesium carbonate, caesium fluoride, tris(dibenzylideneacetone)dipalladium(0), 4-methoxyfluorobenzene, vinyltributylstannane and the boronic acids were obtained from commercial sources and used without further purification. Trimethylphosphine was used as received from the Sigma-Aldrich Company as a 1 M solution in toluene or THF. The known, fully characterised complexes, η^6-(fluorobenzene)tricarbonylchromium(0),[28,29] η^6-(2-methylfluorobenzene)tricarbonylchromium(0)[28] and η^6-(2-methoxyfluorobenzene)tricarbonylchromium(0)[28] and the acetal 2-(4-fluorophenyl)-1,3-dioxolane[24] were prepared according to the indicated literature procedures. Flash column chromatography (FCC)[30] was performed on Sorbisil C-60. Elemental analyses were carried out by Mr Stephen Boyer, SACS, University of North London and are reported as the average of two runs. Infrared spectra were recorded on a Perkin-Elmer RX FT-IR System. NMR spectra were performed in $CDCl_3$ at ambient temperature on a JEOL GSX 270 (270 MHz ^1H and 68 MHz ^{13}C). Mass spectra were recorded on VG Micromass 7070E and AutoSpec-Q spectrometers. Melting points were taken on a Kofler hot stage apparatus and are uncorrected. In spectral assignments, Ar refers to the complexed ring.

General procedure for the synthesis of tricarbonylchromium(0) complexes

Minor variants of the method of Pauson and Mahaffy were used for the synthesis of complexes,[28] by which the arene and hexacarbonylchromium are refluxed in an ether solvent, under an atmosphere of nitrogen, for an empirically determined period. The variations were in the solvent or solvent mixtures used for the complexation process and are given below as appropriate.

η^6-(4-Methoxyfluorobenzene)tricarbonylchromium(0) 1, R^1 = 4-OMe. 4-Methoxyfluorobenzene (15 mL, 158 mmol) and hexacarbonylchromium (14 g, 63 mmol) were refluxed for 60 h in dibutyl ether–THF (300 mL–10 mL). FCC (eluant: 10% ether–hexane) furnished the *complex* **1**, R^1 = 4-OMe as a bright yellow crystalline solid (11.12 g, 42.4 mmol, 68%, lit.[22] 46%), mp 69–71 °C (lit.[22] mp 69–70 °C) (Found: C, 45.72; H, 2.76. $C_{10}H_7CrFO_4$ requires: C, 45.82; H, 2.69%). The spectral data were consistent with literature values.[31,32]

η^6-[4-(1,3-Dioxolan-2-yl)fluorobenzene]tricarbonylchromium(0) 1, R^1 = 4-CH($OCH_2)_2$. 4-(1,3-Dioxolan-2-yl)fluorobenzene[24] (5 g, 30 mmol) and hexacarbonylchromium (7.17 g, 32 mmol) were refluxed for 24 h in dibutyl ether–THF (200 mL–10 mL). FCC (eluant: 40% ether–hexane) furnished the *complex* **1**, R^1 = 4-CH($OCH_2)_2$ as a bright yellow crystalline solid (4.83 g, 15.74 mmol, 53%), mp 79–80 °C (Found: C, 47.30; H, 2.88. $C_{12}H_9CrO_5F$ requires: C, 47.38; H, 2.98%). ν_{max} (KBr)/cm^{-1} 3088m, 2891w, 1968vs, 1885vs, 1480m, 1227s, 1102s, 664s, 624s. δ_H (270 MHz) 5.71 (2 H, dd, J 2.7, 6.7 Hz, ArC(3,5)H), 5.44 (1 H, s, CH), 5.28 (2 H, t, J 4.9 Hz, ArC(2,6)H), 4.12–3.97 (4 H, s, OCH_2CH_2O); δ_C (68 MHz) 231.1 (CO), 143.4 (d, J_{C-F} 731.7 Hz, ArC(1)-F), 101.7 (ArC(4)-C), 100.6 (CH), 91.6 (d, J_{C-F} 8.0 Hz, ArC(3,5)H), 77.5 (d, J_{C-F} 21.1 Hz, ArC(2,6)H), 65.8 (OCH$_2$$CH_2$O). m/z (FAB$^+$) 304 (M^+, 85%) 290 (19), 248 ($M^+ - 2 \times CO$, 100), 220 ($M^+ - 3 \times CO$, 36), 167 ($M^+ - H\ Cr(CO)_3$), 21), 152 (26), 135 (36), 120 (66), 89 (65), 77 (72), 52 (Cr, 26). Found: M^+ 303.9848. $C_{12}H_9CrO_5F$ requires: 303.9855.

η^6-(4-Formylfluorobenzene)tricarbonylchromium(0) 1, R^1 = 4-CHO. η^6-[4-(1,3-Dioxolan-2-yl)fluorobenzene]tricarbonylchromium(0) **1**, R^1 = 4-CH($OCH_2)_2$, (1.7 g, 5.60 mmol) was dissolved in THF (50 mL) and 2 M sulfuric acid (10 mL) was added and the mixture stirred for 1 h. Ether (100 mL) was added and the aqueous layer was separated, washed with water (25 mL) and brine (25 mL) and dried (Mg_2SO_4). The solvent was removed and FCC (eluant: 40% ether–hexane) gave the *complex* **1**, R^1 = 4-CHO as a bright orange crystalline solid (1.34 g, 5.15 mmol, 92%), mp 71–75 °C (Found: C, 46.34; H, 1.74. $C_{10}H_5CrO_4F$ requires: C, 46.17; H, 1.94%); ν_{max} (KBr)/cm^{-1} 3095w, 1985vs, 1915vs, 1884vs, 1681s, 1229s, 1197s, 665s, 613s. δ_H (270 MHz) 9.35 (1 H, s, CHO), 6.02 (2 H, dd, J 2.7, 6.9 Hz, ArC(3,5)H), 5.41 (2 H, dd, J 4.9, 6.43 Hz, ArC(2,6)H); δ_C (68 MHz) 228.4 (CO), 185.9 (CHO), 147.5 (d, J_{C-F} 277.6 Hz, ArC(1)F), 92.7 (d, J 8.0 Hz, ArC(3,5)H), 91.0 (ArC(4)-CHO), 77.84 (d, J 21.1 Hz, ArC(2,6)H). m/z (FAB$^+$) 260 (M^+, 15%), 204 ($M^+ - 2 \times CO$, 10), 176 ($M^+ - 3 \times CO$, 8), 152 (28), 135 (30), 124 ($M^+ - Cr(CO)_3$, 35), 120 (45), 91 (65), 69 (88), 55 (100). Found: M^+ 259.9584. $C_{10}H_5CrO_4F$ requires: 259.9577.

General procedure for the coupling of (fluoroarene)chromium complexes with arylboronic acids

A solution of the (fluoroarene)tricarbonylchromium(0) complex (1 equiv., 1.29 mmol), arylboronic acid (2 equiv., 2.58 mmol), caesium carbonate (2.2 equiv., 0.925 g, 2.84 mmol), $Pd_2(dba)_3$ (5 mol%, 0.060 g, 0.06 mmol) and trimethylphosphine (20 mol%, 0.26 mL, 1 M solution in toluene, 0.26 mmol) in deoxygenated DME (9 mL) was stirred under reflux for 16 h. Ether (20 mL) was added and the solution was washed with 10% $NaOH_{(aq)}$ (10 mL), water (10 mL) and brine (10 mL) and dried over $MgSO_4$. Concentration *in vacuo* followed by column chromatography (FCC) and recrystallisation where necessary furnished the desired complex.

η^6-(Phenylbenzene)tricarbonylchromium(0) 3, R^1 = H. From η^6-(fluorobenzene)tricarbonylchromium(0) **1**, R^1 = H (0.300 g, 1.29 mmol) and phenylboronic acid (0.320 g, 2.58 mmol). FCC (eluant: 5% ether–hexane) furnished the title product **3**, R^1 = H, as a yellow crystalline solid (0.230 g, 0.79 mmol, 61%), mp 84–86 °C (lit.[33] 84–85 °C) (Found: C, 61.86; H, 3.61. $C_{15}H_{10}CrO_3$ requires: C, 62.07; H, 3.47%). ν_{max} (KBr)/cm^{-1} 3187w, 3026w, 1976s, 1866s, 1452m, 760m, 698s, 660s, 622m, 533m. δ_H (270 MHz) 7.51–7.34 (5 H, m, Ph*H*), 5.69 (2 H, dd, *J* 1.0, 6.7 Hz, Ar(2,6)*H*), 5.49 (2 H, t, *J* 6.5 Hz, Ar(3,5)*H*), 5.34 (1 H, tt, *J* 1.0, 6.2 Hz, Ar(4)*H*); δ_C (68 MHz) 232.8 (*C*O), 136.6 (Ph*C*(1)-Ar), 129.1 (Ph*C*(4)H), 128.9 (Ph*C*(3,5)H), 127.2 (Ph*C*(2,6)H), 110.6 (Ar*C*(1)-Ph), 92.6 (Ar*C*(2,6)H), 92.3 (Ar*C*(3,5)H), 91.5 (Ar*C*(4)H). *m*/*z* (EI) 290 (M^+, 23%), 234 ($M^+ - 2 \times CO$, 21), 206 ($M^+ - 3 \times CO$, 79), 154 ($M^+ - Cr(CO)_3$, 30), 77 (Ph, 5), 52 (Cr, 100). Found: M^+ 290.0030. $C_{15}H_{10}CrO_3$ requires: 290.0035. The spectral data were consistent with literature values.[34]

η^6-[(4-Methoxyphenyl)benzene]tricarbonylchromium(0) 7, R^1 = H, R^2 = 4-MeO. From η^6-(fluorobenzene)tricarbonylchromium(0) **1**, R^1 = H (0.300 g, 1.29 mmol) and 4-methoxyphenylboronic acid (0.392 g, 2.58 mmol). FCC (eluant: 5% ether–hexane) furnished the *title product* **7**, R^1 = H, R^2 = 4-MeO, as a yellow crystalline solid (0.360 g, 1.12 mmol, 87%), mp 58–61 °C (Found: C, 59.99; H, 3.69. $C_{16}H_{12}CrO_4$ requires: C, 60.01; H, 3.78%). ν_{max} (KBr)/cm^{-1} 2968w, 2838w, 1977s, 1961s, 1887s, 1868s, 1609m, 1508m, 1454m, 1279m, 1249m, 1176m, 1020m, 840m, 819m, 661m, 629s, 535m. δ_H (270 MHz) 7.43 (2 H, d, *J* 8.9 Hz, Ph(2,6)*H*), 6.93 (2 H, d, *J* 8.9 Hz, Ph(3,5)*H*), 5.64 (2 H, dd, *J* 1.0, 6.7 Hz, Ar(2,6)*H*), 5.49 (2 H, t, *J* 6.4 Hz, Ar(3,5)*H*), 5.28 (1 H, tt, *J* 1.0, 6.2 Hz, Ar(4)*H*), 3.83 (3 H, s, O*Me*); δ_C (68 MHz) 233.0 (*C*O), 160.4 (Ph*C*(4)-OMe), 128.6 (Ph*C*(1)-Ar), 128.3 (Ph*C*(2,6)H), 114.3 (Ph*C*(3,5)H), 111.2 (Ar*C*(1)-Ph), 93.2 (Ar*C*(2,6)H), 91.6 (Ar*C*(3,5)H), 90.9 (Ar*C*(4)H), 55.4 (O*Me*). *m*/*z* (EI) 320 (M^+, 43%), 264 ($M^+ - 2 \times CO$, 39), 236 ($M^+ - 3 \times CO$, 93), 221 (236 − Me, 11), 205 (236 − OMe, 5), 184 ($M^+ - Cr(CO)_3$, 9), 169 (221 − Cr, 4), 52 (Cr, 100). Found: M^+ 320.0130. $C_{16}H_{12}CrO_4$ requires: 320.0141.

η^6-[(2-Methoxyphenyl)benzene]tricarbonylchromium(0) 7, R^1 = H, R^2 = 2-MeO. From η^6-(fluorobenzene)tricarbonylchromium(0) **1**, R^1 = H (0.300 g, 1.29 mmol) and 2-methoxyphenylboronic acid (0.392 g, 2.58 mmol). FCC (eluant: 5% ether–hexane) furnished the *title product* **7**, R^1 = H, R^2 = 2-MeO, as a yellow crystalline solid (0.320 g, 1.01 mmol, 78%), mp 106–108 °C (Found: C, 60.23; H, 3.87. $C_{16}H_{12}CrO_4$ requires: C, 60.01; H, 3.78%). ν_{max} (KBr)/cm^{-1} 2937w, 1951s, 1880s, 1856vs, 1496m, 1266m, 1024m, 755m, 660s, 632s, 529m. δ_H (270 MHz) 7.41–7.30 (2 H, m, Ph*H*), 7.03–6.92 (2 H, m, Ph*H*), 5.74–5.72 (2 H, m, Ar*H*), 5.38–5.31 (3 H, m, Ar*H*), 3.85 (3 H, s, O*Me*); δ_C (68 MHz) 233.2 (*C*O), 156.9 (Ph*C*(2)-OMe), 131.1 (Ph*C*(6)H), 130.2 (Ph*C*(4)H), 125.1 (Ph*C*(1)-Ar), 120.9 (Ph*C*(5)H), 111.3 (Ph*C*(3)H), 108.3 (Ar*C*(1)-Ph), 96.3 (Ar*C*(2,6)H), 92.5 (Ar*C*(4)H), 91.4 (Ar*C*(3,5)H), 55.6 (O*Me*). *m*/*z* (EI) 320 (M^+, 24%), 264 ($M^+ - 2 \times CO$, 13), 236 ($M^+ - 2 \times CO$, 67), 221 (236 − Me, 81), 184 ($M^+ - Cr(CO)_3$, 6), 169 (221 − Cr, 8), 52 (Cr, 100). Found: M^+ 320.0128. $C_{16}H_{12}CrO_4$ requires: 320.0141.

η^6-[(4-Methylphenyl)benzene]tricarbonylchromium(0) 7, R^1 = H, R^2 = 4-Me. From η^6-(fluorobenzene)tricarbonylchromium(0) **1**, R^1 = H (0.300 g, 1.29 mmol) and 4-methylphenylboronic acid (0.350 g, 2.58 mmol). FCC (eluant: 5% ether–hexane) furnished the *title product* **7**, R^1 = H, R^2 = 4-Me, as a yellow crystalline solid (0.329 g, 1.08 mmol, 84%), mp 100–104 °C (Found: C, 63.31; H, 3.94. $C_{16}H_{12}CrO_3$ requires: C, 63.16; H, 3.98%). ν_{max} (KBr)/cm^{-1} 3088w, 1958s, 1896s, 1878s, 1458w, 1151m, 1011m, 810m, 659m, 629s, 531m. δ_H (270 MHz) 7.39 (2 H, d, *J* 8.2 Hz, Ph(2,6)*H*), 7.21 (2 H, d, *J* 7.9 Hz, Ph(3,5)*H*), 5.66 (2 H, dd, *J* 1.0, 6.9 Hz, Ar(2,6)*H*), 5.48 (2 H, t, 6.7 Hz, Ar(3,5)*H*), 5.30 (1 H, tt, *J* 1.0, 6.2 Hz, Ar(4)*H*), 2.37 (3 H, s, *Me*); δ_C (68 MHz) 232.9 (*C*O), 139.3 (Ph*C*(4)-Me), 133.6 (Ph*C*(1)-Ar), 129.6 (Ph*C*(3,5)H), 127.0 (Ph*C*(2,6)H), 111.0 (Ar*C*(1)-Ph), 92.9 (Ar*C*(2,6)H), 91.9 (Ar*C*(3,5)H), 91.2 (Ar*C*(4)H), 21.2 (O*Me*). *m*/*z* (EI) 304 (M^+, 9%), 248 ($M^+ - 2 \times CO$, 12), 220 ($M^+ - 3 \times CO$, 46), 168 ($M^+ - Cr(CO)_3$, 8), 152 (168 − H − Me, 5), 80 (19), 52 (Cr, 100). Found: M^+ 304.0191. $C_{16}H_{12}CrO_4$ requires: 304.0192.

η^6-[(2-Methylphenyl)benzene]tricarbonylchromium(0) 7, R^1 = H, R^2 = 2-Me. From η^6-(fluorobenzene)tricarbonylchromium(0) **1**, R^1 = H (0.300 g, 1.29 mmol) and 2-methylphenylboronic acid (0.350 g, 2.58 mmol). FCC (eluant: 5% ether–hexane) furnished the *title product* **7**, R^1 = H, R^2 = 2-Me, as a yellow crystalline solid (0.311 g, 1.02 mmol, 79%), mp 109–112 °C (Found: C, 63.30; H, 4.14. $C_{16}H_{12}CrO_3$ requires: C, 63.16; H, 3.98%). ν_{max} (KBr)/cm^{-1} 2924w, 1966s, 1869vs, 1640w, 1470w, 1044w, 822m, 765m, 659m, 630s, 529m. δ_H (270 MHz) 7.44–7.39 (2 H, m, Ph*H*), 7.30–7.19 (2 H, m, Ph), 5.51 (2 H, dd, *J* 1.0, 6.9 Hz, Ar(2,6)*H*), 5.45 (1 H, tt, *J* 1.0, 6.2 Hz, Ar(4)*H*), 5.33 (2 H, t, *J* 6.2 Hz, Ar(3,5)*H*), 2.33 (3 H, s, *Me*); δ_C (68 MHz) 232.8 (*C*O), 136.0 (Ph*C*(2)-Me), 135.9 (Ph*C*(6)H), 131.6 (Ph*C*(4)H), 130.4 (Ph*C*(1)-Ar), 128.7 (Ph*C*(5)H), 126.5 (Ph*C*(3)H), 113.2 (Ar*C*(1)-Ph), 96.7 (Ar*C*(2,6)H), 93.5 (Ar*C*(4)H), 90.1 (Ar*C*(3,5)H), 20.4 (*Me*). *m*/*z* (EI) 304 (M^+, 14%), 248 ($M^+ - 2 \times CO$, 18), 220 ($M^+ - 3 \times CO$, 67), 168 ($M^+ - Cr(CO)_3$, 8), 152 (168 − H − Me, 9), 80 (23), 77 (Ph, 8), 52 (Cr, 100). Found: M^+ 304.0194. $C_{16}H_{12}CrO_4$ requires: 304.0192.

η^6-[(4-Chlorophenyl)benzene]tricarbonylchromium(0) 7, R^1 = H, R^2 = 4-Cl. From η^6-(fluorobenzene)tricarbonylchromium(0) **1**, R^1 = H (0.300 g, 1.29 mmol) and 4-chlorophenylboronic acid (1.5 equiv., 0.302 g, 1.94 mmol). FCC (eluant: 10% ether–hexane) furnished the *title product* **7**, R^1 = H, R^2 = 4-Cl, as a yellow crystalline solid (0.312 g, 0.95 mmol, 74%), mp 108–112 °C (Found: C, 55.66; H, 2.73. $C_{15}H_9CrO_3Cl$ requires: C, 55.49; H, 2.79%). ν_{max} (KBr)/cm^{-1} 1949s, 1869s, 805m, 658m, 630s, 536m. δ_H (270 MHz) 7.42 (2 H, d, *J* 8.7 Hz, Ph(2,6)*H*), 7.37 (2 H, d, *J* 8.7 Hz, Ph(3,5)*H*), 5.63 (2 H, d, *J* 6.2 Hz, Ar(2,6)*H*), 5.48 (2 H, t, *J* 6.2 Hz, Ar(3,5)*H*), 5.34 (1 H, t, *J* 6.4 Hz, Ar(4)*H*); δ_C (68 MHz) 232.5 (*C*O), 135.2 (Ph*C*(4)-Cl), 129.2 (Ph*C*(3,5)H), 128.4 (Ph*C*(1)-Ar, Ph*C*(2,6)H), 109.1 (Ar*C*(1)-Ph), 92.5 (Ar*C*(2,6)H), 91.9 (Ar*C*(3,5)H), 91.5 (Ar*C*(4)H). *m*/*z* (EI) 324 (M^+, 100%), 268 ($M^+ - 2 \times CO$, 11), 240 ($M^+ - 3 \times CO$, 26), 188 ($M^+ - Cr(CO)_3$, 14), 152 (188 − Cl, 33), 80 (78), 52 (Cr, 95). Found: M^+ 323.9650. $C_{15}H_9CrO_3Cl$ requires: 323.9645.

η^6-(1-Phenyl-4-methoxybenzene)tricarbonylchromium(0) 7, R^1 = MeO, R^2 = H. From η^6-(4-methoxyfluorobenzene)tricarbonylchromium(0) **1**, R^1 = 4-MeO (0.338 g, 1.29 mmol) and phenylboronic acid (0.320 g, 2.58 mmol). FCC (eluant: 15% ether–hexane) furnished the *title product* **7**, R^1 = MeO,

R^2 = H, as a yellow crystalline solid (0.312 g, 0.99 mmol, 76%), mp 123–124 °C (Found: C, 60.20; H, 3.88. $C_{16}H_{12}CrO_4$ requires: C, 60.01; H, 3.78%). ν_{max} (KBr)/cm^{-1} 3097w, 1942s, 1879s, 1856vs, 1653m, 1543m, 1478m, 1260m, 1156m, 1020m, 764m, 673s, 634m, 534m. δ_H (270 MHz) 7.46–7.28 (5 H, m, Ph*H*), 5.90 (2 H, d, *J* 6.9 Hz, Ar(2,6)*H*), 5.23 (2 H, d, *J* 6.9 Hz, Ar(3,5)*H*), 3.73 (3 H, s, O*Me*); δ_C (68 MHz) 234.0 (*C*O), 142.7 (Ar*C*(1)-OMe), 136.3 (Ph*C*(1)-Ar), 128.9 (Ph*C*(3,5)H), 128.6 (Ph*C*(4)H), 127.1 (Ph*C*(2,6)H), 103.9 (Ar*C*(1)-Ph), 94.6 (Ar*C*(2,6)H), 77.7 (Ar*C*(3,5)H), 55.8 (O*Me*). *m*/*z* (EI) 320 (M^+, 41%), 264 ($M^+ - 2 \times$ CO, 28), 236 ($M^+ - 3 \times$ CO, 100), 221 (236 − Me, 8), 204 (236 − OMe − H, 3), 184 (M^+ − Cr(CO)$_3$, 11), 169 (221 − Cr, 7), 80 (37), 52 (Cr, 63). Found: M^+ 320.0131. $C_{16}H_{12}CrO_4$ requires: 320.0141.

η^6-1-(2-Methylphenyl)-4-methoxybenzene]tricarbonylchromium(0) 7, R^1 = MeO, R^2 = 2-Me. From η^6-(4-methoxyfluorobenzene)tricarbonylchromium(0) **1**, R^1 = 4-MeO (0.338 g, 1.29 mmol) and 2-methylphenylboronic acid (0.350 g, 2.58 mmol). FCC (eluant: 15% ether–hexane) and recrystallisation (ether–hexane) furnished the *title product* **7**, R^1 = MeO, R^2 = 2-Me, as a yellow crystalline solid (0.326 g, 0.98 mmol, 77%), mp 87–90 °C (Found: C, 60.88; H, 4.32. $C_{17}H_{14}CrO_4$ requires: C, 61.08; H, 4.22%). ν_{max} (KBr)/cm^{-1} 3014w, 2933w, 2836w, 1959s, 1872s, 1543m, 1471m, 1249s, 1028m, 769m, 670s, 629s, 523m. δ_H (270 MHz) 7.34–7.16 (4 H, m, Ph*H*), 5.64 (2 H, d, *J* 6.9 Hz, Ar(2,6)*H*), 5.14 (2 H, d, *J* 6.9 Hz, Ar(3,5)*H*), 3.75 (3 H, s, O*Me*), 2.29 (3 H, s, *Me*); δ_C (68 MHz) 233.0 (*C*O), 143.0 (Ar*C*(4)-OMe), 136.1 (Ph*C*(1)-Ar), 135.7 (Ph*C*(2)-Me), 131.9 (Ph*C*(6)H), 130.2 (Ph*C*(4)H), 128.6 (Ph*C*(5)H), 126.5 (Ph*C*(3)H), 107.3 (Ar*C*(1)-Ph), 97.6 (Ar*C*(2,6)H), 76.3 (Ar*C*-(3,5)H), 55.7 (O*Me*), 20.4 (*Me*). *m*/*z* (EI) 334 (M^+, 56%), 278 ($M^+ - 2 \times$ CO, 8), 250 ($M^+ - 3 \times$ CO, 34), 198 (M^+ − Cr(CO)$_3$, 2), 52 (Cr, 100). Found: M^+ 334.0299. $C_{17}H_{14}CrO_4$ requires: 334.0297.

η^6-[1-(4-Methylphenyl)-4-methoxybenzene]tricarbonylchromium(0) 7, R^1 = MeO, R^2 = 4-Me. From η^6-(4-methoxyfluorobenzene)tricarbonylchromium(0) **1**, R^1 = 4-MeO (0.338 g, 1.29 mmol) and 4-methylphenylboronic acid (0.350 g, 2.58 mmol). FCC (eluant: 15% ether–hexane) furnished the *title product* **7**, R^1 = MeO, R^2 = 4-Me, as a yellow crystalline solid (0.319 g, 0.95 mmol, 74%), mp 126–128 °C (Found: C, 60.80; H, 4.29. $C_{17}H_{14}CrO_4$ requires: C, 61.08; H, 4.22%). ν_{max} (KBr)/cm^{-1} 3089w, 2935w, 2843w, 1953vs, 1858vs, 1519m, 1479m, 1438m, 1253m, 1029m, 823m, 668m, 659m, 623m, 530m. δ_H (270 MHz) 7.33 (2 H, d, *J* 8.2 Hz, Ph(3,5)*H*), 7.16 (2 H, d, *J* 8.2 Hz, Ph(2,6)*H*), 5.87 (2 H, d, *J* 6.9 Hz, Ar(2,6)*H*), 5.22 (2 H, d, *J* 6.9 Hz, Ar(3,5)*H*), 3.72 (3 H, s, O*Me*), 2.35 (3 H, s, *Me*); δ_C (68 MHz) 233.1 (*C*O), 142.4 (Ar*C*(4)-OMe), 138.6 (Ph*C*(1)-Ar), 133.4 (Ph*C*(4)-Me), 129.5 (Ph*C*(2,6)H), 126.8 (Ph*C*(3,5)H), 110.5 (Ar*C*(1)-Ph), 94.4 (Ar*C*(2,6)H), 77.8 (Ar*C*(3,5)H), 55.8 (O*Me*), 21.1 (*Me*). *m*/*z* (EI) 334 (M^+, 24%), 278 ($M^+ - 2 \times$ CO, 18), 250 ($M^+ - 3 \times$ CO, 100), 198 (M^+ − Cr(CO)$_3$, 8), 80 (13), 52 (Cr, 79). Found: M^+ 334.0296. $C_{17}H_{14}CrO_4$ requires: 334.0297.

General procedure for the coupling of (fluoroarene)chromium complexes with vinyltributylstannane

A solution of a (fluoroarene)tricarbonylchromium(0) complex (1 equiv., 1.29 mmol), vinyltributylstannane (2 equiv., 0.75 mL, 2.58 mmol), caesium fluoride (4 equiv., 0.780 g, 5.16 mmol), Pd$_2$(dba)$_3$ (5 mol%, 0.060 g, 0.06 mmol) and trimethylphosphine (20 mol%, 0.26 mL, 1 M solution in THF, 0.26 mmol) in deoxygenated DME (9 mL) was stirred under reflux for 16–40 h. Ether (20 mL) was added and the solution was washed with saturated KF$_{(aq)}$ (10 mL), water (10 mL) and brine (10 mL) and dried over MgSO$_4$. Concentration *in vacuo* followed by flash column chromatography (FCC) and recrystallisation were necessary to furnish the desired complex.

η^6-(Vinylbenzene)tricarbonylchromium(0) 8, R^1 = H. From η^6-(fluorobenzene)tricarbonylchromium(0) **1**, R^1 = H (0.300 g, 1.29 mmol); column chromatography (eluant: 10% ether–hexane) furnished the title product **8**, R^1 = H, as a yellow crystalline solid (0.146 g, 0.61 mmol, 48%), mp 79–80 °C (lit.[35] 78–79 °C) (Found: C, 54.92; H, 3.20. $C_{11}H_8CrO_3$ requires: C, 55.01; H, 3.36%). ν_{max} (KBr)/cm^{-1} 3080w, 1952vs, 1861vs, 1405m, 821m, 630s. δ_H (270 MHz) 6.26 (1 H, dd, *J* 10.6, 17.6 Hz, =C*H*), 5.65 (1 H, d, *J* 17.6 Hz, *trans* =CH*H*), 5.32 (1 H, d, *J* 10.6 Hz, *cis* =C*H*H), 5.43–5.24 (5 H, m, Ar*H*); δ_C (68 MHz) 232.8 (*C*O), 133.6 (*C*H), 116.6 (*C*H$_2$), 105.6 (Ar*C*(1)-C), 92.7 (Ar*C*(2,6)H), 91.3 (Ar*C*(4)H), 90.6 (Ar*C*(3,5)H). *m*/*z* (EI) 240 (M^+, 44%), 217 (5), 212 (M^+ − CO, 6), 204 (37), 184 ($M^+ - 2 \times$ CO, 15), 156 ($M^+ - 3 \times$ CO, 75), 128 (30), 104 (M^+ − Cr(CO)$_3$, 8), 77 (6), 52 (Cr, 100) Found: M^+ 239.9875. $C_{11}H_8CrO_3$ requires: 239.9879. The spectral data were consistent with the literature values.[35]

η^6-[(4-Methoxy)vinylbenzene]tricarbonylchromium(0) 8, R^1 = 4-MeO. From η^6-(4-methoxyfluorobenzene)tricarbonylchromium(0) **1**, R^1 = 4-MeO (0.338 g, 1.29 mmol); column chromatography (eluant: 15% ether–hexane) furnished the *title product* **8**, R^1 = 4-MeO, as a yellow crystalline solid (0.172 g, 0.52 mmol, 40%), mp 60–61 °C (Found: C, 53.29; H, 3.52. $C_{12}H_{10}CrO_4$ requires: C, 53.34; H, 3.73%). ν_{max} (KBr)/cm^{-1} 1956vs, 1850vs, 1628m, 1253s, 673s. δ_H (270 MHz) 6.17 (1 H, dd, *J* 10.9, 17.3 Hz, =C*H*), 5.65 (2 H, d, *J* 6.7 Hz, Ar(2,6)*H*), 5.55 (1 H, d, *J* 17.6 Hz, *trans* =CH*H*), 5.17 (1 H, d, *J* 11.1 Hz, *cis* =C*H*H), 5.15 (2 H, d, *J* 5.4 Hz, Ar(3,5)*H*), 3.69 (3 H, s, O*Me*); δ_C (68 MHz) 232.9 (*C*O), 143.1 (Ar*C*(4)-OMe), 132.7 (*C*H), 114.8 (*C*H$_2$), 105.7 (Ar*C*(1)-C), 92.6 (Ar*C*(2,6)H), 77.9 (Ar*C*(3,5)H), 55.8 (O*Me*). *m*/*z* (EI) 270 (M^+, 44%), 262 (13), 214 ($M^+ - 2 \times$ CO, 9), 186 ($M^+ - 3 \times$ CO, 46), 178 (13), 134 (M^+ − Cr(CO)$_3$, 8), 80 (42), 52 (Cr, 100). Found: M^+ 269.9983. $C_{12}H_{10}CrO_4$ requires: 269.9984.

η^6-[(2-Methoxy)vinylbenzene]tricarbonylchromium(0) 8, R^1 = 2-MeO. From η^6-(2-methoxyfluorobenzene)tricarbonylchromium(0) **1**, R^1 = 2-MeO (0.140 g, 0.53 mmol); column chromatography (eluant: 15% ether–hexane) furnished the *title product* **8**, R^1 = 2-MeO, as a yellow crystalline solid (0.061 g, 0.27 mmol, 42%), mp 78–80 °C (Found: C, 53.48; H, 3.96. $C_{12}H_{10}CrO_4$ requires: C, 53.34; H, 3.73%). ν_{max} (KBr)/cm^{-1} 1956vs, 1847vs, 1535m, 1247s, 672s. δ_H (270 MHz) 6.72 (1 H, dd, *J* 11.1, 17.6 Hz, =C*H*), 5.86 (1 H, dd, *J* 1.5, 6.4 Hz, Ar(6)*H*), 5.63 (1 H, d, *J* 17.6 Hz, *trans* =CH*H*), 5.52 (1 H, dt, *J* 1.5, 6.2 Hz, Ar(4)*H*), 5.27 (1H, d, *J* 11.1 Hz, *cis* =C*H*H), 5.09 (1 H, d, *J* 6.9 Hz, Ar(3)*H*), 4.96 (1 H, t, *J* 6.2 Hz, Ar(5)*H*), 3.78 (3 H, s, O*Me*); δ_C (68 MHz) 233.2 (*C*O), 141.0 (Ar*C*(2)-O), 129.1 (*C*H), 116.8 (*C*H$_2$), 107.8 (Ar*C*(1)-C), 93.5 (Ar*C*(6)H), 92.5 (Ar*C*(4)H), 85.5 (Ar*C*(5)H), 74.1 (Ar*C*(3)H), 55.9 (O*Me*). *m*/*z* (EI) 270 (M^+, 51%), 242 (M^+ − CO, 6), 214 ($M^+ - 2 \times$ CO, 26), 186 ($M^+ - 3 \times$ CO, 12), 135 (M^+ + H − Cr(CO)$_3$, 28), 120 (40), 91 (54), 55 (100). Found: M^+ 269.9996. $C_{12}H_{10}CrO_4$ requires: 269.9984. The ^{1}H NMR was consistent with the literature values.[36]

η^6-[(4-Methyl)vinylbenzene]tricarbonylchromium(0) 8, R^1 = 4-Me. From η^6-(4-methylfluorobenzene)tricarbonylchromium(0) **1**, R^1 = 4-Me (0.317 g, 1.29 mmol); column chromatography (eluant: 10% ether–hexane) furnished the *title product* **8**, R^1 = 4-Me, as a yellow crystalline solid (0.170 g, 0.67 mmol, 52%), mp 68 °C (Found: C, 56.94; H, 4.05. $C_{12}H_{10}CrO_3$ requires: C, 56.70; H, 3.97%). ν_{max} (KBr)/cm^{-1} 3074w, 1960vs, 1856vs, 1538m, 922s, 624s. δ_H (270 MHz) 6.22 (1 H, dd, *J* 10.9, 17.6 Hz, =C*H*), 5.61 (1 H, d, *J* 17.3 Hz, *trans* =CH*H*), 5.51 (2 H, d, *J* 6.7 Hz, Ar(3,5)*H*), 5.24 (1 H, d, *J* 11.1 Hz, *cis* =C*H*H), 5.21 (2 H, d, *J* 7.4 Hz, Ar(2,6)*H*), 2.17 (3 H, s, *Me*); δ_C (68 MHz) 233.2 (*C*O), 133.2 (*C*H), 115.6 (*C*H$_2$), 108.5 (Ar*C*(4)-Me), 102.9 (Ar*C*(1)-C), 92.8 (Ar*C*(2,6)H), 92.1 (Ar*C*(3,5)H), 20.5 (*Me*).

m/*z* (EI) 254 (M^+, 30%), 198 ($M^+ - 2 \times$ CO, 16), 170 ($M^+ - 3 \times$ CO, 93), 118 ($M^+ -$ Cr(CO)$_3$, 6), 91 (6), 52 (100). Found: M^+ 254.0042. $C_{12}H_{10}CrO_3$ requires: 254.0035.

***η*^{6}-[(3-Methyl)vinylbenzene]tricarbonylchromium(0) 8, R^1 = 3-Me.** From *η*^{6}-(3-methylfluorobenzene)tricarbonylchromium(0) **1**, R^1 = 3-Me (0.317 g, 1.29 mmol); column chromatography (eluant: 10% ether–hexane) and recrystallisation (ether–hexane) furnished the *title product* **8**, R^1 = 3-Me, as a yellow crystalline solid (0.173 g, 0.67 mmol, 52%), mp 62–64 °C (Found: C, 57.06; H, 3.99. $C_{12}H_{10}CrO_3$ requires: C, 56.70; H, 3.97%). ν_{max} (KBr)/cm^{-1} 1948s, 1871s, 1032w, 926w, 838w, 663m, 631m, 536w. δ_H (270 MHz) 6.28 (1H, dd, *J* 10.6, 17.3 Hz, =C*H*), 5.66 (1 H, d, *J* 17.6 Hz, *trans* =CH*H*), 5.46 (1 H, t, *J* 6.4 Hz, Ar(5)*H*), 5.38 (1 H, d, *J* 10.9 Hz, *cis* =C*H*H), 5.25 (1 H, s, Ar(2)*H*), 5.23 (1 H, d, *J* 6.4 Hz, Ar(4)*H*), 5.09 (1 H, d, *J* 6.5 Hz, Ar(6)*H*), 2.22 (3 H, s, *Me*); δ_C (68 MHz) 233.3 (*C*O), 133.8 (*C*H), 116.9 (*C*H$_2$), 109.3 (Ar*C*(3)-Me), 106.7 (Ar*C*(1)-C), 94.1, 91.6, 91.1, 87.9 (Ar*C*H), 20.9 (*Me*). *m*/*z* (EI) 254 (M^+, 25%), 198 ($M^+ - 2 \times$ CO, 11), 170 ($M^+ - 3 \times$ CO, 83), 118 ($M^+ -$ Cr(CO)$_3$, 4), 91 (5), 52 (100). Found: M^+ 254.0028. $C_{12}H_{10}CrO_3$ requires: 254.0035.

***η*^{6}-[4-(1,3-Dioxolan-2-yl)vinylbenzene]tricarbonylchromium(0) 8, R^1 = 4-CH(OCH$_2$)$_2$.** From *η*^{6}-[4-fluoro(1,3-dioxolan-2-yl)-benzene]tricarbonylchromium(0) **1**, R^1 = 4-CH(OCH$_2$)$_2$ (0.392 g, 1.29 mmol); column chromatography (eluant: 20% ether–hexane) furnished the *title product* **8**, R^1 = 4-CH(OCH$_2$)$_2$, as a yellow crystalline solid (0.149 g, 0.48 mmol, 37%), mp 56–58 °C. (Found: C, 53.87; H, 3.76. $C_{14}H_{10}CrO_5$ requires: C, 53.85; H, 3.87%). ν_{max} (KBr)/cm^{-1} 3083w, 2890w, 1962s, 1890s, 1880s, 1350w, 1227w, 1080w, 985w, 664m, 625m, 531w. δ_H (270 MHz) 6.28 (1 H, dd, *J* 10.6, 17.6 Hz, =C*H*), 5.66 (1 H, d, *J* 17.6 Hz, *trans* =CH*H*), 5.60 (2 H, d, *J* 6.7 Hz, ArC(3,5)*H*), 5.55 (1 H, s, C*H*), 5.38 (2 H, d, *J* 6.7 Hz, ArC(2,6)*H*), 5.34 (1 H, d, *J* 10.9 Hz, *cis* =C*H*H), 4.12–3.97 (4 H, s, OC*H*$_2$C*H*$_2$O); δ_C (68 MHz) 232.3 (*C*O), 133.4 (*C*H), 116.9 (*C*H$_2$), 105.9 (Ar*C*(4)-CH), 101.4 (*C*H), 100.6 (Ar*C*(1)-C), 91.2 (Ar*C*(3,5)H), 88.9 (Ar*C*(2,6)H), 65.9 (O*C*H$_2$*C*H$_2$O). *m*/*z* (EI) 312 (M^+, 36%), 256 ($M^+ - 2 \times$ CO, 15), 228 ($M^+ - 3 \times$ CO, 84), 200 (62), 184 (36), 52 (100). Found: M^+ 312.0064. $C_{14}H_{12}CrO_5$ requires: 312.0090.

***η*^{6}-(Phenylbenzene)tricarbonylchromium(0) 3, R^1 = H, *via* the Stille reaction.** *η*^{6}-(Fluorobenzene)tricarbonylchromium(0) **1**, R^1 = H (0.300 g, 1.29 mmol) and trimethylstannylbenzene[25] (0.62 g, 2.58 mmol) were treated as described above for the vinylstannane series. FCC (eluant: 5% ether–hexane) furnished the title product **3**, R^1 = H as a yellow crystalline solid (0.030 g, 0.10 mmol, 13%) with spectral data identical to those of the Suzuki reaction product.

***η*^{6}-[4-Methoxy(phenyl)benzene]tricarbonylchromium(0) 3, R^1 = MeO, *via* the Stille reaction.** *η*^{6}-(4-Methoxyfluorobenzene)tricarbonylchromium(0) **1**, R^1 = MeO (0.338 g, 1.29 mmol) and trimethylstannylbenzene[25] (0.62 g, 2.58 mmol) were treated as described above for the vinylstannane series. FCC (eluant: 15% ether–hexane) furnished the title product **3**, R^1 = MeO, as a yellow crystalline solid (0.020 g, 0.06 mmol, 6%) with spectral data identical to those of the Suzuki reaction product.

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