

Pd-Catalyzed Cross-Coupling of Haloarenes and Chloroarene-Cr(CO)₃ Complexes with Stabilized Vinyl- and Allylaluminium Reagents

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Abstract: The palladium-catalyzed cross-coupling of intramolecularly stabilized divinyl- and diallylaluminium compounds **1** and **2** with haloarenes and chloroarene-Cr(CO)₃ complexes has been studied. The coupling products were obtained in high yields (up to 98%) under relatively mild conditions (40–60 °C in THF, 3–12 h) in the presence of 5–10 mol% of PdCl₂(PPh₃)₂.

Key words: allyl complexes, aluminium reagents, arene complexes, cross-coupling, palladium, vinyl complexes

Throughout the last decades palladium-catalyzed cross-coupling reactions of electrophiles with organometallic reagents have become one of the most important procedures for carbon–carbon bond formation.¹ For the transfer of various organic residues the range of possible organometallics include tin (Stille coupling),² boron (Suzuki coupling),³ zinc (Negishi coupling),⁴ and Grignard reagents.⁵ But there are still considerable problems specific to alkenyl organometallics. Some of them are readily polymerized and cannot be isolated. Others are of high toxicity and their inorganic by-products cannot be removed by simple work up procedures.

In the course of our work on intramolecularly stabilized organometallic complexes of group 13 metals⁶ we have demonstrated their great potential in synthetic application. Herein, we show that the intramolecularly stabilized organoaluminium compounds **1**⁷ and **2**⁸ (Figure 1), are also useful reagents for the Pd-catalyzed cross-alkenylation of haloarenes. The vinyl- and allyl-reagents are readily synthesized crystalline solids, which are easily isolated and keep indefinitely stable under nitrogen.

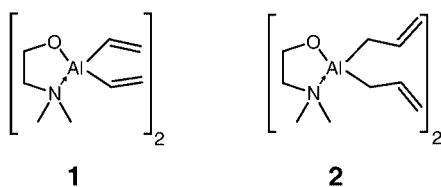
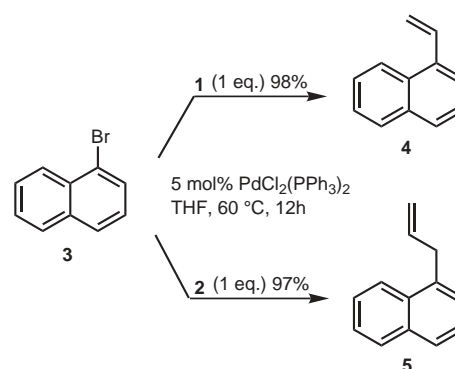


Figure 1

At first, Pd-catalyzed cross-coupling reactions of α -bromonaphthalene (**3**) with aluminium reagents **1** and **2** were investigated (Scheme 1). The results are shown in Table 1.



Scheme 1

After a reaction time of 12 h at 60 °C in the presence of 10 mol% of the Pd-catalyst, complete conversion was observed (TLC monitoring). The analytically pure coupling product **4** was isolated in 98% yield after chromatography (Table 1, entry 1). The high efficiency of the vinyl⁹ (entry 2) as well as the allyl coupling (entry 6) was preserved when the amount of catalyst was lowered to 5 mol%. Further reduction to 1 mol% lowered the yield to 18% (entry 3). However, no reaction occurred at ambient temperature (entry 4). It should be pointed out that only one of the two alkenyl groups at aluminium can be efficiently transferred, as entries 5 and 7 indicate. This fact has already been observed in the transfer of the alkyl group from dimethylmetal reagents of group 13 elements.^{6–8}

After optimizing the reaction conditions for the cross-coupling, we turned our attention to a wider field of substrates (Table 2). In the case of bromo- (**6**) and iodobenzene (**7**) similar high yields of styrene (**8**) (Table 2, entry 1 and 2) were obtained. When 1,2-dibromo-benzene (**9**) was treated with **1** under the reaction conditions reported above, the expected product 1,2-divinylbenzene (**10**) was obtained in 35% yield only (Table 2, entry 3). However, when the amount of catalyst was increased to 10 mol% and the amount of vinyl reagent to 3 equivalents, **10** could be isolated in a 65% yield (Table 2, entry 4). In a similar

Table 1 Pd-Catalyzed Cross-Coupling of α -Bromonaphthalene (**3**) using Aluminium Reagents **1** and **2** according to Scheme 1

Entry	Cat. amount (mol%)	T (°C)	Reagent (equiv)	Conv. ^a (%)	Yield ^b (%)
1	10	60	1 (1)	100	98
2	5	60	1 (1)	100	98
3	1	60	1 (1)	20	18
4	5	r.t.	1 (1)	–	–
5	5	60	1 (0.5)	78	76
6	5	60	2 (1)	100	97
7	5	60	2 (0.5)	60	56

^a Conversion based on recovered starting material.^b Isolated yields after column chromatography.

manner the cross-coupling product **12** of 4-bromo-1,2-dimethoxybenzene (**11**) was isolated in 59% yield (Table 2, entry 5). The reaction of 4-bromoaniline (**13**) with **1** failed and the expected product could only be found in trace amounts (Table 2, entry 6). Probably, the amino function of **13** is capable of coordinating or even reacting with the aluminium center and thus preventing

the vinyl transfer. The *o*- and *p*-bromobenzoates (**14** and **16**) reacted rather smoothly with **1** to the corresponding coupling products 2- (**15**) (Table 2, entry 7) and 4-vinyl-bromobenzoic acid methyl ester (**17**) (Table 2, entry 8), when the amount of Pd-catalyst was increased to 10 mol%. The desired coupling products could be isolated in 85% and 72% yield.

This rather simple and reliable procedure was then applied for the cross-coupling of allylalane **2** (Table 2, entries 9–13). The allylcoupling product **18** of bromobenzene (**6**) (Table 2, entry 9) was isolated in a high yield of 93%. In analogy to the vinyl coupling of 1,2-dibromobenzene (**9**), 10 mol% of Pd-catalyst and 3 equivalents of aluminium reagent **2** were needed to achieve a high yield (95%) of 1,2-diallylbenzene (**19**) (Table 2, entry 10). In contrast to **1** the allylcoupling of 4-bromo-1,2-dimethoxybenzene (**11**) resulted in an astonishingly efficient formation of 4-allyl-1,2-dimethoxybenzene (**20**) in an isolated yield of 99% (Table 2, entry 11). Using 10 mol% of the catalyst for the coupling of the bromobenzoates **14** and **16** the desired products 2- (**21**) and 4-allyl-benzoate (**22**) were isolated in a yield of 72% (Table 2, entry 12) and 59% (Table 2, entry 13), respectively. Finally it is noteworthy to mention that the allylarenes do not undergo any palladium-catalyzed isomerization.

Table 2 PdCl₂(PPh₃)₂ Catalyzed Cross-Coupling of Various Substrates Using Vinylalane **1** or Allylalane **2** According to Scheme 1


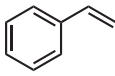


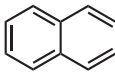
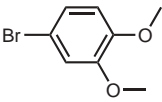
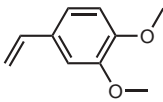
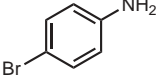
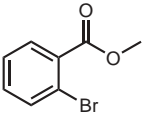
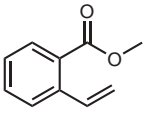
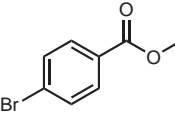
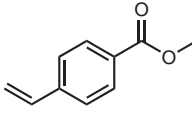
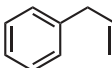
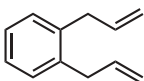
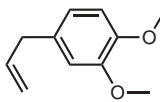
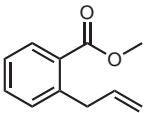
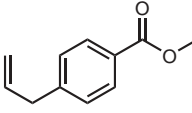
Entry	Substrate	Cat. amount (mol%)	Reagent (equiv)	Product	Conv. ^a (%)	Yield ^b (%)
1		5	1 (1)		100	97
	6			8		
2		5	1 (1)	8	100	96
	7					
3		5	1 (2)		35	30
	9			10		
4	9	10	1 (3)	10	68	65
5		5	1 (1)		61	59
	11			12		
6		5	1 (1)	–	<2	–
	13					

Table 2 PdCl₂(PPh₃)₂ Catalyzed Cross-Coupling of Various Substrates Using Vinylallane **1** or Allyllallane **2** According to Scheme 1 (continued)

Entry	Substrate	Cat. amount (mol%)	Reagent (equiv)	Product	Conv. ^a (%)	Yield ^b (%)
7		10	1 (1)		92	85
8		10	1 (1)		75	72
9	6	5	2 (1)		100	93
10	9	10	2 (3)		100	95
11	11	5	2 (1)		100	99
12	14	10	2 (1)		73	72
13	16	10	2 (1)		70	59

^a Conversion based on recovered starting material.^b Isolated yields after column chromatography.

Due to the positive results⁶ of our work on palladium-catalyzed cross-coupling reactions of chloroarene-Cr(CO)₃ complexes with intramolecularly stabilized organoindium and -aluminium reagents, we were interested to see whether the vinyl reagent **1** could be employed in an analogous way in order to establish another entry¹⁰ to the synthetically important¹¹ class of styrene-Cr(CO)₃ derivatives. Accordingly, a selection of mono- and bis-chloroarene-Cr(CO)₃ complexes (**23–27**, Schemes 2 and 3, Table 3) was reacted with **1** under standard reaction conditions.¹² The substrates (Tables 3 and 4) were chosen in order to address the general question of feasibility (**23** + **24**), selectivity (**25** + **26**) and tolerance of the vinylation reaction towards an ester functionality. Moreover, meso-

compounds **25** and **26** represent prochiral structures and selective substitution of one enantiotopic chlorine for vinyl leads to planar-chiral complexes. Accordingly, the general possibility of enantioselective desymmetrization via vinylation employing a chiral catalyst (**35**) was to be elucidated. The results of the various experiments are shown in Tables 3 and 4.

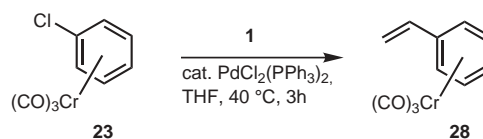
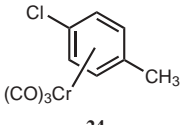
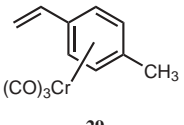
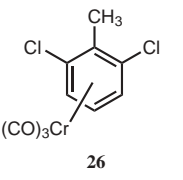
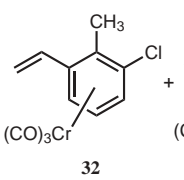
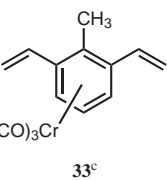
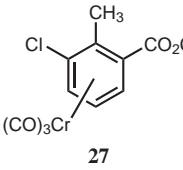
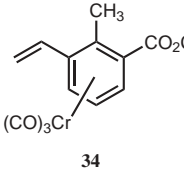
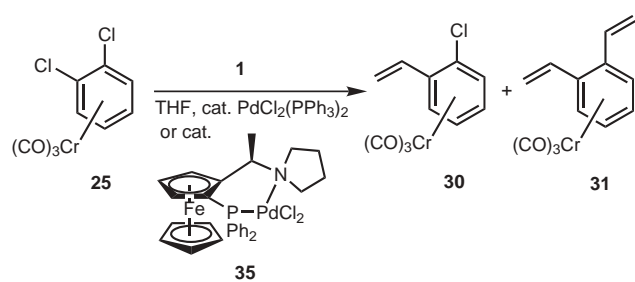
**Scheme 2**

Table 3 PdCl₂(PPh₃)₂ Catalyzed Cross-Coupling of Various Chloroarene-Cr(CO)₃ Complexes Using Vinylalane **1** (T = 40 °C)

Entry	Substrate	Equiv of 1	Cat. amount (mol%)	Time (min)	Product	Yield (%)
1	23	1	5	180	28	95 ^a
2		1	5	180		92 ^a
3		1	5	60	 + 	–
4	26	2	5	180	33	92 ^a
5		1	5	180		73 ^{b,a}

^a After recrystallization.^b After column chromatography.^c An inseparable mixture of **26**, **32** and **33** was obtained. The relative composition was determined by means of NMR as **26:32:33** = 10:40:78.**Scheme 3**

First of all, the coupling experiments conducted with the monochloroarene-Cr(CO)₃ complexes **23** and **24** show the high efficiency of the vinylation reaction as high yields

(95% for **28**¹³ and 92% for **29**,¹⁴ Table 3) of the corresponding styrene complexes were obtained. Moreover, a lower reaction temperature of 40 °C and a distinctly shorter reaction time (3 h) were sufficient compared to the experiments carried out with the uncomplexed haloarenes (i.e. Table 2, entries 1 and 2). This result again demonstrates the power of the Cr(CO)₃ fragment to facilitate or even enable palladium catalyzed cross coupling reactions on chloroarenes.¹⁵

In order to test for a selective monovinylation, complexes **25** and **26** were employed in the reaction. The results of these experiments were rather disappointing, as on variation of the reaction time and catalyst amount in the case of complex **25** a 63:37 ratio of the mono- and bis-vinylated

Table 4 Pd-Catalyzed Cross-Coupling of Complex **25** Using Vinylalane **1** (T = 40 °C, 1 equiv **1**)

Entry	Catalyst	Cat. amount (mol%)	Time (min)	Coupling yield ^a (%)	Molar ratio 30 ^a : 31 ^a	ee% ^b
1	PdCl ₂ (PPh ₃) ₂	5	180	87	0:100	–
2	PdCl ₂ (PPh ₃) ₂	1	180	34	61:39	–
3	PdCl ₂ (PPh ₃) ₂	2	180	85	16:84	–
4	PdCl ₂ (PPh ₃) ₂	2	60	55	63:37	–
5	35	2	150	82	46:54	16 (1 <i>R</i> ,2 <i>S</i>)

^a Yields of isolated compounds after column chromatography.^b Determination of ee% was conducted via HPLC: Chiralcel OD-H, *n*-hexane/*i*-PrOH = 90/10, Volume = 1 mL/min, λ = 254 nm, r.t.; R_t[(1*R*,2*S*)-**30**] = 12.1 min; R_t[(1*S*,2*R*)-**30**] = 16.4 min.²¹

products (**30**¹⁶ and **31**¹⁷ respectively) could not be surpassed (Table 4, entries 1–4). Additionally, the total coupling yield for the most selective case is rather poor (Table 4, entry 4). The selectivity of the vinylation of **26** (Table 3, entry 3) is even worse as it displays a 1:2 ratio of the mono- and bis-vinylated product (**32**¹⁸ and **33**¹⁹ respectively). Moreover, it was not possible to separate the obtained mixture of **26**, **32** and **33** by means of flash chromatography nor HPLC. Nevertheless, the reaction of **26** with two equivalents of the vinylalane **1** under the proven reaction conditions afforded 92% of the bis-vinylated product **33** (Table 3, entry 4).

The tested desymmetrization of compound **25** employing the chiral catalyst **35** furnished the monovinylated complex **30** with poor selectivity (Table 4, entry 5) and small enantioselectivity (16% ee of the (1*R*,2*S*)-enantiomer).

Finally, the reaction of the ester complex **27** afforded the vinyolated trifunctional compound **34**²⁰ in satisfying yield.

In summary, we have demonstrated that the intramolecularly stabilized vinyl- and allylaluminum compounds **1** and **2** are highly useful reagents for Pd-catalyzed cross-alkenylation of bromo- and iodoarenes as well as chloroarene-Cr(CO)₃ complexes. The developed procedure is characterized by high yields of products and operational simplicity.

Acknowledgment

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 - (9) Typical experimental procedure: The vinylaluminum reagent **1** (0.21 mg, 1.25 mmol), PdCl₂(PPh₃)₂ (5 mol%, 0.06 mmol), and 2-bromonaphthalene(**3**) (0.26 g, 1.25 mmol) were placed in a flame dried Schlenk-flask equipped with a reflux condenser, evacuated and flushed with N₂. Deoxygenated anhyd THF (20 mL) was added via syringe. The reaction mixture was stirred at 60 °C for 12 h under a N₂ atmosphere, cooled to ambient temperature, diluted with *n*-hexane (20 mL), filtered through a short pad of silica gel, washed with hexane and concentrated under reduced pressure. The residue was purified by chromatography on silica gel (20 g) with *n*-hexane–ethyl acetate = 10:1 to give the product **4** as (0.19 g, 1.23 mmol, 98%) a colorless oil. ¹H NMR (CDCl₃, 200 MHz): δ = 8.27–8.32 (m, 1 H, H_{aryl}), 7.93–8.04 (m, 2 H, H_{aryl}), 7.80 (m, 1 H, H_{aryl}), 7.57–7.72 (m, 4 H, H_{aryl}, –CH=CH₂), 5.97 (dd, 1 H, J = 1.58, 17.3 Hz, –CH=CHH_{trans}), 5.65 (dd, 1 H, J = 1.58, 10.9 Hz, –CH=CHH_{cis}). ¹³C NMR (CDCl₃, 50 MHz): δ = 135.5, 134.3 (C_q), 133.6 (–CH=CH₂), 131.1 (C_q), 128.5, 128.1, 126.0, 125.7, 125.6, 123.7, 123.6 (C_{aryl}), 116.97 (–CH=CH₂).
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 - (12) Typical experimental procedure: η⁶-(Vinylbenzene)-tricarboxylchromium(0) (**28**). η⁶-(Chlorobenzene)tricarboxylchromium(0) (**23**) (124.3 mg, 0.5 mmol), vinylalane **1** (84.6 mg, 0.5 mmol) and PdCl₂(PPh₃)₂ (17.6 mg, 0.025 mmol) were placed under Ar in a flame dried Schlenk flask equipped with a reflux condenser. Deoxygenated anhydrous THF (5.0 mL) was added via a syringe and the reaction mixture was degassed three times. After stirring at 40 °C for 3 h the reaction mixture was cooled in an ice-bath, diluted with *n*-hexane (5 mL), filtered through a short column of silica gel (30 × 50 mm), eluted with *n*-hexane–MTBE = 8:1 (40 mL) and finally with *n*-hexane–MTBE = 4:1 (40 mL). Upon concentration of the filtrate the obtained orange-yellowish solid was recrystallized from MTBE–*n*-hexane to afford **28** (114.3 mg, 0.476 mmol, 95.2%) as yellow-orange crystals.
 - (13) η⁶-(Vinylbenzene)tricarboxylchromium(0) (**28**). ¹H NMR (C₆D₆, 250 MHz): δ = 5.69 (dd, 1 H, J = 10.9, 17.5 Hz, –CH=CH₂), 5.11 (d, 1 H, J = 17.5 Hz, –CH=CHH_{trans}), 4.85 (d, 1 H, J = 10.9 Hz, –CH=CHH_{cis}), 4.53 (ψd, 2 H, H_{aryl}), 4.43 (ψt, 2 H, H_{aryl}), 4.30 (m, 1 H, H_{aryl}). ¹³C NMR (C₆D₆,

- 63 MHz): $\delta = 233.2$ (CO), 133.7 ($-\text{CH}=\text{CH}_2$), 115.8 ($-\text{CH}=\text{CH}_2$), 105.3 (C_q), 92.5, 90.9, 90.3 (C_{aryl}). Mp 80 °C (lit.²¹ 79–80 °C).
- (14) **η^6 -(4-Methyl-1-vinylbenzene)tricarbonylchromium(0) (29)**. ^1H NMR (C_6D_6 , 250 MHz): $\delta = 5.73$ (dd, 1 H, $J = 10.9$, 17.5 Hz, $-\text{CH}=\text{CH}_2$), 5.16 (d, 1 H, $J = 17.5$ Hz, $-\text{C}=\text{CHH}_{\text{trans}}$), 4.84 (d, 1 H, $J = 10.9$ Hz, $-\text{CH}=\text{CH}_{\text{cis}}\text{H}$), 4.77 (d, 2 H, $J = 6.3$ Hz, H_{aryl}), 4.36 (d, 2 H, $J = 6.3$ Hz). ^{13}C NMR (C_6D_6 , 63 MHz): $\delta = 233.5$ (CO), 133.4 ($-\text{CH}=\text{CH}_2$), 114.9 ($-\text{CH}=\text{CH}_2$), 108.0, 102.7 (C_q), 92.5, 91.9 (C_{aryl}), 19.9 (Ar- CH_3). Mp 80 °C.
- (15) For a review about $C_{\text{Ar}}-\text{Cl}$ bond activation through $\text{Cr}(\text{CO})_3$ complexation, see: (a) Carpentier, J.-F.; Petit, F.; Mortreux, A.; Dufaud, V.; Basset, J.-M.; Thivolle-Cazat, J. *J. Mol. Catal.* **1993**, *81*, 1. (b) For some recent work, see: Müller, T. J. J.; Ansorge, M.; Aktah, D. *Angew. Chem.* **2000**, *112*, 1323. (c) Crousse, B.; Xu, L.-H.; Bernardinelli, G.; Kündig, E. P. *Synlett* **1998**, 658. (d) Bräse, S. *Tetrahedron Lett.* **1999**, *40*, 6757.
- (16) **η^6 -(1-Chloro-2-vinylbenzene)tricarbonylchromium(0) (30)**. ^1H NMR (CDCl_3 , 250 MHz): $\delta = 6.75$ (dd, 1 H, $J = 10.9$, 17.4 Hz, $-\text{CH}=\text{CH}_2$), 5.72 (d, 1 H, $J = 17.4$ Hz, $-\text{C}=\text{CHH}_{\text{trans}}$), 5.72 (dd, 1 H, H_{aryl}), 5.49 (dd, 1 H, H_{aryl}), 5.43 (d, 1 H, $J = 10.9$ Hz, $-\text{CH}=\text{CH}_{\text{cis}}\text{H}$), 5.39–5.34 (m, 1 H, H_{aryl}), 5.16–5.10 (m, 1 H, H_{aryl}). ^{13}C NMR (CDCl_3 , 63 MHz): $\delta = 231.5$ (CO), 130.5 ($-\text{CH}=\text{CH}_2$), 117.9 ($-\text{CH}=\text{CH}_2$), 102.6 (C_q), 91.8, 91.6 (C_{aryl}), 90.2 (C_q), 89.4, 88.8 (C_{aryl}). Mp 73 °C.
- (17) **η^6 -(1,2-Divinylbenzene)tricarbonylchromium(0) (31)**. ^1H NMR (CDCl_3 , 250 MHz) $\delta = 6.62$ (dd, 2 H, $J = 10.9$, 17.3 Hz, $-\text{CH}=\text{CH}_2$), 5.64 (d, 2 H, $J = 17.3$ Hz, $-\text{CH}=\text{CHH}_{\text{trans}}$), 5.54–5.49 (m, 2 H, H_{aryl}), 5.41 (d, 2 H, $J = 10.9$ Hz, $-\text{CH}=\text{CH}_{\text{cis}}\text{H}$), 5.37–5.34 (m, 2 H, H_{aryl}). ^{13}C NMR (CDCl_3 , 63 MHz) $\delta = 232.8$ (CO), 131.7 ($-\text{CH}=\text{CH}_2$), 188.8 ($-\text{CH}=\text{CH}_2$), 105.1 (C_q), 91.6, 90.2 (C_{aryl}). Mp 85 °C.
- (18) **η^6 -(1-Chloro-2-methyl-3-vinylbenzene)tricarbonylchromium(0) (32)**. ^1H NMR (C_6D_6 , 300 MHz) $\delta = 6.12$ (dd, 1 H, $J = 11.0$, 17.2 Hz, $-\text{CH}=\text{CH}_2$), 5.07 (d, 1 H, $J = 17.2$, $-\text{CH}=\text{CHH}_{\text{trans}}$), 4.92 (d, 1 H, $J = 11.0$ Hz, $-\text{CH}=\text{CH}_{\text{cis}}\text{H}$), 4.81 (m, 1 H, H_{aryl}), 4.50 (m, 1 H, H_{aryl}), 4.34 (m, 1 H, H_{aryl}), 1.84 (s, 1 H, Ar- CH_3). ^{13}C NMR (C_6D_6 , 75 MHz) $\delta = 232.5$ (CO), 132.2 ($-\text{CH}=\text{CH}_2$), 119.0 ($-\text{CH}=\text{CH}_2$), 112.7, 106.0, 104.1 (C_q), 91.9, 90.5, 88.1 (C_q), 1.84 (Ar- CH_3). (Shifts were taken from crude product NMR).
- (19) **η^6 -(1-Methyl-2,6-divinylbenzene)tricarbonylchromium(0) (33)**. ^1H NMR (C_6D_6 , 250 MHz) $\delta = 6.20$ (dd, 2 H, $J = 10.9$, 17.1 Hz, $-\text{CH}=\text{CH}_2$), 5.16 (d, 2 H, $J = 17.1$ Hz, $-\text{CH}=\text{CHH}_{\text{trans}}$), 4.96–4.91 (m, 4 H, H_{aryl} , $-\text{CH}=\text{CH}_{\text{cis}}\text{H}$), 4.51 (t, 1 H, $J = 6.6$ Hz), 1.70 (s, 3 H, Ar- CH_3). ^{13}C NMR (C_6D_6 , 63 MHz) $\delta = 233.6$ (CO), 132.8 ($-\text{CH}=\text{CH}_2$), 118.1 ($-\text{CH}=\text{CH}_2$), 105.7, 105.5 (C_q), 91.1, 90.0 (C_{aryl}), 14.8 (Ar- CH_3). Mp 85 °C.
- (20) **η^6 -(2-Methyl-3-vinyl-methylbenzoate)tricarbonylchromium(0) (34)**. ^1H NMR (C_6D_6 , 250 MHz) $\delta = 6.10$ (dd, 1 H, $J = 10.7$, 17.1 Hz, $-\text{CH}=\text{CH}_2$), 5.62 (dd, 1 H, $J = 1.2$, 6.6 Hz, H_{aryl}), 5.11 (dd, 1 H, $J = 0.8$, 17.1 Hz, $-\text{CH}=\text{CHH}_{\text{trans}}$), 5.05 (dd_{br}, 1 H, $J = 1.2$, 6.6 Hz, H_{aryl}), 4.87 (dd, 1 H, $J = 0.7$, 10.7 Hz, $-\text{CH}=\text{CH}_{\text{cis}}\text{H}$), 4.27 (wt, 1 H, $J = 6.6$ Hz, H_{aryl}), 3.30 (s, 3 H, OCH_3), 2.29 (s, 3 H, Ar- CH_3). ^{13}C NMR (C_6D_6 , 63 MHz) $\delta = 231.8$ (CO), 166.4 (CO_2CH_3), 132.3 ($-\text{CH}=\text{CH}_2$), 118.4 ($-\text{CH}=\text{CH}_2$), 109.0, 104.6 (C_q), 95.8, 93.7 (C_{aryl}), 92.0 (C_q), 87.3 (C_{aryl}), 52.1 (OCH_3), 16.3 (Ar- CH_3). Mp 50 °C.
- (21) Uemura, M.; Nishimura, H.; Hayashi, T. *J. Organomet. Chem.* **1994**, *473*, 129.