# Notiz / Note

# Palladium-Catalyzed Coupling of Vinylferrocene with Aromatic Halides – A Highly Efficient Route to (Ferrocenylvinyl)arenes

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(Ferrocenylvinyl)arenes **3**, **5**, and **7** are obtained from vinylferrocene (**1**) and substituted aromatic and heteroaromatic halides by palladium-catalyzed Heck-type reactions. Up to three ferrocene units are introduced in one step by the multifold reaction of 1,2-dibromo- (**4**) or 1,3,5-tribromobenzene (**6**) with **1**. The first crystal structure of a bis(ferrocenylvinyl)benzene chromophore (**5**) is reported.

There is considerable interest in the synthesis of new materials with large second-order optical non-linearities because of their potential use in optical devices for information processing[1]. It is now well established that molecular structures that possess both differences between ground-state and excited-state dipole moments and large transition dipole moments will have large second-order non-linearities[2]. Molecules with $\pi$ donor-acceptor interactions are promising candidates to fulfil these requirements. But in comparison with the great efforts focussed on the synthesis of organic materials such properties[3], organometallic compounds have received little attention until recently. The vinylferrocene moiety has now been used as a $\pi$ electron donor in several compounds[4] with high second harmonic generation[5] (SHG) efficiencies.

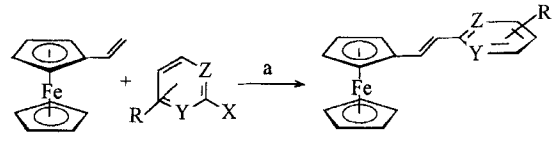
However, most synthetic routes to (ferrocenylvinyl)arenes are based on the Wittig reaction of ferrocenecarboxaldehyde with ylides[6a,4e] or (ferrocenylmethyl)triphenylphosphonium iodide with aldehydes[6b]. Over the last decade palladium-catalyzed coupling reactions of vinyl and aryl halides with alkenes (Heck reactions[7]) have become a useful synthetic method with numerous applications. In the course of our studies of an application of this powerful methodology to the synthesis of defined polynuclear metal complexes, we have observed the facile coupling of vinylferrocene with various aryl halides.

Iodobenzene reacts with vinylferrocene under the phase-transfer conditions described by Jeffery[8] to yield (*E*)-styrylferrocene[9] as the only product. The coupling reaction can be extended to electron-deficient or electron-rich aromatic rings with nitro or methoxy substituents. Heterocyclic examples[10] of the procedure are the reactions of **1** with 2-bromo-6-methylpyridine (**2d**) and 2-bromo-pyrimidine (**2e**).

Two or three ferrocene units are introduced in a one-pot reaction by the multifold coupling of **1** with 1,2-di-(**4**) and 1,3,5-tribromobenzene (**6**)[11].

Suitable crystals for an X-ray analysis of **5** have been obtained from dichloromethane. The crystal structure determination[12] shows that only one of the two vinylferrocene moieties is essentially parallel to the central aromatic ring (Figure 1). The interplanar angles to this ring are 17° for C9–13 and 60° for C9′-13′, with corresponding torsion angles C1–7–8–9 179, C7–8–9–10 -7, C6–7′–8′–9′ -175, and C7′–8′–9′–10′ -158°.

Scheme 1. Coupling reactions of vinylferrocene (**1**) with aromatic halides. [a] $Pd(OAc)_2$, DMF, $K_2CO_3$, $NBu_4Br$




**1** **2** **3**

| **2** | X | Y | Z | R | Yield **3** [%] |
|---|---|---|---|---|---|
| **a**[9] | I | CH | CH | H | 85 |
| **b**[4c] | I | CH | CH | *para*-$NO_2$ | 84 |
| **c**[16] | I | CH | CH | *para*-$OCH_3$ | 45 |
| **d** | Br | N | CH | 6-Me | 37 |
| **e** | Br | N | N | H | 13 |

The palladium-catalyzed coupling of **1** with aryl halides is a simple and effective procedure for the synthesis of (ferrocenylvinyl)arenes with obvious advantages over stoichiometric reactions in terms of "atom economy"[13]. Practical applications to the synthesis of ferrocene derivatives as electrochemically switchable non-linear optical materials[14] and photodegradation protection units[15] of conjugated chain molecules might be envisaged.

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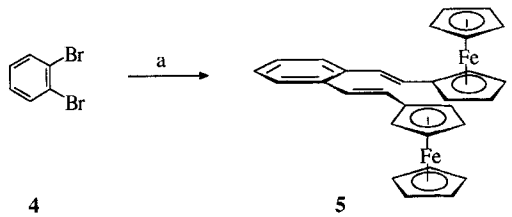
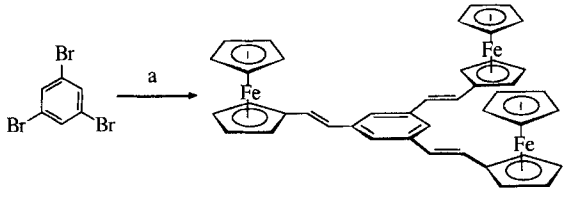



4 5

a: 2 equiv. of **1**, $Pd(OAc)_2$ [5 mol-%], DMF, $K_2CO_3$, $NBu_4Br$. Yield: 74 %.




6 7

a: 3 equiv. of **1**, $Pd(OAc)_2$ [5 mol-%], DMF, $K_2CO_3$, $NBu_4Br$. Yield: 46 %.

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## Experimental

$^1H$ NMR: Bruker AM 400; $\delta = 0$ for tetramethylsilane as internal standard, $\delta = 7.26$ for chloroform. – $^{13}C$ NMR: AM 400; $\delta = 77.0$ for deuteriochloroform; the multiplicity of the $^{13}C$-NMR signals was determined by the DEPT technique and quoted as (+) for $CH_3$ and CH groups, (–) for $CH_2$- and ($C_{quart}$) for quaternary carbons. – IR: Nicolet 320 FT-IR. – MS: Finnigan MAT 8430. – UV/Vis: Hewlett Packard 8452A. – Melting points: Hot-plate microscope apparatus, not corrected. – Column chromatography (CC): Merck silica gel 60, mesh 70–230; PE (60/70) means petroleum ether with a boiling range of 60–70°C. – TLC: silica gel (Macherey-Nagel; Sil G/$UV_{254}$).

*X-Ray Structure Determination of Compound* **5**[12]: $C_{30}H_{26}Fe_2$, $M = 498.21$, monoclinic, space group $C2/c$, $a = 2711.3(3)$, $b = 722.2(1)$, $c = 2337.2(3)$ pm, $\beta = 102.28(2)°$, $V = 4.4718(10)$ nm$^3$, $Z = 8$, $\lambda$(Mo-$K\alpha$) = 0.71073 Å, $\mu = 1.3$ mm$^{-1}$, $D_x = 1.480$ Mg m$^{-3}$, $F(000) = 2064$, $T = 143$ K. A red prism with the dimensions 0.6 × 0.3 × 0.15 mm was mounted on a glass fiber in inert oil (type RS3000, donated by Fa. Riedel-de Haën) and transferred to the cold gas stream of a Stoe STADI-4 diffractometer with a Siemens LT-2 low-temperature attachment. Cell constants were refined from $\pm\omega$ values of 54 reflections in the $2\theta$ range 20–23°. A total 4051 intensities (3940 unique, $R_{int} = 0.0208$) were measured to $2\theta$ 50°. – The structure was solved by direct methods and refined anisotropically on $F^2$ (program SHELXL-93, G. M. Sheldrick, University of Göttingen). Hydrogen atoms were included with a riding model. The final $wR(F^2)$ for all reflections was 0.121, with a conventional $R(F)$ of 0.046, for 289 parameters.

*General Procedure (GP) for the Palladium-Catalyzed Coupling of Vinylferrocene* (**1**): A mixture of 1.0 mmol of **1**, 10.0 mmol of potassium carbonate, 4.0 mmol of tetrabutylammonium bromide, the given amount of the appropriate halide, and 25 mg (0.11 mmol) of $Pd(OAc)_2$ in 20 ml of dimethylformamide (DMF) was heated in a capped pyrex tube under nitrogen for the time stated. The reaction mixture was filtered, diluted with 100 ml of dichloromethane and washed with six portions of 50 ml of water. The organic phase was dried with $K_2CO_3$, filtered, and the solvent was removed from the filtrate in vacuo. The crude products were purified by column chromatography (CC) on silica gel and subsequent recrystallization.

*(E)-Styrylferrocene* (**3a**)[9]: **2a** (214 mg, 1.0 mmol) was allowed to react with **1** (204 mg, 1.0 mmol) according to the GP for 2 d at 70°C, and the crude product was chromatographed on silica gel (PE/$CH_2Cl_2$, 100:3) to yield 245 mg (85%) of pure **3a** ($R_f = 0.17$) as a red solid, m.p. 119°C[9].

*(E)-(4-Nitrostyryl)ferrocene* (**3b**)[4c]: **2b** (125 mg, 0.5 mmol) and **1** (107 mg, 0.5 mmol) were heated to 55°C for 2 d according to the GP. The crude product was chromatographed on silica gel (PE/$CH_2Cl_2$, 2:3) to yield 141 mg (84%) of **3b** ($R_f = 0.44$) as a dark red solid, m.p. 196°C[4c].

*(E)-(4-Methoxystyryl)ferrocene* (**3c**)[16]: **2c** (187 mg, 1.0 mmol) and **1** (214 mg, 1.0 mmol) were allowed to react according to the GP for 2 d at 80°C. The crude product was purified by CC on

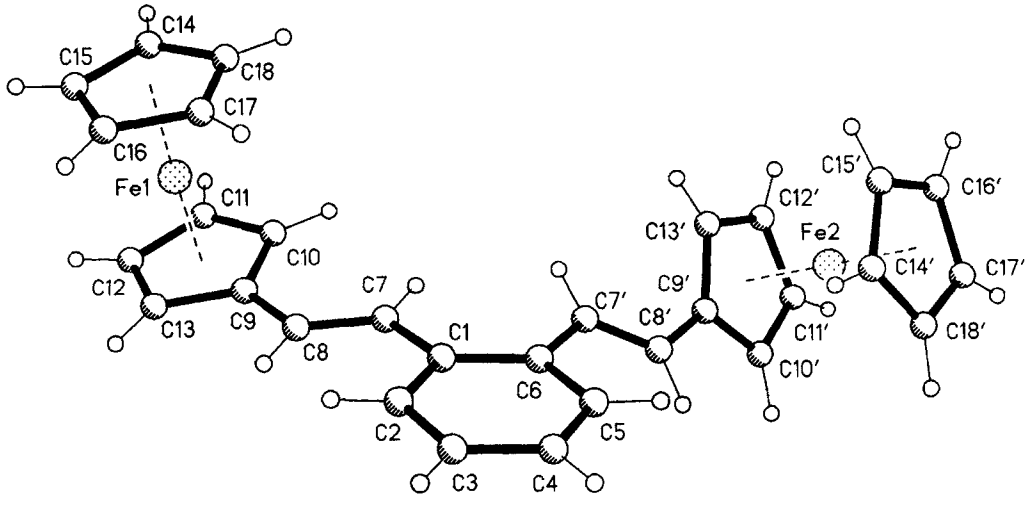


Figure 1. Crystal structure of **5**. Selected bond lengths [pm]: C(7)–C(8) 133.2(5), C(1)–C(7) 146.7(6), C(8)–C(9) 146.1(6); bond angles [°]: C(8)–C(7)–C(1) 126.2(4), C(7)–C(8)–C(9) 127.1(4)

silica gel (PE/$CH_2Cl_2$, 7:3) to afford 142 mg (45%) of **3c** ($R_f$ = 0.27) as orange plates, m.p. 128°C).

*(E)-2-(2-Ferrocenylvinyl)-6-methylpyridine* (**3d**): **2d** (170 mg, 1.0 mmol) and **1** (214 mg, 1.0 mmol) were allowed to react for 2 d at 80°C. By CC on silica gel ($CH_2Cl_2$/MeOH, 98:2) 112 mg (37%) of **3d** ($R_f$ = 0.38) was obtained as an orange solid, m.p. 53°C. – IR (KBr): $\tilde{\nu}$ = 1636 $cm^{-1}$, 1565, 816, 782, 489. – UV ($CH_3CN$): $\lambda_{max}$ (lg ε) = 194 nm (4.584), 260 (4.028), 320 (4.323), 414 (3.603). – $^1H$ NMR ($CDCl_3$): δ = 2.56 (s, 3H), 4.13 (s, 5H), 4.39 (m, 2H), 4.50 (m, 2H), 6.77 (d, $J$ = 16.0 Hz, 1H), 6.96 (d, $J$ = 7.6 Hz, 1H), 7.17 (d, $J$ = 7.8 Hz, 1H), 7.30 (d, $J$ = 16.0 Hz, 1H), 7.49 (dd, $J$ = 7.7/7.6 Hz, 1H). – $^{13}C$ NMR ($CDCl_3$): δ = 24.64 (+), 67.39 (+), 69.27 (+), 69.36 (+), 82.25 ($C_{quart}$), 117.46 (+), 120.78 (+), 126.14 (+), 131.26 (+), 136.49 (+), 156.30 ($C_{quart}$), 158.10 ($C_{quart}$). – MS (70 eV), *m/z* (%): 303 (50) [$M^+$], 238 (100) [$M^+$ – Cp]. – $C_{18}H_{17}FeN$: calcd. 303.0710; found 303.0710 (MS).

*(E)-2-(2-Ferrocenylvinyl)pyrimidine* (**3e**): **2e** (110 mg, 0.7 mmol) was allowed to react with **1** (200 mg, 0.9 mmol) for 16 h at 110°C according to the GP. CC on silica gel ($CH_2Cl_2$/MeOH, 97:3) yielded 27 mg (14%) of **3e** ($R_f$ = 0.64) as a dark red solid, m.p. 143°C. – IR (KBr): $\tilde{\nu}$ = 1635 $cm^{-1}$, 1565, 1437. – UV ($CH_3CN$): $\lambda_{max}$ (lg ε) = 208 nm (4.382), 264 (4.042), 310 (4.202), 464 (3.174). – $^1H$ NMR ($CDCl_3$): δ = 4.16 (s, 5H), 4.37 (m, 2H), 4.56 (m, 2H), 6.82 (d, $J$ = 15.8 Hz, 1H), 7.05 (t, $J$ = 4.9 Hz, 1H), 7.80 (d, $J$ = 15.7 Hz, 1H), 8.65 (d, $J$ = 4.8 Hz, 2H). – $^{13}C$ NMR ($CDCl_3$): δ = 68.08 (+), 69.47 (+), 70.12 (+), 81.10 ($C_{quart}$), 117.70 (+), 124.51 (+), 138.31 (+), 157.00 (+), 160.30 ($C_{quart}$). – MS (70 eV), *m/z* (%): 290 (52) [$M^+$], 225 (66) [$M^+$ – Cp], 132 (100). – $C_{16}H_{14}FeN_2$: calcd. 290.0506; found 290.0502 (MS).

*(E,E)-1,2-Bis(2-ferrocenylvinyl)benzene* (**5**): **4** (188 mg, 0.8 mmol) and **1** (360 mg, 1.7 mmol) were heated for 3 d to 70°C according to the GP, and the crude product was chromatographed on silica gel (1. PE/$CH_2Cl_2$, 95:5; 2. $CH_2Cl_2$) to yield 313 mg (74%) of **5** ($R_f$ = 0.8) as a red solid, m.p. 182°C. – IR (KBr): $\tilde{\nu}$ = 1626 $cm^{-1}$, 1104, 957, 833, 716, 487. – UV ($CH_3CN$): $\lambda_{max}$ (lg ε) = 196 nm (4.770), 204 (4.905), 256 (4.389), 298 (4.473), 456 (3.383). – $^1H$ NMR ($CDCl_3$): δ = 4.18 (s, 10H), 4.31 (m, 4H), 4.52 (m, 4H), 6.77 (d, $J$ = 16.0 Hz, 2H), 7.04 (d, $J$ = 16 Hz, 2H), 7.26 (m, 2H), 7.51 (m, 2H). – $^{13}C$ NMR ($CDCl_3$): δ = 66.95 (+), 69.10 (+), 69.27 (+), 83.60 (+), 124.19 (+), 126.31 (+), 126.99 (+), 129.17 (+), 135.71 ($C_{quart}$). – MS (70 eV), *m/z* (%): 498 (100) [$M^+$], 433 (10) [$M^+$ – Cp]. – $C_{30}H_{26}Fe_2$ (498.2): calcd. C 72.32, H 5.26; found C 72.29, H 5.22. – Mol. mass 498 (MS).

*(E,E,E)-1,3,5-Tris(2-ferrocenylvinyl)benzene* (**7**): 500 mg (0.236 mmol) of **1** and 189 mg (0.6 mmol) of 1,3,5-tribromobenzene (**6**) were allowed to react according to the GP for 2 d at 60°C. The crude product was chromatographed on silica gel (PE/$CH_2Cl_2$, 1:1) to yield 195 mg (46%) of **7** ($R_f$ = 0.47) as a red solid, m.p. 172°C. – IR (KBr): $\tilde{\nu}$ = 1635 $cm^{-1}$, 491. – UV ($CHCl_3$): $\lambda_{max}$ (lg ε) = 242 nm (4.328), 316 (4.681), 362 (3.995), 456 (3.552). – $^1H$ NMR ($CDCl_3$): δ = 4.16 (s, 15H), 4.31 (m, 6H), 4.49 (m, 6H), 6.73 (d, $J$ = 16.1 Hz, 3H), 6.95 (d, $J$ = 16.1 Hz), 7.36 (s, 3H). – MS (70 eV), *m/z* (%): 708 (97) [$M^+$], 44 (100). – $C_{42}H_{36}Fe_3$: calcd. 708.0868, found 708.0867 (MS).

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[11] The reaction of **1** with hexabromobenzene yielded a sixfold coupling product, as clearly indicated by mass spectroscopy. However, the compound was obtained as a mixture of conformers giving rise to complicated $^1H$- and $^{13}C$-NMR spectra.

[12] [12a] Full details of the crystal structure investigation are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, on quoting the depository number CSD-400973, the names of the authors, and the journal citation. – [12b] For the structure of (*Z*)-(1,2-diphenylethylenyl)-ferrocene see: Ch. J. Cardin, W. Crawford, W. E. Watts, B. J. Hathaway, *J. Chem. Soc., Dalton Trans.* **1979**, 970–974.

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